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Abstract

Full Text

Physical Chemistry

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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 $\text{NbO}_{2.5}$ to $\text{NbO}_{2.4}^*$, 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.

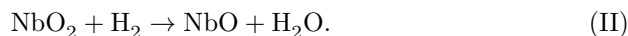
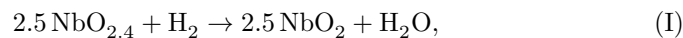
[Figure 1 schematic not reproduced]

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 $1200-1550^\circ\text{C}$ 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



The values of the equilibrium constants $K_p = P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ are presented in Table 1 and in Fig. 1. In the composition range from $\text{NbO}_{2.4}$ to $\text{NbO}_{2.5}$, 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

* Nb_2O_5 remains homogeneous within the limits from $\text{NbO}_{2.5}$ to $\text{NbO}_{2.39}$ according to ⁽¹⁾ and from $\text{NbO}_{2.5}$ to $\text{NbO}_{2.42}$ according to ⁽⁶⁾.

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

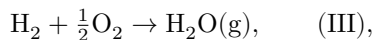
$$\lg K_{\text{pI}} = -15050/4.575T + 1.3306 \quad (1480 - 1673^\circ\text{K}),$$

$$\lg K_{\text{pII}} = -29490/4.575T + 1.3334 \quad (1673 - 1823^\circ\text{K}),$$

whence

$$\Delta G_{\text{I}}^0(\text{cal}) = 15050 - 6.087T, \quad \Delta G_{\text{II}}^0(\text{cal}) = 29490 - 6.10T.$$

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

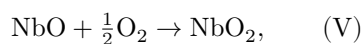
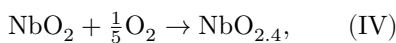


whose isobaric potential according to Chipman ⁽⁹⁾ is expressed by the equation

$$\Delta G_{\text{III}}^0(\text{cal}) = -59251 + 2.006T \lg T - 7.5 \cdot 10^{-5}T^2 + 4.08 \cdot 10^5T^{-1} + 6.8085T,$$

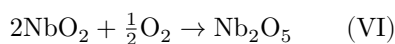
and using literature data on the heat capacities of NbO_2 and NbO according to ⁽¹⁰⁾ and for O_2 according to ⁽¹¹⁾, one can calculate ΔG_{VI}^0 (respectively ΔH_{VI}^0 and ΔH_{V}^0) for the reactions of formation of $\text{NbO}_{2.4}$ and NbO_2 at 298.2°K for the reactions

Fig. 2



$$\begin{aligned} \Delta G_{\text{IV}}^0 &= -26.2 \text{ kcal}; \quad \Delta H_{\text{IV}}^0 = -28.1 \text{ kcal}; \quad \Delta S_{\text{IV}}^0 = -6.36 \text{ e.u.}; \quad \Delta G_{\text{V}}^0 = \\ &= -87.33 \text{ kcal}; \quad \Delta H_{\text{V}}^0 = -94.95 \text{ kcal}; \quad \Delta S_{\text{V}}^0 = -25.57 \text{ e.u.} \end{aligned}$$

For the reaction of formation of Nb_2O_5 from NbO_2 :



linearly extrapolating from the composition $\text{NbO}_{2.4}$ to $\text{NbO}_{2.5}$, we obtain at 298.2°K:

$$\Delta H_{\text{VI}}^0 = -70.25 \text{ kcal}; \quad \Delta G_{\text{VI}}^0 = -65.5 \text{ kcal}; \quad \Delta S_{\text{VI}}^0 = -15.91 \text{ e.u.}^*$$

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



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

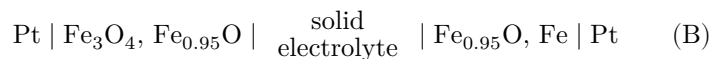
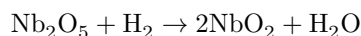


Fig. 3

Figure 2: Fig. 3

*

The calculation of ΔG_{VI}^0 (respectively ΔH_{VI}^0 and ΔS_{VI}^0) under the assumption that reduction of Nb_2O_5 proceeds according to the reaction



gives for 298.2°K:

$$\Delta H_{\text{VI}}^0 = -70.5 \text{ kcal}; \quad \Delta G_{\text{VI}}^0 = -65.9 \text{ kcal}; \quad \Delta S_{\text{VI}}^0 = -15.6 \text{ kcal}.$$

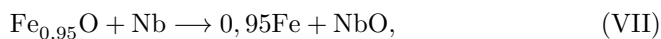
As an example, we give the values of E of cell B obtained for one experiment:

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 ($\text{Fe}_{0,95}\text{O}$, 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 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 ($\Delta G_{\text{VII}}^0 = -2FE$) of the reaction



