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Thermodynamic Study of Niobium Oxides with O/Nb Ratios from 2.47 to 2.50 Using a High-Temperature Galvanic Cell

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The partial molar free energy, enthalpy, and entropy of oxygen in niobium oxides with O/Nb ratios from 2.47 to 2.50 were measured with a galvanic cell in the temperature range from 1084 to 1325 K. The partial molar enthalpies of oxygen of the Nb_2O_{5-x} and V phases were observed to be nearly independent of composition, indicating the presence of only weak interactions between defects. The value of the slope for the plots of log x in Nb_2O_{5-x} against log P_{O_2} was observed to be $-1/5.2$ which is interpreted in terms of a defect structure involving both singly ionized and doubly ionized oxygen vacancies. The previously proposed phase diagram in the vicinity of Nb_2O_{5-x} was confirmed by the present emf measurements.

Introduction

The phase relations, defect structures, and thermodynamic properties in the niobium–oxygen system have been studied by many investigators, and the results have been recently reviewed by the present authors (*1*).

As indicated in the review, thermodynamic quantities such as the partial molar enthalpy and entropy of oxygen in niobium oxides near Nb_2O_5 reported previously are inconsistent; for example, the values of the partial molar enthalpy of oxygen vary from -531 to -1074 kJ · mole^{-1} (*3–7*), and the presence of intermediate phases (*1, 2, 6, 8, 9*) between NbO_2 and Nb_2O_5 was scarcely considered in most studies. It is also noted that the compositional dependence of the partial molar entropy has not been discussed in relation to defect structures in the papers previously reported.

In the present study, the oxygen partial pressure of the Nb_2O_{5-x}, V, IV, V + II, and V + IV phases (*2*) (see Fig. 4) was measured with a galvanic cell in the temperature range from 1084 to 1325 K to determine the partial molar enthalpy and entropy of oxygen, to elucidate the defect structure of Nb_2O_{5-x}, and also to confirm the previously reported phase diagram in the vicinity of Nb_2O_5.

Experimental

1. *Samples*

The Nb_2O_5 powder (99.99% purity) purchased was heated in air at 1023 K for about 3 hr before use to adjust the composition to be stoichiometric. Spectroscopic analysis of Nb_2O_5 powder showed the following main impurities (oxide in Nb_2O_5, weight ppm): Mn < 1, Mg < 1, Cr < 1, Al < 2, Fe < 2, V < 2, Sn < 2, Ti < 3, Zr < 3, W < 5, Mo < 10, Si < 10, and Ta < 30. The NbO_2

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powder was prepared by reducing Nb_2O_5 powder in a stream of dried hydrogen gas at 1273 K for 30 hr. The samples with O/Nb ratios from 2.4700 to 2.4994 were prepared by mixing the NbO_2 and Nb_2O_5 powders in appropriate ratios. The mixed powders were pressed into pellets and then sintered in evacuated and sealed quartz tubes at 1298 K for about 1080 hr. After sintering, the size of the pellets was about 8 mm in diameter and from 3 to 7 mm thick. The phases existing in the samples were identified by X-ray diffractometry. The oxygen content of the sample pellets was determined from the weight gain by oxidizing them to stoichiometric Nb_2O_5 in air at 1023 K for 50 hr.

2. *Electromotive Force Measurements*

The galvanic cell employed in this study was of the type

$$Nb_2O_{5-x}|\text{solid electrolyte}|\text{air}. \qquad (1)$$

The cell system is schematically shown in Fig. 1. A calcia (or yttria) stabilized zirconia tube (ZrO_2 + 15% mole% CaO (or Y_2O_3)) with a flat closed end with inner diameter 17 mm, thickness 2 mm, and length 500 mm was used, as the solid electrolyte. Platinum paste was coated on the bottom of the inside surface of the closed end of the zirconia tube.

Platinum gauze with a platinum lead wire was then pushed against this paste with an alumina tube to obtain good contact. The alumina tube was also used for the air flow path into the inside of the zirconia tube. A sample pellet was placed against the outer flat surface of the closed end of the zirconia tube, and platinum foil was in turn placed against the sample. The platinum foil was pushed with a quartz pellet and a spring to ensure good contact with the sample. Argon gas, purified by passing through a titanium sponge oxygen getter, was used as the atmosphere on the sample side. This inert atmosphere ensures that the emf measured by the cell is due to the sample, and not to the P_{O_2} of the atmosphere on the outside of the zirconia cell. On the sample side, several pieces of pellets with the same O/Nb composition as the sample pellet were placed near the sample to prevent it from being oxidized.

