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Abstract

Full Text

PHYSICAL CHEMISTRY

M. V. SMIRNOV, L. A. TSIOVKINA, and N. A. LOGINOV

THE OXIDATION-REDUCTION POTENTIAL OF THE Ti2+/Ti3+ SYSTEM AND THE EQUILIBRIUM CONSTANT OF THE REACTION $2Ti^{3+} + Ti \rightleftarrows 3Ti^{2+}$ IN CHLORIDE MELTS

(Presented by Academician A. N. Frumkin, September 5, 1960)

The equilibrium of the reaction

$$Ti^{3+}\,(\text{melt}) + \frac{1}{2}Ti_{(s)} \rightleftarrows \frac{3}{2}Ti^{2+}\,(\text{melt}) \qquad (1)$$

has been studied by a number of investigators ([1–3]), but none of them gives an expression for the temperature dependence of the equilibrium constant. An attempt to measure the oxidation-reduction potential of the Ti^{2+}/Ti^{3+} system by potentiometric titration with hydrogen of titanium trichloride in a molten eutectic mixture of lithium and potassium chlorides was made only in work ([4]). The value of the formal oxidation-reduction potential $E^0_{Ti^{2+}/Ti^{3+}}$ determined in this way is approximately 0.6 V more positive than the equilibrium potential of titanium measured by us ([5]) under almost the same conditions. If it corresponded to reality, then in melts in equilibrium with metallic titanium the ratio of ion-mole concentrations should have a value of the order of 10^{-3}. In fact, however, according to the results of direct determinations ([1–3]), $[Ti^{3+}]/[Ti^{2+}] \simeq 10^{-1}$.

In studying cathodic polarization during the electrolysis of chloride melts containing trivalent titanium ([6]), we estimated the value of $E^0_{Ti^{3+}/Ti^{2+}}$ to be about -1.7 V relative to the chlorine reference electrode at 700–800°. It agrees well not only with the kinetic data for the cathodic process, but also with the results of determining the concentrations of Ti^{2+} and Ti^{3+} in equilibrium with metallic titanium.

The reliability of the method of potentiometric titration of $TiCl_3$ with hydrogen in a molten salt medium is highly questionable, since the reduction reaction to $TiCl_2$ at 400–500° proceeds slowly and incompletely ([7]). The authors of work ([4])

evidently measured not the value of $E^0_{Ti^{3+}/Ti^{2+}}$, but the potential of the system corresponding to attainment of equilibrium in the reaction

$$TiCl_3\,(melt) + \frac{1}{2}H_{2(g)} \rightleftarrows TiCl_2\,(melt) + HCl_{(g)}.$$

To verify this conclusively, we carried out analogous experiments on the potentiometric titration with hydrogen of titanium trichloride in a molten equimolar mixture of sodium and potassium chlorides at 700°. The potential of the indicator molybdenum electrode was measured directly relative to a chlorine reference electrode.

Figure 1 gives three typical experimental curves obtained by us. As can be seen, the experimental curves do not have the course characteristic of potentiometric titration corresponding to the equation

$$E = E^0_{Ti^{2+}/Ti^{3+}} + \frac{RT}{F}\ln\frac{[Ti^{3+}]}{[Ti^{2+}]}$$

with an inflection or a small plateau at $[Ti^{3+}] = [Ti^{2+}]$, when $E = E^0_{Ti^{2+}/Ti^{3+}}$. They tend toward a constant value of the oxidation–reduction potential of the system, lying approximately 0.5 V more positive than the equilibrium potential of titanium.

In our measurements we also used the method of potentiometric titration, but replaced hydrogen with metallic titanium. This reducing agent, unlike hydrogen, unquestionably ensures, in the course of the reduction of Ti^{3+} to Ti^{2+}, passage through the region where their concentrations become equal.

