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Formation Gibbs energy of K_2NbF_7, K_2NbOF_5, and $K_2NbO_2F_3$ from electrochemical measurements

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Abstract

The formation Gibbs energies of molten K_2NbF_7, K_2NbOF_5, and $K_2NbO_2F_3$ at the temperature of 750°C were calculated from the previously performed voltammetric and chronopotentiometric measurements in the system LiF–NaF–K_2NbF_7–Na_2O [1–3] and from the equilibrium constants of reactions leading to the formation in the melts of the individual oxyfluoroniobates.

For the formation Gibbs energy of K_2NbF_7 the average value $\Delta_f G^0(K_2NbF_7) = -(1340 \pm 25)$ kJ mol^{-1} was obtained. For K_2NbOF_5 the formation Gibbs energy is $\Delta_f G^0(K_2NbOF_5) = -(1526 \pm 16)$ kJ mol^{-1}. This value may, however, not be exactly correct since the product of the electrochemical reduction was not pure niobium, but the solid solution of oxygen in niobium. For the formation Gibbs energy of $K_2NbO_2F_3$ the value $\Delta_f G^0(K_2NbO_2F_3) = -(1100 \pm 100)$ kJ mol^{-1} was calculated. This value may be charged by a substantial error as well due to the probably incorrect value of the formation Gibbs energy of K_2NbOF_5. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electrochemistry; Gibbs energy; Oxofluoroniobates

1. Introduction

Electrolytic deposition of niobium from molten salts is a rather known process, but the mechanism of its electrolytic deposition in the presence of oxide ions has not previously been clarified satisfactorily. The necessity to know details of both complex formation and redox chemistry of the species present in the melts is required in order to optimise the process. In order to calculate any equilibrium in the melt, the values of the formation Gibbs energies of the individual oxyfluoroniobates are unavoidable. Unfortunately, in the literature they are missing.

The reduction process of niobium and the influence of oxide ions in an equimolar molten mixture of LiF and KF have been investigated using a cyclic voltametric technique in our previous paper [1]. A two step mechanism of reduction of Nb(V) to Nb(0) in LiF–KF melt was proposed

$$[\mathrm{Nb(V)F_7}]^{2-} + \mathrm{e}^- = [\mathrm{Nb(IV)F_6}]^{2-} + \mathrm{F}^- \tag{A}$$

$$[\mathrm{Nb(IV)F_6}]^{2-} + 4\mathrm{e}^- = \mathrm{Nb(0)} + 6\mathrm{F}^- \tag{B}$$

taking place at the potentials $E^0_{(A)} = -0.29$ V and $E^0_{(B)} = -1.02$ V, respectively [1]. The same results were obtained also in the system LiF–NaF–K_2NbF_7.

In [2], it was found that the presence of oxide ions strongly influences the redox properties and the structure of niobium ions in the melt. In the voltammograms, new reduction peaks were observed when the

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oxide ions were purposely added to the melt. It was suggested that the presence of oxide ions leads to the formation of monoxyfluoride complex $[Nb(V)OF_5]^{2-}$ according to the chemical reaction

$$[Nb(V)F_7]^{2-} + O^{2-} = [Nb(V)OF_5]^{2-} + 2F^- \qquad (C)$$

This reaction, however, does not proceed quantitatively. $[Nb(V)OF_5]^{2-}$ decomposes at the cathode in one-step reaction at the potential $E^0_{(D)}$, approximately by 100 mV lower than $E^0_{(B)}$ [4–6], according to the reaction

$$[Nb(V)F_7]^{2-} + 3e^- = Nb(0), O(ss) + 5F^- \qquad (D)$$

forming, in accordance with [5,7], a light-gray surface layer of the solid solution Nb(0),O(ss). At higher oxide concentrations ($n_O/n_{Nb(V)} > 0.7$) the monoxyfluoride complex $[Nb(V)OF_5]^{2-}$ transforms to the dioxyfluoride complex $[Nb(V)O_2F_3]^{2-}$ according to the chemical reaction [3]

