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Abstract

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Thermodynamic Characteristics of Niobium Oxides

(Equilibrium with Hydrogen and Electrochemical Measurements)

In the niobium-oxygen system there exist, at least, three oxides: Nb_2O_5, with a homogeneity range from $NbO_{2\cdot5}$ to $NbO_{2\cdot4}$*, NbO_2, and NbO, with very narrow homogeneity ranges (^{1}-^{7}). The equilibrium conditions in the reduction of Nb_2O_5 to NbO_2 by hydrogen and carbon monoxide have been studied in works (^{3}-^{7}). However, the results of works (^{3},^{4}) are not free from errors associated with the influence of thermal diffusion; in work (^{5}) only approximate values of the equilibrium constants are given. Work (^{6}) is known to us only from a brief description in the monograph (^{22}), where values of the equilibrium constants are absent. In the later work (^{7}), the equilibrium of niobium pentoxide with hydrogen was measured only for one temperature. The equilibrium of the lower oxides of niobium with hydrogen apparently has not been studied by anyone. In the present work the equilibrium reduction of niobium pentoxide to NbO was investigated, and the e.m.f. of a galvanic cell containing the lower niobium oxide NbO and metallic niobium was measured. In the work, niobium pentoxide (99.9% Nb_2O_5) and metallic niobium (98.6% Nb; 0.08% Fe; 0.06% Ti; 0.10% Pb; 0.04% Si; 0.12% C) were used.

[Figure 1 schematic not reproduced]

Fig. 1. Reduction isotherms of Nb_2O_5 for temperatures:
a –1207°, *b* –1400°, *c* –1550°

The equilibrium of niobium oxides with hydrogen in the temperature interval 1200–1550° C was studied by the circulation method in an apparatus described in (^{8}). The sample under investigation, in the form of a pellet, was placed in a molybdenum short-circuit furnace on a platinum support so that the pellet touched the platinum in a few places. The gross composition of the reduction products was determined from the gain in weight of the preparation upon ignition in air to Nb_2O_5; the phase composition was determined by X-ray diffraction. Two stages of reduction of Nb_2O_5 were investigated:

Fig. 2

Figure 1: Fig. 2

$$2.5\,\mathrm{NbO_{2.4}} + \mathrm{H_2} \rightarrow 2.5\,\mathrm{NbO_2} + \mathrm{H_2O}, \qquad \text{(I)}$$

$$\mathrm{NbO_2} + \mathrm{H_2} \rightarrow \mathrm{NbO} + \mathrm{H_2O}. \qquad \text{(II)}$$

The values of the equilibrium constants $K_p = P_{\mathrm{H_2O}}/P_{\mathrm{H_2}}$ are presented in Table 1 and in Fig. 1. In the composition range from $\mathrm{NbO_{2\cdot4}}$ to $\mathrm{NbO_{2\cdot5}}$, the values of K_p increase rapidly and cannot be measured sufficiently accurately in our apparatus. The logarithmic polytherms of the equilibrium constants for the two stages

* $\mathrm{Nb_2O_5}$ remains homogeneous within the limits from $\mathrm{NbO_{2\cdot5}}$ to $\mathrm{NbO_{2\cdot39}}$ according to (^{1}) and from $\mathrm{NbO_{2\cdot5}}$ to $\mathrm{NbO_{2\cdot42}}$ according to (^{6}).

the reduction of $\mathrm{Nb_2O_5}$ (Fig. 2) are described (with an accuracy of $±$0.2% for the first and $±$0.3% for the second) by the following equations:

$$\lg K_{\mathrm{p1}} = -15050/4.575T + 1.3306 \qquad (1480 - 1673°\mathrm{K}),$$

$$\lg K_{\mathrm{p_{II}}} = -29490/4.575T + 1.3334 \qquad (1673 - 1823°\mathrm{K}),$$

whence

$$\Delta G^0_{\mathrm{I}}(\mathrm{cal}) = 15050 - 6.087T, \qquad \Delta G^0_{\mathrm{II}}(\mathrm{cal}) = 29490 - 6.10T.$$

Combining reactions I and II with the reaction of formation of water vapor

$$\mathrm{H_2} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{H_2O(g)}, \qquad \text{(III)},$$

whose isobaric potential according to Chipman (^{9}) is expressed by the equation

$$\Delta G^0_{\mathrm{III}}(\mathrm{cal}) = -59251 + 2.006\,T\lg T - 7.5\cdot10^{-5}T^2 + 4.08\cdot10^5T^{-1} + 6.8085\,T,$$

and using literature data on the heat capacities of $\mathrm{NbO_2}$ and NbO according to (^{10}) and for $\mathrm{O_2}$ according to (^{11}), one can calculate ΔG^0_{VI} (respectively ΔH^0_{IV} and ΔH^0_{V}) for the reactions of formation of $\mathrm{NbO_{2\cdot4}}$ and $\mathrm{NbO_2}$ at 298.2°K for the reactions