The initial salt mixtures were prepared by passing $TiCl_4$ vapor through a molten equimolar mixture of sodium and potassium chlorides in a stream of pure hydrogen. The reduction of $TiCl_3$ was carried out with metallic titanium, in the apparatus shown schematically in Fig. 2. The oxidation–reduction potential of the system was measured by means of an indicator molybdenum electrode relative to a chlorine reference electrode of ordinary design. Measurements were made every half minute throughout the experiment. In order to ensure more rapid equalization of the concentrations of Ti^{2+} and Ti^{3+} throughout the entire volume of the melt, the indicator molybdenum electrode was rotated at a speed of 60 rpm. The temperature was maintained constant at the specified value within ±2°.

Fig. 1. Curves of potentiometric titration of $TiCl_3$ (4 wt.%) in a molten equimolar mixture of NaCl–KCl at 700°, obtained in 3 repeated experiments.

The form of the potentiometric curves (potential–reduction time) depends on the conditions (temperature, concentration, stirring of the melt, etc.). An in-

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crease in the surface area of the metallic titanium has an especially strong effect on the rate of the reduction reaction. This can be seen in Fig. 3.

However, all the experimental curves have the shape typical of potentiometric titration; namely, they have an inflection, which corresponds to attainment of equality of the concentrations of tri- and divalent titanium in the course of the reduction reaction. The potentials of the molybdenum electrode corresponding to these inflection points obviously give us the values of the formal oxidation-reduction potential $E^0_{Ti^{2+}/Ti^{3+}}$; they are given in Table 1.

Table 1

Experiment no.	Initial conc. of $TiCl_3$, wt.%	t, °C	$E^0_{Ti^{2+}/Ti^{3+}}$, V	Experiment no.	Initial conc. of $TiCl_3$, wt.%	t, °C	$E^0_{Ti^{2+}/Ti^{3+}}$, V
1	1.93	711	−1.720	9	4.52	733	−1.731
2	1.93	725	−1.718	10	4.52	818	−1.722
3	1.93	734	−1.731	11	4.52	827	−1.720
4	1.93	737	−1.729	12	4.52	848	−1.717
5	1.93	740	−1.734	13	4.52	897	−1.723
6	2.26	713	−1.731	14	6.12	717	−1.727
7	3.96	711	−1.721	15	6.12	727	−1.728
8	3.96	724	−1.729	16	6.12	728	−1.731

As can be seen from the table, the formal oxidation-reduction potential of the Ti^{2+}/Ti^{3+} system remains, within the limits of the measurement errors, a constant value equal to

$$E^0_{Ti^{2+}/Ti^{3+}} = -1.726 \pm 0.005 \text{ V}$$

relative to the chlorine reference electrode.

Earlier we[1] found the temperature dependence of $E^0_{Ti/Ti^{2+}}$ under the assumption that, at equilibrium with the metal, the overwhelming part of titanium in the melt is in the divalent state; we obtained the expression

$$E^0_{Ti/Ti^{2+}} = (-2.371 + 6.09 \cdot 10^{-4} T) \text{ V}.$$

Fig. 2. Cell for studying the oxidation-reduction potential of the Ti^{2+}/Ti^{3+} system:

[1]Reference as cited in the source.

1 –quartz electrolyzer, 2 –graphite protective screen, 3 –molybdenum electrode, 4 –molybdenum lead to titanium, 5 –corundum crucible, 6 –electrode of titanium iodide, 7 –chlorine reference electrode.

According to [^1,^2], in this equilibrium the fraction of divalent titanium is about 90%. Taking this circumstance into account, the equation changes somewhat:

$$E^0_{\mathrm{Ti/Ti^{2+}}} = (-2.371 + 5.73 \cdot 10^{-4} T) \ \mathrm{V}$$

relative to the chloride reference electrode.