$$[Nb(V)OF_5]^{2-} + O^{2-} = [Nb(V)O_2F_3]^{2-} + 2F^- \qquad (E)$$

The aim of the present paper is the calculation of the formation Gibbs energies from the previously performed voltammetric and chronopotentiometric measurements [1,2] and from the equilibrium constants of reactions leading to the formation in the melts of the individual oxyfluoroniobates as well as on the basis of the X-ray diffraction and IR spectroscopic investigations [3] in the systems LiF–KF–K_2NbF_7, LiF–KF–K_2NbF_7–K_2O, LiF–NaF–K_2NbF_7, and LiF–NaF–K_2NbF_7–Na_2O.

2. Results of calculation

2.1. Voltammetry

For the half-peak potential, $E_{p/2}$, in a Nernst's system it holds (when $i = i_p/2$)

$$E_{p/2} - E_{1/2} = 1.09\frac{RT}{nF} \qquad (1)$$

where $E_{1/2} = (E_p - E_{p/2})/2$. From Eq. (1) it follows, that:

$$E_{1/2} = E_p - 1.09\frac{RT}{nF} \qquad (2)$$

For the half-peak potential it also holds

$$E_{1/2} = E^0 - \frac{RT}{2nF}\ln\frac{D_{ox}}{D_{red}} = E^0, \qquad D_{ox} = D_{red} \qquad (3)$$

where D_{ox} and D_{red} are the diffusion coefficients of the oxidised and reduced forms of the electroactive species, respectively. For the Gibbs energy of the individual electrochemical reduction it then holds

$$\Delta G^0 = -nFE^0 \qquad (4)$$

The decomposition of $K_2Nb(V)F_7$ at the cathode proceeds in two steps. The first step can be described by the following electrochemical reaction scheme:

$$\begin{array}{ll} \text{cathodic part:} & K_2Nb(V)F_7 + e^- = K_2Nb(IV)F_6 + F^- \\ \text{anodic part:} & 4F^- - e^- = 0.5F_2 \\ \text{cell reaction:} & K_2Nb(V)F_7 = K_2Nb(IV)F_6 + 0.5F_2 \end{array} \qquad (F)$$

while the second one involves the electrochemical reaction scheme

$$\begin{array}{ll} \text{cathodic part:} & K_2Nb(IV)F_6 + 4e^- = Nb(0) + 4F^- \\ \text{anodic part:} & 4F^- - e^- = 2F_2 \\ \text{cell reaction:} & K_2Nb(V)F_7 = Nb(0) + 2KF + 2F_2 \end{array} \qquad (G)$$

For the total electrochemical reaction, we then get

$$\begin{array}{ll} \text{cathodic part:} & K_2Nb(V)F_7 + 5e^- = Nb(0) + 2KF + 4F^- \\ \text{anodic part:} & 5F^- - 5e^- = 2.5F_2 \\ \text{cell reaction:} & K_2Nb(V)F_7 = Nb(0) + 2KF + 2.5F_2 \end{array} \qquad (H)$$

The results of the voltammetric measurements in the system LiF–NaF–K_2NbF_7 at the temperature of 750°C are given in Table 1 [1]. The resulting mean value of the Gibbs energy of reaction (F), which refers to the reduction $Nb(V) \rightarrow Nb(IV)$, obtained at different concentrations of $K_2Nb(V)F_7$ is $\Delta_r G^0_{(F)} = (29 \pm 5)\,kJ\,mol^{-1}$. For the Gibbs energy of reaction (G), which corresponds to the reduction $Nb(IV) \rightarrow Nb(0)$, the mean value $\Delta_r G^0_{(G)} = (395 \pm 16)\,kJ\,mol^{-1}$ was obtained. The resulting Gibbs energy of the total cell reaction (H) is, thus $\Delta_r G^0_{(H)} = (424 \pm 21)\,kJ\,mol^{-1}$. The Gibbs energy of formation of K_2NbF_7 can then be calculated from the relation

$$\Delta_f G^0(K_2NbF_7) = 2\Delta_f G^0(KF) - \Delta_r G^0_{(H)} \qquad (5)$$

Using the literature data for the formation Gibbs energy of KF [8] for the formation Gibbs energy of K_2NbF_7, we get the final value $\Delta_f G^0(K_2NbF_7) = -(1346 \pm 25)\,kJ\,mol^{-1}$.