Fig. 2

$$NbO_2 + \tfrac{1}{5}O_2 \rightarrow NbO_{2.4}, \qquad (IV)$$

$$NbO + \tfrac{1}{2}O_2 \rightarrow NbO_2, \qquad (V)$$

$$\Delta G^0_{IV} = -26.2\ \text{kcal}; \quad \Delta H^0_{IV} = -28.1\ \text{kcal}; \quad \Delta S^0_{IV} = -6.36\ \text{e.u.}; \quad \Delta G^0_V =$$

$$= -87.33\ \text{kcal}; \quad \Delta H^0_V = -94.95\ \text{kcal}; \quad \Delta S^0_V = -25.57\ \text{e.u.}$$

For the reaction of formation of Nb_2O_5 from NbO_2:

$$2NbO_2 + \tfrac{1}{2}O_2 \rightarrow Nb_2O_5 \qquad (VI)$$

linearly extrapolating from the composition $NbO_{2\cdot 4}$ to $NbO_{2\cdot 5}$, we obtain at 298.2°K:

$$\Delta H^0_{VI} = -70.25\ \text{kcal}; \quad \Delta G^0_{VI} = -65.5\ \text{kcal}; \quad \Delta S^0_{VI} = -15.91\ \text{e.u.}^*$$

We were unable to carry out equilibrium reduction of niobium oxides by hydrogen to the metal. Therefore, to determine the thermodynamic functions of the lower niobium oxide NbO, the emf method was used. Measurements of the cell E

$$\text{Pt} \mid \text{Fe, Fe}_{0.95}\text{O} \mid \begin{matrix}\text{solid}\\ \text{electrolyte}\end{matrix} \mid \text{NbO, Nb} \mid \text{Pt} \qquad (A)$$

were carried out in an apparatus described in (^{12}), in the temperature interval 841–1073°C. Mixed crystals in the ThO_2—La_2O_3 system were used as the solid electrolyte in the experiments. In individual cases, after carrying out an experiment with cell A, the electrolyte pellet was used to measure the E of the cell

$$\text{Pt} \mid \text{Fe}_3\text{O}_4, \text{Fe}_{0.95}\text{O} \mid \begin{matrix}\text{solid}\\ \text{electrolyte}\end{matrix} \mid \text{Fe}_{0.95}\text{O, Fe} \mid \text{Pt} \qquad (B)$$

Fig. 3

Figure 2: Fig. 3

*

The calculation of ΔG^0_{VI} (respectively ΔH^0_{VI} and ΔS^0_{VI}) under the assumption that reduction of $\mathrm{Nb_2O_5}$ proceeds according to the reaction

$$\mathrm{Nb_2O_5 + H_2 \rightarrow 2NbO_2 + H_2O}$$

gives for 298.2°K:

$$\Delta H^0_{\mathrm{VI}} = -70.5\ \mathrm{kcal}; \quad \Delta G^0_{\mathrm{VI}} = -65.9\ \mathrm{kcal}; \quad \Delta S^0_{\mathrm{VI}} = -15.6\ \mathrm{kcal}.$$

As an example, we give the values of E of cell B obtained for one experiment:

Temperature, °C	900	1000	1100
E, V* (our data)	0,102	0,131; 0,131	0,166
E, V (according to ([13]))	0,101–0,103	0,132–0,136	0,165–0,166

Fig. 3

The agreement of the values obtained with the literature data ([13]) confirms the correctness of the choice of electrolyte*. The reference electrode ($\mathrm{Fe_{0,95}O}$, Fe) and the electrolyte were prepared as described in ([12]). The electrode under investigation was prepared by pressing pellets from a mixture of calculated amounts of Nb and $\mathrm{Nb_2O_5}$, followed by annealing them at 1700°C for 3 h in vacuum.