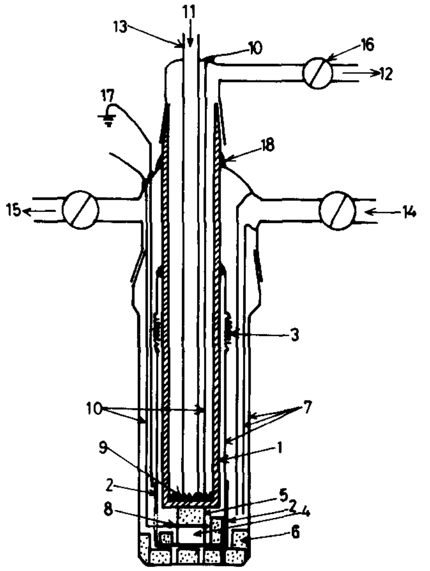

FIG. 1. Schematic diagram of the galvanic cell assembly (1) solid electrolyte tube, (2) Pt cover, (3) spring (4) quartz pellet, (5) sample pellet, (6) pellets for oxygen getter, (7) quartz tube, (8) Pt foil, (9) Pt paste and gauze, (1) Pt lead wire, (11) air inlet, (12) air outlet, (13) alumina tube, (14) Ar inlet, (15) Ar outlet, (16) glass stopcock, (17) ground, (18) araldite seal.

Electrical noise from the furnace was eliminated by placing a platinum foil cover around the sample and a grounded stainless-steel tube between the furnace and the quartz tube. The electromotive force measurements were carried out with a high impedance ($>10^9$ ohm) microvoltmeter.

The partial molar free energy of oxygen in niobium oxide samples ($\Delta\bar{G}_{O_2}$) is obtained from the equation

$$\Delta\bar{G}_{O_2} = 4EF + \Delta\bar{G}_{O_2}(\text{r}), \qquad (2)$$

where E is the electromotive force in millivolts, F the Faraday constant (23.069 cal/mV equivalent), and $\Delta\bar{G}_{O_2}$ (r) the partial molar free energy of oxygen in the reference gas. The partial molar enthalpy and entropy of oxygen of samples were calculated from the value of $\Delta\bar{G}_{O_2}$ thus obtained.

The galvanic cell was calibrated by measuring the oxygen potential of a two-phase mixture of Ni and NiO. The results obtained were in good agreement with those of Kiukkola and Wagner (*10*) and Saito (*11*) using a galvanic cell. Uncertainty in the $\Delta\bar{G}_{O_2}$ values is estimated to be at most ±1.1 kJ · mole^{-1} in the temperature range from 1073 to 1373 K.

Results and Discussion

1. *Thermodynamic Quantities*

The partial molar free energies of oxygen ($\Delta\bar{G}_{O_2}$) of Nb_2O_{5-x} and intermediate phases (V, IV, V + IV, V + II) between NbO_2 and Nb_2O_5 which are calculated from the electromotive force by Eq. (2) are shown against temperature in Figs. 2 and 3, respectively. A good linear relationship between $\Delta\bar{G}_{O_2}$ and temperature and also good reproducibility of the $\Delta\bar{G}_{O_2}$ values with increasing and decreasing temperature are seen in these figures; the former fact indicates little temperature dependence of the partial molar enthalpy ($\Delta\bar{H}_{O_2}$) and entropy ($\Delta\bar{S}_{O_2}$) of oxygen of each phase in the temperature range measured in this study and the latter indicates no compositional change of the sample pellets within the experimental error during measurements. A change of slope in the plot of $\Delta\bar{G}_{O_2}$ vs temperature was observed at 1258 K for both $NbO_{2.4802}$ and $NbO_{2.4700}$ as shown in Fig. 3, although no slope change was seen for Nb_2O_{5-x} and $NbO_{2.4900}$. X-ray analysis of the samples quenched above and below 1258 K revealed that this temperature corresponded to the transition temperature from single phase V to a two-phase mixture of IV + V for $NbO_{2.4802}$ and from a two-phase mixture of II + V to single phase IV for $NbO_{2.4700}$. These phase transitions are consistent with the phase diagram for the