Table 1
Experimental voltammetric data in the system LiF–NaF–K_2NbF_7 at 750°C[a]

$c_{Nb(V)}$/(mol m^{-3})	$-E^0_{(A)}$/(V)	$\Delta G^0_{(F)}$/(J mol^{-1})	$-E^0_{(B)}$/(V)	$\Delta G^0_{(G)}$/(J mol^{-1})
57.1	0.258	24894	1.03	398289
166.5	0.326	31455	1.03	397517
239.1	0.365	35218	0.97	372816
512.1	0.258	24894	1.06	409867

[a] Platinum quasi-reference electrode.

2.2. Chronopotentiometry

Next information we can get also from the chronopotentiometric measurement [2]. For fast reversible diffusion-controlled electrode reaction, the dependence of the potential on time in an ideal case is expressed by the equation

$$E = E_{\tau/4} + \frac{RT}{nF} \ln \frac{\tau^{1/2} - t^{1/2}}{t^{1/2}} \quad (6)$$

where $E_{\tau/4}$ is the quart-wave potential. For $E_{\tau/4}$ it holds

$$E_{\tau/4} = E^0_{(B)} - \frac{RT}{2nF} \ln \frac{D_{ox}}{D_{red}} = E^0_{(B)}, \quad D_{ox} = D_{red} \quad (7)$$

In Eq. (6), the first reduction step, $Nb(V) \rightarrow Nb(IV)$, was neglected due to very short transition time of the first step compared with that of the second one. For the relation between $E^0_{(B)}$ and the formation Gibbs energy of K_2NbF_7 again Eq. (4) is valid. The results of the chronopotentiometric measurements are given in Table 2.

The potential of the first wave, $E^0_{(A)}$, was obtained from the linear dependence of the potential on $\ln\{(\tau/t)^{1/2} - 1\}$, which describes the chronopotentiometric wave for a simple reversible electrode reaction. The slope of this plot was equal to 0.082 V and intersects the potential axis at the potential of −0.32 V. This means that the number of transferred electrons equals to one. This chronopotentiometric wave, thus corresponds to the electrode reaction $Nb(V) + e^- = Nb(IV)$ with the formal potential $E^0_{(A)} = -0.32$ V.

Table 2
Experimental chronopotentiometric data in the system LiF–NaF–K_2NbF_7 at 750°C with platinum working electrode

$c_{Nb(V)}$/ (mol m^{-3})	j/(A cm^{-2})	$-E_{\tau/4}$/(V)	$\Delta G^0_{(G)}$/ (J mol^{-1})
57.1	625–1896	0.99	382089
51.8	689–7769	0.99	382089
46.8	937–1437	0.98	378229
43.9	1250–2159	0.97	374370
38.3	776–1442	1.03	396562
18.8	1154.00	0.98	378229

Using the similar procedure as in the previous case, the resulting mean value of the Gibbs energy of reaction (F) is $\Delta_r G^0_{(F)} = (30 \pm 5)$ kJ mol^{-1}. For the Gibbs energy of reaction (G), the mean value $\Delta_r G^0_{(G)} = (382 \pm 7)$ kJ mol^{-1} was obtained. The resulting Gibbs energy of the total cell reaction (H) is, thus in this case $\Delta_r G^0_{(H)} = (412 \pm 12)$ kJ mol^{-1}. From the chronopotentiometric measurements, we now get for the formation Gibbs energy of K_2NbF_7 the final value $\Delta_f G^0(K_2NbF_7) = -(1334 \pm 15)$ kJ mol^{-1}. With regard to the previously obtained value based on voltammetric measurements the average value $\Delta_f G^0(K_2NbF_7) = -(1340 \pm 25)$ kJ mol^{-1} was accepted.