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 ΔG_{VII}^0 (cal) = $-34500 + 3,15T$. Using ΔG_T^0 of the reactions $\text{Fe}_{0,95}\text{O} + \text{CO} \rightarrow 0,95\text{Fe} + \text{CO}_2$ ⁽¹⁴⁾ and $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$ ⁽¹⁵⁾, and the temperature dependence of the heat capacities of NbO according to ⁽¹⁰⁾, Nb and O₂ according to ⁽¹¹⁾, one can calculate for the reaction of formation of NbO:



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

Table 1

T, °C	Composition of the equilibrium preparation, gross phase			K_p	T, °C	Composition of the equilibrium preparation, gross phase			K_p
	Composition of the equilibrium preparation, gross phase	Composition of the equilibrium preparation, gross phase	Composition of the equilibrium preparation, gross phase			Composition of the equilibrium preparation, gross phase	Composition of the equilibrium preparation, gross phase	Composition of the equilibrium preparation, gross phase	
1207	NbO _{2,44}	Nb ₂ O ₅		0,191	1400	NbO _{2,00}	NbO ₂		0,0225
1207	NbO _{2,37}	Nb ₂ O ₅ , NbO ₂		0,131	1400	NbO _{2,00}	Same		0,00508
1207	NbO _{2,30}	Same		0,127	1400	NbO _{1,79}	NbO ₂ , NbO		0,00306
1207	NbO _{2,21}	Same		0,129	1400	NbO _{1,73}	Same		0,00303
1207	NbO _{2,19}	Same		0,126	1400	NbO _{1,40}	Same		0,00301
1207	NbO _{2,00}	NbO ₂		0,115	1400	NbO _{1,01}	NbO		0,00207
1300	NbO _{2,42}	Nb ₂ O ₅		0,261	1450	NbO _{1,63}	NbO ₂ , NbO		0,00389
1300	NbO _{2,33}	Nb ₂ O ₅ , NbO ₂		0,176	1500	NbO _{1,55}	Same		0,00496
1300	NbO _{2,21}	Same		0,170	1500	NbO _{1,70}	Same		0,00500
1300	NbO _{2,07}	Same		0,175	1550	NbO _{2,00}	NbO ₂		0,0352
1400	NbO _{2,20}	Same		0,229	1550	NbO _{1,77}	NbO ₂ , NbO		0,00628
1400	NbO _{2,09}	Same		0,236	1550	NbO _{1,64}	Same		0,00618
1400	NbO _{2,34}	Same		0,228	1550	NbO _{1,35}	Same		0,00638

T, °C	Composition of the equilibrium preparation, gross			K_p	T, °C	Composition of the equilibrium preparation, gross		
	of the equilibrium preparation, gross	of the equilibrium preparation, phase				of the equilibrium preparation, gross	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

* In preliminary experiments it was established that mixed crystals in the ZrO₂–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.

whence, for 298.2°K: $\Delta G_{\text{VIII}}^0 = -92.36$ kcal; $\Delta H_{\text{VIII}}^0 = -98.39$ kcal; $\Delta S_{\text{VIII}}^0 = -20.19$ e.u. Combining reactions V, VI, and VIII, one can calculate for the reaction of formation of Nb₂O₅ from the elements:



at 298.2°K: $\Delta H_{\text{IX}}^0 = -456.9$ kcal; $\Delta G_{\text{IX}}^0 = -424.9$ kcal; $\Delta S_{\text{IX}}^0 = -107.43$ e.u. and for the reaction of formation of NbO₂ from the elements:



at 298.2°K: $\Delta H_{\text{X}}^0 = -193.3$ kcal; $\Delta G_{\text{X}}^0 = -179.7$ kcal; $\Delta S_{\text{X}}^0 = -45.76$ e.u.

Table 2

Reaction	ΔH_{298}^0 , kcal	ΔS_{298}^0	Source	Reaction	ΔH_{298}^0 , kcal	ΔS_{298}^0	Source
2NbO ₂ + $\frac{1}{2}$ O ₂ → Nb ₂ O ₅	-73.3	-17.77	(17)	Nb + O ₂ → NbO ₂	-190.4		(17)
2NbO ₂ + $\frac{1}{2}$ O ₂ → Nb ₂ O ₅	-74.0		(18)	Nb + O ₂ → NbO ₂	-199.3	-44.68	(18)
2NbO ₂ + $\frac{1}{2}$ O ₂ → Nb ₂ O ₅	-75.2		(19)	Nb + O ₂ → NbO ₂	-190.4		(23)