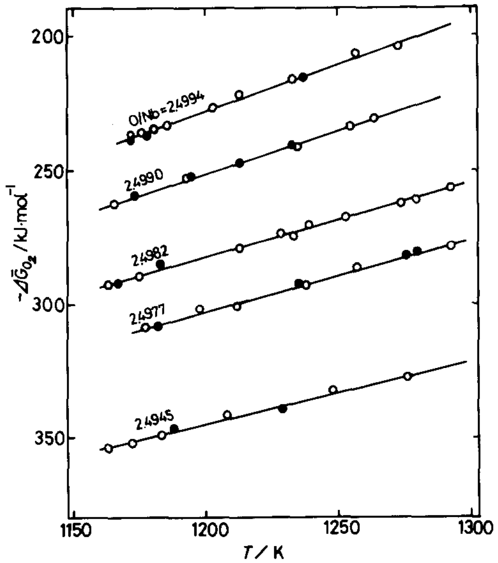

FIG. 2. Temperature dependence of the partial molar free energy of oxygen of Nb_2O_{5-x}. (○) Increasing temperature, (●) decreasing temperature.

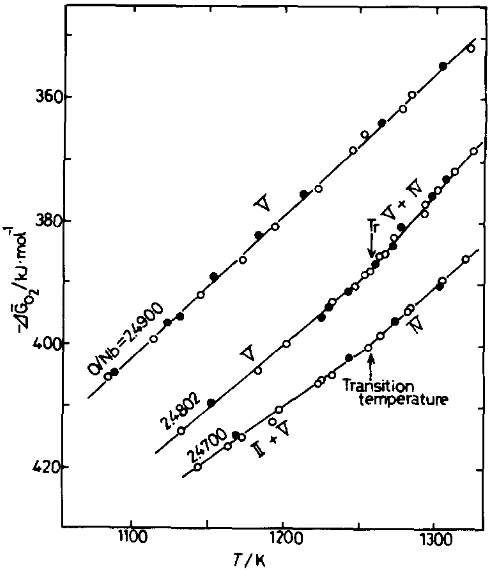

FIG. 3. Temperature dependence of the partial molar free energy of oxygen of $NbO_{2.4700}$, $NbO_{2.4802}$, and $NbO_{2.4900}$. (○) Increasing temperature, (●) decreasing temperature.

system between NbO_2 and Nb_2O_5 based on the electrical conductivity measurements by Naito *et al.* (*2*), which is shown in Fig. 4.

The partial molar enthalpy and entropy of oxygen in Nb_2O_{5-x} calculated from $\Delta\bar{G}_{O_2}$ values are shown in Figs. 5 and 6, respectively, and summarized in Table I together with the results previously reported (*3–7*). The partial molar enthalpy of oxygen of Nb_2O_{5-x} was observed to be nearly independent of composition, suggesting the presence of only a weak interaction between defects (line g). An absence in compositional dependence of $\Delta\bar{H}_{O_2}$ of Nb_2O_{5-x} has been also reported by Blumenthal *et al.* (line d) (*3*), Kofstad and Anderson (line b) (*4*), and Wimmer and Tripp (line c) (*5*), though their values of $\Delta\bar{H}_{O_2}$ are lower than the present result. According to the phase diagram shown in Fig. 4, the compositional regions, where the measurements by Blumenthal *et al.* (*3*) and Kofstad and Anderson (*4*) were carried out, do not correspond to a single Nb_2O_5 phase region, but also include other intermediate phases: II, IV, and V phases for the case of Blumenthal *et al.* and III, IV, V, X, Y, and Z phases for Kofstad and Anderson. Hence, the partial molar enthalpies of oxygen reported as those of Nb_2O_{5-x} by them (*3, 4*) are considered to correspond to the average values for many homologous phases including Nb_2O_{5-x}. Only the partial molar enthalpy reported by Wimmer and Tripp (line c) (*5*) is thought to be that for single-phase Nb_2O_{5-x}, considering the compositional region measured by them. The disagreement in the partial molar enthalpy of Nb_2O_{5-x} between the present (1163–1293 K) and the previous results by Wimmer and Tripp (1223–1573 K) may be caused partly by the difference in the temperature of the measurements. The partial molar enthalpy and entropy of oxygen of phases V, IV, and two-phase mixtures V + IV and V + II ($Nb_{12}O_{29}$) obtained in this