As it was mentioned above, in the presence of oxide ions two electrochemical reductions take place simultaneously in the system LiF–NaF–K_2NbF_7–Na_2O. It is the reduction $Nb(IV) \rightarrow Nb(0)$ and the reduction $Nb(V)O \rightarrow Nb(0)$, O (ss). In the system with two parallel reductions, the potential of the second chronopotentiometric wave in case of a reversible electrode reaction is given by the relation

$$E = \varepsilon + \frac{RT}{n_2 F} \ln \left\{ \frac{\tau_2^{1/2} - (\tau_2 + t')^{1/2} + \tau_3^{1/2}}{[(\tau_2 + t')^{1/2} - \tau_2^{1/2}]} \right\} \quad (8)$$

where t' is the time period from the first transition time and ε represents the expression

$$\varepsilon = E_{\tau/4,2} = E^0_{(D)} - \frac{RT}{n_2 F} \ln \frac{f_{red_2}}{f_{ox_2}} + \frac{RT}{2n_2 F} \ln \frac{D_{red_2}}{D_{ox_2}} = E^0_{(D)}, \quad D_{red_2} = D_{ox_2}, f_{red_2} = f_{ox_2} \quad (9)$$

where f_{ox_2} and f_{red_2} are the fugacities of the oxidised and reduced forms of the second electrochemically active species, respectively. For the second reduction, which represents the one-step five-electron reduction according to the following electrochemical reaction scheme:

$$\begin{array}{ll} \text{cathodic part:} & \mathrm{K_2Nb(V)OF_5 + 5e^- = Nb(0), O^{2-}(ss) + 2KF + 3F^-} \\ \text{anodic part:} & \mathrm{Nb(0), O^{2-}(ss) + 3F^- - 5e^- = Nb(0), O(ss) + 1.5F_2} \\ \text{cell reaction:} & \mathrm{K_2Nb(V)OF_5 = Nb(0), O(ss) + 2KF + 1.5F_2} \end{array} \qquad \text{(I)}$$

we can apply all relations valid for the simple reduction. The results of the chronopotentiometric measurements are given in Table 3. For the Gibbs energy of reaction (G) the mean value $\Delta_r G^0_{(G)} = (386 \pm 19)$ kJ mol^{-1} was obtained, which is very close to the previously obtained values. For the reaction Gibbs energy of reaction (I), taking place at the cathodic potential $E^0_{(D)} = -1.25$ V, the mean value $\Delta_r G^0_{(I)} = (604 \pm 16)$ kJ mol^{-1} was calculated. With respect to the total cell reaction (I), the formation Gibbs energy of K_2NbOF_5 can thus be calculated according to the equation

$$\Delta_f G^0(\mathrm{K_2NbOF_5}) = 2\Delta_f G^0(\mathrm{KF}) - \Delta_r G^0_{(I)} \qquad (10)$$

The final value $\Delta_f G^0(\mathrm{K_2NbOF_5}) = -(1526 \pm 16)$ kJ mol^{-1} was obtained. It should be, however, stressed that the obtained value is not exactly equal to the formation Gibbs energy of $K_2Nb(V)OF_5$, since the product of the electrochemical reduction is not pure niobium, but the solid solution of oxygen in niobium.

2.3. Chemical equilibrium

The formation Gibbs energy of $K_2Nb(V)O_2F_3$ can be calculated from the obtained value of the formation Gibbs energy of $K_2Nb(V)OF_5$, the material balance in the system LiF–NaF–K_2NbF_7–Na_2O, and from the literature data of the formation Gibbs energy of NaF and Na_2O. The derivation of equation for the equilibrium constant of the chemical reactions leading to the formation of $K_2Nb(V)O_2F_3$ was performed in the following way.

At $n_O/n_{Nb(V)} > 0.7$ two chemical reactions take place simultaneously in the melt. It is the reaction

$$\mathrm{K_2Nb(V)F_7 + Na_2O = K_2Nb(V)OF_5 + 2NaF} \qquad \text{(J)}$$

with the degree of conversion α_1 and the reaction

$$\mathrm{K_2Nb(V)OF_5 + Na_2O = K_2Nb(V)O_2F_3 + 2NaF} \qquad \text{(K)}$$

with the degree of conversion α_2.