Knowing $E^0_{\mathrm{Ti/Ti^{2+}}}$ and $E^0_{\mathrm{Ti^{2+}/Ti^{3+}}}$, one can readily find an expression for the temperature dependence of $E^0_{\mathrm{Ti/Ti^{3+}}}$ in the thermodynamic equation for the equilibrium potential of titanium relative to its trivalent ions in a chloride melt:

$$E = E^0_{\mathrm{Ti/Ti^{3+}}} + \frac{RT}{3F} \ln[\mathrm{Ti^{3+}}].$$

From the relation

$$E^0_{\mathrm{Ti^{2+}/Ti^{3+}}} = 3E^0_{\mathrm{Ti/Ti^{3+}}} - 2E^0_{\mathrm{Ti/Ti^{2+}}}$$

it follows that

$$E^0_{\mathrm{Ti/Ti^{3+}}} = (-2.156 + 3.82 \cdot 10^{-4} T) \ \mathrm{V}$$

relative to the chlorine reference electrode.

The equilibrium constant of reaction (1), expressed through the ionic-fraction concentrations of its components, is related to $E^0_{\mathrm{Ti/Ti^{2+}}}$ and $E^0_{\mathrm{Ti/Ti^{3+}}}$ by the relation:

$$\ln K = \ln \frac{[\mathrm{Ti^{2+}}]^{3/2}}{[\mathrm{Ti^{3+}}]} = \frac{3F}{RT} \left(E^0_{\mathrm{Ti/Ti^{3+}}} - E^0_{\mathrm{Ti/Ti^{2+}}} \right).$$

Passing to common logarithms and substituting here the temperature dependences of the quantities E^0 in parentheses, we obtain the expression for the equilibrium constant

$$\lg K = -2.888 + 3.251/T.$$

Table 2

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Fig. 3. Curves of potentiometric titration by metallic titanium of TiCl3 in a molten equimolar NaCl–KCl mixture

Figure 1: Fig. 3. Curves of potentiometric titration by metallic titanium of TiCl3 in a molten equimolar NaCl–KCl mixture

Temp., °C	Equilibrium constants, according to our data	Equilibrium constants, according to data of other authors
700	2.82	1.21–0.56 (1)2.95–1.65 (2)
800	1.35	1.33 (at 780°) (2)$8.6 \cdot 10^{-4}$–$6.14 \cdot 10^{-2}$ (at 825°) (3)
900	0.76	–
1000	0.46	–

It is of interest to compare the values of the equilibrium constant, calculated from this equation, with data from other authors, given in Table 2.

The equilibrium constant decreases with increasing temperature, i.e., the equilibrium of reaction (1) shifts to the left.

To some extent this phenomenon accounts for the "spraying" of titanium in salt melts, when the metal is deposited on the vessel walls. With external heating their temperature is higher than that of the piece of metal inside the melt. The temperature gradient may reach a considerable magnitude in the case of large heat removal from metallic titanium. The equilibrium mixture of Ti^{2+} and Ti^{3+} ions formed near metallic titanium is carried away by convective

by streams of the salt melt and enters a hotter zone near the walls of the vessel. As a result, the equilibrium is disturbed in the direction of the deposition of metallic titanium; moreover, contact with a solid surface favors the nucleation of a new phase.

Fig. 3. Curves of potentiometric titration by metallic titanium of $TiCl_3$ in a molten equimolar mixture of NaCl–KCl, recorded: **1** –at 710° and 1.93 wt.% $TiCl_3$; **2** –at 897° and 3.96 wt.% $TiCl_3$; **3** –at 824° and 3.96 wt.% $TiCl_3$; curve **1** was recorded with a larger surface area of the metal reductant than **2** and **3**.

The assertion of previous authors that the equilibrium constant depends on the concentration of titanium in the melt, even if only slightly, is highly doubtful. In our experiments, the initial $TiCl_3$ content in the electrolyte varied by more than a factor of 3. At the same time, however, no definite dependence of the

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formal oxidation-reduction potential of the Ti^{2+}/Ti^{3+} system on the titanium concentration was observed.

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