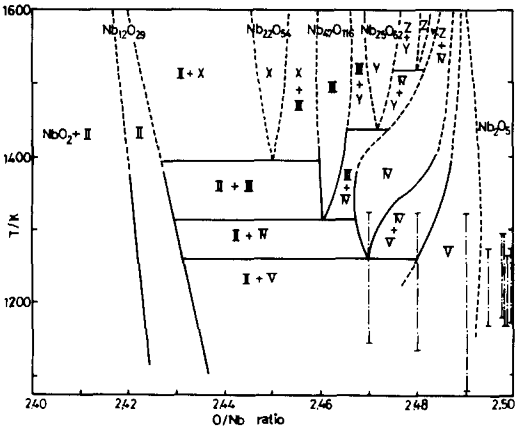

FIG. 4. Phase diagram of the system between NbO_2 and the Nb_2O_5. (–·–·) The composition and temperature range measured in this study.

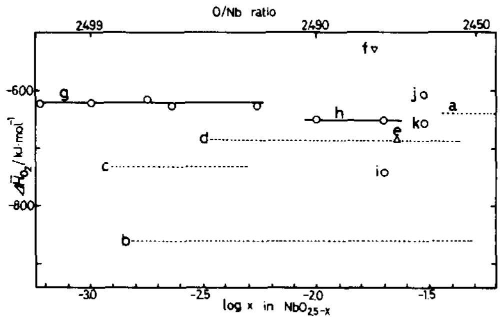

FIG. 5. The compositional dependence of the partial molar enthalpy of oxygen. (a) $NbO_{2.42}$ + $NbO_{2.47}$ (*6*); (b) Nb_2O_{5-x} (*4*); (c) Nb_2O_{5-x} (*5*); (d) Nb_2O_{5-x} (*3*); (e) $NbO_{2.477}$ (*7*); (f) $NbO_{2.482}$ (*7*). Present results (○) for: (g) Nb_2O_{5-x}; (h) phase V; (i) V + IV; (j) V + II; and (k) IV.

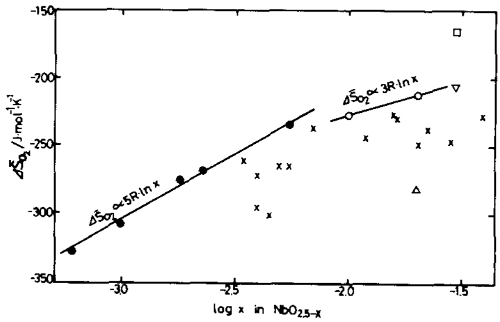

FIG. 6. The compositional dependence of the partial molar entropy of oxygen. (×) Previous results (*3*); present study: (●) Nb_2O_{5-x}, (○) V, (△) V + IV, (▽) IV, and (□) V + II.

TABLE I

PARTIAL MOLAR ENTHALPIES AND ENTROPIES OF OXYGEN OF Nb_2O_{5-x}

Phases	O/Nb	$-\Delta\bar{H}_{O_2}$ (kJ · mole^{-1})	$-\Delta\bar{S}_{O_2}$ (J K^{-1} · mole^{-1})	Temp. (K)	Method	Ref.
(II, III, IV, V, Nb_2O_5)[a]	2.461 -2.497	722–667 (av. 686)	228–301	1073–1343	EMF	*3*
(X, Y, Z, III, IV, V, Nb_2O_{5-x})[a]	2.4500–2.4985	862	—	1200–1683	TGA	*4*
Nb_2O_{5-x}	2.4950–2.4988	732	—	1223–1573	TGA	*5*
Nb_2O_{5-x}	2.4994 ± 0.0002	622 ± 20	329 ± 16	1163–1293	EMF	This study
	0.4990 ± 0.0002	621 ± 8	308 ± 6			
	2.4982 ± 0.0002	613 ± 7	275 ± 6			
	2.4977 ± 0.0002	625 ± 8	269 ± 7			
	2.4945 ± 0.0002	627 ± 15	235 ± 12			

[a] The phases in parentheses are estimated from the original data in the literature (*3*, *4*) by the present authors according to the classification reported by Naito *et al.* (*2*).