Let us consider 1 mol of melt with the composition $x_1\mathrm{LiF} + x_2\mathrm{NaF} + x_3\mathrm{K_2NbF_7} + x_4\mathrm{Na_2O}$. Since the amount of originated $K_2Nb(V)OF_5$ according to reaction (J) depends on the amount of added Na_2O, the resulting amounts of substances in equilibrium, when reaction (J) is at equilibrium, are

$$\begin{aligned} n_1 &= x_1\ \mathrm{mol} \\ n_2 &= x_2 + 2\alpha_1 x_4\ \mathrm{mol} \\ n_3 &= x_3 - \alpha_1 x_4\ \mathrm{mol} \\ n_4 &= x_4 - \alpha_1 x_4\ \mathrm{mol} \\ n_5 &= \alpha_1 x_4\ \mathrm{mol} \end{aligned} \qquad (11)$$

where n_5 is the amount of originated $K_2Nb(V)OF_5$. The resulting amounts of substances, when both simultaneous reactions (J) and (K) are in equilibrium,

Table 3
Chronopotentiometric data for the system LiF–NaF–K_2NbF_7–Na_2O with different $n_O/n_{Nb(V)}$ ratios at 750°C[a]

$c_{Nb(V)}$/(mol m^{-3})	$n_O/n_{Nb(V)}$	$-E^0_{(B)}$/(V)	$\Delta G^0_{(G)}$/(J mol^{-1})	$-E^0_{(D)}$/(V)	$\Delta G^0_{(I)}$/(J mol^{-1})
70.3	0.23	1.03	397526	1.24	599828
70.3	0.62	1.05	405245	1.26	607868
113.9	0.67	0.91	349283	1.20	576510
70.3	0.68	1.01	387878	1.25	603044
38.3	0.80	1.01	387878	1.26	607868
64.7	1.00	1.01	387878	1.30	627166

[a] Platinum working electrode.

are

$$\begin{aligned} n'_1 &= x_1\ \text{mol} \\ n'_2 &= x_2 + 2\alpha_1 x_4 + 2\alpha_2(x_2 + 2\alpha_1 x_4)\ \text{mol} \\ n'_3 &= x_3 - \alpha_1 x_4 - \alpha_2(x_3 - \alpha_1 x_4)\ \text{mol} \\ n'_4 &= x_4 - \alpha_1 x_4 - \alpha_2(x_4 - \alpha_2 x_4)\ \text{mol} \\ n'_5 &= \alpha_1 x_4 - \alpha_1\alpha_2 x_4\ \text{mol} \\ n'_6 &= \alpha_1\alpha_2 x_4\ \text{mol} \end{aligned} \tag{12}$$

where $n_6{}'$ is the amount of originated $K_2Nb(V)O_2F_3$. The total amount of all substances is $\sum n' = 1 + \alpha_1 x_4 + \alpha_2(2x_2 - x_3 - x_4 + 6\alpha_1 x_4)$ mol. For the molar fractions of components at equilibrium, we then get

$$\begin{aligned} y_1 &= \frac{x_1}{\sum n'} & y_2 &= \frac{x_2 + 2\alpha_1 x_4 + 2\alpha_2(x_2 + 2\alpha_1 x_4)}{\sum n'} \\ y_3 &= \frac{x_3 - \alpha_1 x_4 - \alpha_2(x_3 - \alpha_1 x_4)}{\sum n'} & y_4 &= \frac{x_4 - \alpha_1 x_4 - \alpha_2(x_4 - \alpha_2 x_4)}{\sum n'} \\ y_5 &= \frac{\alpha_1 x_4 - \alpha_1\alpha_2 x_4}{\sum n'} & y_6 &= \frac{\alpha_1\alpha_2 x_4}{\sum n'} \end{aligned} \tag{13}$$