For the equilibrium e.m.f. of cell A, the following values were obtained, corresponding to the change in the isobaric potential ($\Delta G^0_{\mathrm{VII}} = -2FE$) of the reaction

$$\mathrm{Fe_{0,95}O + Nb \longrightarrow 0,95Fe + NbO}, \qquad \text{(VII)}$$

Temperature, °C	841	900	900	905	935	940	1000	1000	1000	1071	1071	1073
E, V	0,671	0,675	0,664	0,666	0,666	0,670	0,657	0,669	0,654	0,653	0,658	0,660

From the data presented and from Fig. 3 it is seen that the greatest deviation from the linear dependence of E on T does not exceed $\pm 0,008$ V, i.e., about 1,2% of the measured quantity. The experimental data in the temperature interval studied are described (with an accuracy of $\pm 0,7\%$) by the equation $\Delta G^0_{\mathrm{VII}}$ (cal) $= -34500 + 3,15T$. Using ΔG^0_T of the reactions $\mathrm{Fe}_{0,95}\mathrm{O} + \mathrm{CO} \rightarrow 0,95\mathrm{Fe} + \mathrm{CO}_2$ ([14]) and $\mathrm{CO} + \frac{1}{2}\mathrm{O}_2 \rightarrow \mathrm{CO}_2$ ([15]), and the temperature dependence of the heat capacities of NbO according to ([10]), Nb and O_2 according to ([11]), one can calculate for the reaction of formation of NbO:

$$\mathrm{Nb} + \frac{1}{2}\mathrm{O}_2 \rightarrow \mathrm{NbO}, \qquad \text{(VIII)}$$

$$\Delta G^0_{\mathrm{VIII}}(\mathrm{cal}) = -98450 - 0,564T \lg T - 0,63 \cdot 10^{-3} T^2 - 0,08 \cdot 10^5 T^{-1} + 22,10T \ (298\text{—}1346°\mathrm{K}),$$

Table 1

T, °C	Composition of the equilibrium preparation, gross	Composition of the equilibrium preparation, phase	K_p	T, °C	Composition of the equilibrium preparation, gross	Composition of the equilibrium preparation, phase	K_p
1207	$\mathrm{NbO}_{2,44}$	$\mathrm{Nb_2O_5}$	0,191	1400	$\mathrm{NbO}_{2,00}$	$\mathrm{NbO_2}$	0,0225
1207	$\mathrm{NbO}_{2,37}$	$\mathrm{Nb_2O_5}$, $\mathrm{NbO_2}$	0,131	1400	$\mathrm{NbO}_{2,00}$	Same	0,00508
1207	$\mathrm{NbO}_{2,30}$	Same	0,127	1400	$\mathrm{NbO}_{1,79}$	$\mathrm{NbO_2}$, NbO	0,00306
1207	$\mathrm{NbO}_{2,21}$	Same	0,129	1400	$\mathrm{NbO}_{1,73}$	Same	0,00303
1207	$\mathrm{NbO}_{2,19}$	Same	0,126	1400	$\mathrm{NbO}_{1,40}$	Same	0,00301
1207	$\mathrm{NbO}_{2,00}$	$\mathrm{NbO_2}$	0,115	1400	$\mathrm{NbO}_{1,01}$	NbO	0,00207
1300	$\mathrm{NbO}_{2,42}$	$\mathrm{Nb_2O_5}$	0,261	1450	$\mathrm{NbO}_{1,63}$	$\mathrm{NbO_2}$, NbO	0,00389
1300	$\mathrm{NbO}_{2,33}$	$\mathrm{Nb_2O_5}$, $\mathrm{NbO_2}$	0,176	1500	$\mathrm{NbO}_{1,55}$	Same	0,00496
1300	$\mathrm{NbO}_{2,21}$	Same	0,170	1500	$\mathrm{NbO}_{1,70}$	Same	0,00500
1300	$\mathrm{NbO}_{2,07}$	Same	0,175	1550	$\mathrm{NbO}_{2,00}$	$\mathrm{NbO_2}$	0,0352
1400	$\mathrm{NbO}_{2,20}$	Same	0,229	1550	$\mathrm{NbO}_{1,77}$	$\mathrm{NbO_2}$, NbO	0,00628
1400	$\mathrm{NbO}_{2,09}$	Same	0,236	1550	$\mathrm{NbO}_{1,64}$	Same	0,00618
1400	$\mathrm{NbO}_{2,34}$	Same	0,228	1550	$\mathrm{NbO}_{1,35}$	Same	0,00638