TABLE II

PARTIAL MOLAR ENTHALPIES AND ENTROPIES OF OXYGEN OF INTERMEDIATE PHASES BETWEEN NbO_2 AND Nb_2O_5

Phases	O/Nb	$-\Delta\bar{H}_{O_2}$ (kJ · mole^{-1})	$-\Delta\bar{S}_{O_2}$ (J K^{-1} · mole^{-1})	Temp. (K)	Method	Ref.
$NbO_{2.42}$ + $NbO_{2.47}$	2.424–2.468	645.4[b]	185.6[b]	1273–1373	TGA	*6*
$NbO_{2.47}$ + $NbO_{2.50}$	2.472–2.488	1073.5[b]	528.0[b]	1273–1373	TGA	*6*
(II + V)[a]	2.477	690.4	—	1253	TGA	*7*
(V)[a]	2.482	531.4	—	1253	TGA	*7*
IV	2.4700 ± 0.0005	658 ± 20	206 ± 1	1258–1325	EMF	This study
V + II($Nb_{12}O_{29}$)	2.4700 ± 0.0005	609 ± 25	166 ± 2	1144–1258		
V	2.4802 ± 0.0002	653 ± 5	211 ± 4	1124–1258		
V	2.4900 ± 0.0002	652 ± 12	227 ± 1	1084–1323		
V + IV	2.4802 ± 0.0002	739 ± 29	280 ± 2	1258–1324		

[a] The phases in parentheses are estimated from the original data in the literature (*7*) by the present authors according to the classification reported by Naito *et al.* (*2*).

[b] These values are calculated from the original data in the literature (*6*) by the present authors.

study are also shown in Figs. 5 and 6, respectively. Though the partial molar enthalpy of oxygen of a two-phase mixture of V + II is a little higher than that of Nb_2O_{5-x}, those of phases V, IV, and a two-phase mixture of V + IV are lower than those of Nb_2O_{5-x}. It is noted that the partial molar enthalpy of oxygen of Nb_2O_{5-x} reported by Blumenthal *et al.* (*3*) nearly corresponds to the average value of the phases V + IV, V + II, IV, and V determined in this study. The partial molar enthalpy of oxygen of phase V was observed to be nearly independent of composition, similar to that of Nb_2O_{5-x}.

The enthalpies of formation of niobium oxides (NbO_x, $0.324 \leqq x \leqq 2.490$) have been measured by Inaba *et al.* (*13*) with a Tian-Calvet-type calorimeter and they suggested a higher value (-476 kJ $\cdot$ mole^{-1}) than the literature values (*3–6*) as the average of the partial molar enthalpy of oxygen in the region between $NbO_{2.42}$ and $NbO_{2.50}$. Although the partial molar enthalpies of oxygen obtained in this study were found to be higher than the values reported previously (*3–6*), except that of $NbO_{2.482}$ by Grude and Flad (*7*) as seen in Fig. 5, they are still not high enough to explain the average value -476 kJ $\cdot$ mole^{-1} proposed by calorimetry. This discrepancy suggests that the partial molar enthalpy of oxygen of phase IV may vary largely with the composition, $2.468 \leqq$ O/Nb $\leqq 2.472$ at 1300 K. To clarify the discrepancy, a thermodynamic study of niobium oxides with O/Nb ratio less than 2.47 with a galvanic cell utilizing a thoria–yttria solid electrolyte is required, in order to measure very low oxygen partial pressures.