Reaction	ΔH_{298}^0 , kcal	ΔS_{298}^0	Source	Reaction	ΔH_{298}^0 , kcal	ΔS_{298}^0	Source
$2\text{NbO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{Nb}_2\text{O}_5$	-70.3	-15.9	Our data	$\text{Nb} + \text{O}_2 \rightarrow \text{NbO}_2$	-191.7		(19)
$\text{NbO} + \frac{1}{2}\text{O}_2 \rightarrow \text{NbO}_2$	-90.5	-22.98	(18)	$\text{Nb} + \text{O}_2 \rightarrow \text{NbO}_2$	-193.3	-45.8	Our data
$\text{NbO} + \frac{1}{2}\text{O}_2 \rightarrow \text{NbO}_2$	-94.0		(19)	$2\text{Nb} + \frac{5}{2}\text{O}_2 \rightarrow \text{Nb}_2\text{O}_5$	-455.2	-107.21	(20)
$\text{NbO} + \frac{1}{2}\text{O}_2 \rightarrow \text{NbO}_2$	-95.0	-25.6	Our data	$2\text{Nb} + \frac{5}{2}\text{O}_2 \rightarrow \text{Nb}_2\text{O}_5$	-472.6		(18)
$\text{Nb} + \frac{1}{2}\text{O}_2 \rightarrow \text{NbO}$	-108.8	-21.57	(18)	$2\text{Nb} + \frac{5}{2}\text{O}_2 \rightarrow \text{Nb}_2\text{O}_5$	-454.8		(23)
$\text{Nb} + \frac{1}{2}\text{O}_2 \rightarrow \text{NbO}$	-99.9		(23)	$2\text{Nb} + \frac{5}{2}\text{O}_2 \rightarrow \text{Nb}_2\text{O}_5$	-458.6		(19)
$\text{Nb} + \frac{1}{2}\text{O}_2 \rightarrow \text{NbO}$	-97.7	-20.2	(19)	$2\text{Nb} + \frac{5}{2}\text{O}_2 \rightarrow \text{Nb}_2\text{O}_5$	-455.1		(21)
$\text{Nb} + \frac{1}{2}\text{O}_2 \rightarrow \text{NbO}$	-98.4		Our data	$2\text{Nb} + \frac{5}{2}\text{O}_2 \rightarrow \text{Nb}_2\text{O}_5$	-456.9	-107.4	Our data

In Table 2, for comparison, ΔH_{298}^0 and ΔS_{298}^0 of reactions V, VI, VIII, IX, and X are presented according to the data of various authors: ΔH_{298}^0 —calorimetric values obtained (18–21), and ΔS_{298}^0 —calculated using entropies at 298.2°K: $S_{\text{Nb}}^0 = 8.73$ (11); $S_{\text{NbO}}^0 = 11.5$ (11); $S_{\text{NbO}_2}^0 = 13.07$ (16); $S_{\text{Nb}_2\text{O}_5}^0 = 32.8$ (11) and $S_{\text{O}_2}^0 = 49.02$ (11).

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CITED LITERATURE

1. G. Brauer, *Zs. anorg. u. allgem. Chem.*, **248**, 1 (1941).
2. S. I. Alyamovskii, G. P. Shveikin, P. V. Gel'd, *ZhNKh*, issue 3, 2437 (1958).

3. R. Süe, *C. R.*, **208**, 1088 (1939).
4. R. Süe, *J. Chim. Phys.*, **36**, 280 (1939).
5. G. Grube, O. Kubaschewski, K. Zwiauer, *Zs. Elektrochem.*, **45**, 885 (1939).
6. G. Grube, M. Flad, *KWJ Metallforschung*, Stuttgart, 1945.
7. H. Schäfer, I. Breil, *Zs. anorg. Chem.*, **267**, 265 (1952).
8. L. A. Zharkova, V. M. Lavrent'ev et al., *DAN*, **134**, 872 (1960).
9. I. Chipman, *Trans. Am. Soc. Metals*, **22**, 385 (1934).
10. P. V. Gel'd, R. G. Kusenko, *Izv. AN SSSR, OKhN*, 1960, No. 2, 79.
11. O. Kubaschewski, E. Evans, *Metallurgical thermochemistry*, 1958.
12. T. N. Rezhukhina, V. I. Lavrent'ev et al., *ZhFKh*, in press.
13. K. Kiukkola, C. Wagner, *J. Electrochem. Soc.*, **104**, 379 (1957).
14. L. S. Darken, R. W. Gurry, *J. Am. Chem. Soc.*, **67**, 1938 (1945).
15. H. Peters, H. H. Möbius, *Zs. phys. Chem.*, **209**, 298 (1958).
16. E. G. King, *J. Am. Chem. Soc.*, **76**, 3289 (1954).
17. A. Mah, *J. Am. Chem. Soc.*, **80**, 3872 (1958).
18. M. P. Morozova, L. L. Getskina, *ZhOKh*, **29**, 1049 (1959).
19. F. G. Kusenko, P. V. Gel'd, Siberian Branch, Academy of Sciences of the USSR, No. 2 (1960).
20. G. L. Humphrey, *J. Am. Chem. Soc.*, **76**, 978 (1954).
21. F. G. Kusenko, P. V. Gel'd, *ZhOKh*, **30**, No. 11 (1960).
22. O. Kubaschewski, A. A. Catteral, *Thermochemical data of alloys*, 1956.
23. M. P. Morozova, T. A. Stolyarova, *ZhOKh*, **30**, 3848 (1960).

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