T, °C	Composition of the equilibrium preparation, gross	Composition of the equilibrium preparation, phase	K_p	T, °C	Composition of the equilibrium preparation, gross	Composition of the equilibrium preparation, phase	K_p
1400	$NbO_{2,02}$	NbO_2	0,144	1550	$NbO_{1,12}$	Same	0,00617
1400	$NbO_{2,01}$	Same	0,0812	1550	$NbO_{1,00}$	NbO	0,00234

whence, for 298.2°K: $\Delta G^0_{\mathrm{VIII}} = -92.36$ kcal; $\Delta H^0_{\mathrm{VIII}} = -98.39$ kcal; $\Delta S^0_{\mathrm{VIII}} = -20.19$ e.u. Combining reactions V, VI, and VIII, one can calculate for the reaction of formation of Nb_2O_5 from the elements:

$$2\mathrm{Nb} + \frac{5}{2}\mathrm{O}_2 \rightarrow \mathrm{Nb}_2\mathrm{O}_5 \qquad \text{(IX)}$$

at 298.2°K: $\Delta H^0_{\mathrm{IX}} = -456.9$ kcal; $\Delta G^0_{\mathrm{IX}} = -424.9$ kcal; $\Delta S^0_{\mathrm{IX}} = -107.43$ e.u. and for the reaction of formation of NbO_2 from the elements:

$$\mathrm{Nb} + \mathrm{O}_2 \rightarrow \mathrm{NbO}_2 \qquad \text{(X)}$$

at 298.2°K: $\Delta H^0_{\mathrm{X}} = -193.3$ kcal; $\Delta G^0_{\mathrm{X}} = -179.7$ kcal; $\Delta S^0_{\mathrm{X}} = -45.76$ e.u.

Table 2

Reaction	ΔH^0_{298}, kcal	ΔS^0_{298}	Source	Reaction	ΔH^0_{298}, kcal	ΔS^0_{298}	Source
$2NbO_2 + \frac{1}{2}O_2 \rightarrow Nb_2O_5$	−73.3	−17.77	(17)	$Nb + O_2 \rightarrow NbO_2$	−190.4		(17)
$2NbO_2 + \frac{1}{2}O_2 \rightarrow Nb_2O_5$	−74.0		(18)	$Nb + O_2 \rightarrow NbO_2$	−199.3	−44.68	(18)
$2NbO_2 + \frac{1}{2}O_2 \rightarrow Nb_2O_5$	−75.2		(19)	$Nb + O_2 \rightarrow NbO_2$	−190.4		(23)

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* In preliminary experiments it was established that mixed crystals in the ZrO_2 —CaO system could not serve as the electrolyte because of penetration of the electrode material (apparently, Nb, NbO) into the electrolyte, although for other cells investigated in (12, 13) this electrolyte proved suitable.

Reaction	ΔH^0_{298}, kcal	ΔS^0_{298}	Source	Reaction	ΔH^0_{298}, kcal	ΔS^0_{298}	Source
$2NbO_2 + \frac{1}{2}O_2 \rightarrow Nb_2O_5$	−70.3	−15.9	Our data	$Nb + O_2 \rightarrow NbO_2$	−191.7		(19)
				$Nb + O_2 \rightarrow NbO_2$	−193.3	−45.8	Our data
$NbO + \frac{1}{2}O_2 \rightarrow NbO_2$	−90.5	−22.98	(18)	$2Nb + \frac{5}{2}O_2 \rightarrow Nb_2O_5$	−455.2	−107.21	(20)
$NbO + \frac{1}{2}O_2 \rightarrow NbO_2$	−94.0		(19)	$2Nb + \frac{5}{2}O_2 \rightarrow Nb_2O_5$	−472.6		(18)
$NbO + \frac{1}{2}O_2 \rightarrow NbO_2$	−95.0	−25.6	Our data	$2Nb + \frac{5}{2}O_2 \rightarrow Nb_2O_5$	−454.8		(23)
$Nb + \frac{1}{2}O_2 \rightarrow NbO$	−108.8	−21.57	(18)	$2Nb + \frac{5}{2}O_2 \rightarrow Nb_2O_5$	−458.6		(19)
$Nb + \frac{1}{2}O_2 \rightarrow NbO$	−99.9		(23)	$2Nb + \frac{5}{2}O_2 \rightarrow Nb_2O_5$	−455.1		(21)
$Nb + \frac{1}{2}O_2 \rightarrow NbO$	−97.7	−20.2	(19)	$2Nb + \frac{5}{2}O_2 \rightarrow Nb_2O_5$	−456.9	−107.4	Our data
$Nb + \frac{1}{2}O_2 \rightarrow NbO$	−98.4		Our data				

In Table 2, for comparison, ΔH^0_{298} and ΔS^0_{298} of reactions V, VI, VIII, IX, and X are presented according to the data of various authors: ΔH^0_{298}—calorimetric values obtained (18—21), and ΔS^0_{298}—calculated using entropies at 298.2°K: $S^0_{Nb} = 8.73$ (11); $S^0_{NbO} = 11.5$ (11); $S^0_{NbO_2} = 13.07$ (16); $S^0_{Nb_2O_5} = 32.8$ (11) and $S^0_{O_2} = 49.02$ (11).

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