For the equilibrium constant of reaction (K), we get the equation

$$\begin{aligned} K_{(K)} &= \frac{y_2^2 y_6}{y_4 y_5} \\ &= \frac{(x_2 + 2\alpha_1 x_4 + 2\alpha_2 x_2 + 4\alpha_1\alpha_2 x_4)^2 \alpha_1\alpha_2 x_4}{\sum n'(\alpha_1 x_4 - \alpha_1\alpha_2 x_4)(x_4 - \alpha_1 x_4 - \alpha_2 x_4 + \alpha_1\alpha_2 x_4)} \end{aligned} \tag{14}$$

It is obvious, that in general both α_1 and α_2 depend on composition. However, in our particular case, when x_3, $x_4 \ll x_1$, x_2 and the electrochemical measurements were carried out in a narrow concentration interval of K_2NbF_7 and Na_2O, the following simplifications can be made: $x_1 + x_2 \approx 1$; $1 - x_3 - x_4 \approx 1$; $\alpha_1 =$ constant; $\alpha_2 =$ constant. Inserting these simplifications into Eq. (14) and rearranging, the following final equation was obtained for the equilibrium constant $K_{(K)}$:

$$K_{(K)} = \frac{\alpha_2 x_2^2 (1 + 2\alpha_2)^2}{x_4(1 + 2\alpha_2 x_2)(1 - \alpha_1)(1 - \alpha_2)^2} \tag{15}$$

From electrochemical measurements, the value $\alpha_1 = 0.7$ was obtained. Since it is very unlikely that some free Na_2O is left in the melt, for the degree of conversion of reaction (K) the value $\alpha_2 = 0.9999$ was adopted. The results of calculation are summarised in Table 4. The equilibrium constant of reaction (K) attains then the value $K_{(K)} = 6.66 \times 10^{11}$ and for the reaction Gibbs energy the value $\Delta_r G^0_{(K)} = -232\ \text{kJ mol}^{-1}$ was obtained. The formation Gibbs energy of $K_2Nb(V)O_2F_3$ can then be calculated using the previously obtained formation Gibbs energy of $K_2Nb(V)OF_5$ and the literature data for NaF and Na_2O [8] according to the equation

$$\begin{aligned} -RT \ln K_{(K)} = \Delta_r G^0_{(K)} &= \Delta_f G^0(K_2NbO_2F_3) \\ &\quad + 2\Delta_f G^0(\text{NaF}) - \Delta_f G^0(K_2NbOF_5) \\ &\quad - \Delta_f G^0(Na_2O) \end{aligned} \tag{16}$$

The value $\Delta_f G^0(K_2NbO_2F_3) = -(1100 \pm 100)$ kJ mol^{-1} was obtained. As it was already mentioned above, the obtained value of the formation Gibbs energy of $K_2Nb(V)O_2F_3$ may be charged by a substantial error due to the probably incorrect value of the formation Gibbs energy of $K_2Nb(V)OF_5$. Further uncertainty is introduced also by the accepted value $\alpha_2 = 0.9999$, since every 9 in the next decimal place

Table 4
Results of calculation of the equilibrium constant $K_{(K)}$

$c_{Nb(V)}$/(mol m^{-3})	$n_O/n_{Nb(V)}$	x_1	x_2	$x_3 \times 10^4$	$x_4 \times 10^4$	$K_{(K)} \times 10^{-11}$	$\Delta G^0_{(K)}$/(J mol^{-1})
38.3	0.8	0.399	0.599	6.77	5.42	9.04	−234151
64.7	1	0.399	0.599	11.4	11.4	4.28	−227789

Table 5
Formation Gibbs energies of substances

Substance	$\Delta_f G^0$/(kJ mol^{-1})	Reference
Na_2O	−263	[8]
NaF	−461	[8]
KF	−461	[8]
K_2NbF_7	−1340	This work
K_2NbOF_5	−1526	This work
$K_2NbO_2F_3$	−1100	This work

decreases the formation Gibbs energy by −39 kJ mol^{-1}. The literature data used in the calculation as well as the data obtained in this work from electrochemical measurements are summarised in Table 5.

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