The partial molar entropies of oxygen of Nb_2O_{5-x}, V, IV, a two-phase mixture of V + II and that of V + IV obtained in this study are given in Fig. 6 together with the results reported previously (*3*). A linear relationship between $\Delta\bar{S}_{O_2}$ and log x is seen for Nb_2O_{5-x} and phase V, indicating the presence of a single type of defects with a weak interaction between them. In the $\Delta\bar{S}_{O_2}$ data for the phase Nb_2O_{5-x} reported by Blumenthal *et al.* (*3*), which is shown if Fig. 6, it is difficult to observe the presence of a linear relationship between $\Delta\bar{S}_{O_2}$ and log x, presumably owing to the scatter of the data. It is also noted from the figure that the values of $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ obtained for a two-phase mixture of V + II and those for V + IV are higher and lower than those of phase V, respectively, which indicates that the values of $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ for phases II and IV near the phase boundary with phase V are higher and lower than those of phase V, respectively. The values of $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ for phase IV (O/Nb = 2.4700) obtained in this study, however, are close to those of phase V as seen in Figs. 5 and 6, which implies that the values of $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ for phase IV decrease rapidly with increasing O/Nb ratio. The partial molar enthalpy and entropy of oxygen for a two-phase mixture of V + IV calculated preliminary, $\Delta\bar{H}_{O_2} = -1005$ kJ $\cdot$ mole^{-1} and $\Delta\bar{S}_{O_2} = -469$ J $\cdot$ mole^{-1} $\cdot$ K^{-1} by the present authors (*1*) from the data of the electrical conductivity measurements (1283–1473 K) by Naito *et al.* (*2*) are lower than those of V + IV obtained in this study. Since the O/Nb ratio of phase IV at the phase boundary with phase V increases rapidly with temperature as seen in Fig. 4, it is expected that the values of $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ for a two-phase mixture of V + IV obtained at higher temperature from the electrical conductivity measurements are lower than those obtained in this study at lower temperature.

2. *Defect Structure*

The relations between log x in Nb_2O_{5-x} and log P_{O_2} obtained in this study are shown in Fig. 7 together with the results reported previously for homologous phases between NbO_2 and Nb_2O_5 (*2–5, 10*). The discontinuities in the figure (line a) show the presence of homologous phases (*2*).

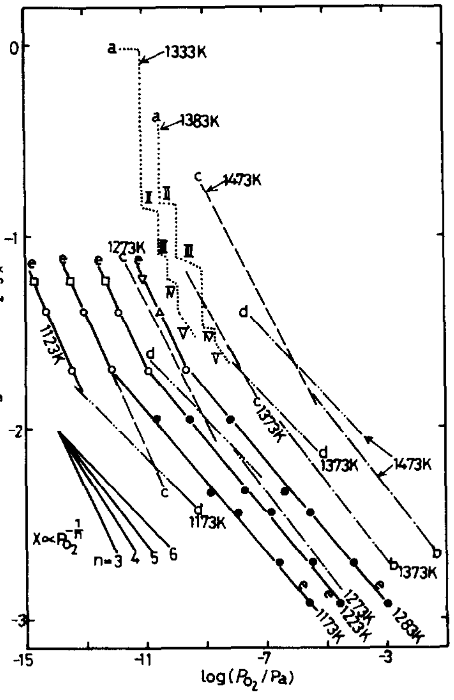

FIG. 7. The relation between log x in Nb_2O_{5-x} and oxygen partial pressure for the phases between NbO_2 and Nb_2O_5. (a, . . .) Naito *et al.* (*2*); (b, —·—·) Wimmer and Tripp (*5*); (c, ----) Blumenthal *et al.* (*3*); (d, —··—··) Kofstad and Anderson (*4*, *12*); (e, present results): –●–, Nb_2O_{5-x}; –○–, phase V; ▽, phase IV; △, V + IV; □, V + II.

The value of the slope for the plots of log x in Nb_2O_{5-x} against log P_{O_2} in this study is $-1/5.2$ in the temperature range from 1173 to 1283 K. This value is in good agreement with the value $-1/5$ for Nb_2O_{5-x} reported by Wimmer and Tripp (*3*), although the composition x in Nb_2O_{5-x} in the present study is a little larger than their composition at the same oxygen partial pressure. The value of the slope $-1/5.2$ is close to $-1/5$. The latter can be interpreted by a defect model involving both singly ionized oxygen vacancies ($V_O^{\cdot}$) and doubly ionized oxygen vacancies ($V_O^{\cdot\cdot}$) with the concentration ratio $V_O^{\cdot}/V_O^{\cdot\cdot} = 2$, provided that the concentration ratio scarcely varies with the oxygen partial pressure. The value $-1/5.2$ obtained in this study, which can be interpreted by a defect ratio of $V_O^{\cdot}/V_O^{\cdot\cdot} = 1.3$, is somewhat different from the values $-1/4.2$ to $-1/4.8$ determined from the oxygen partial pressure dependence of the electrical conductivity in the temperature range from 1283 to 1573 K by Naito *et al.* (*2*). This difference in slope is probably due to the different in temperature measured, which causes the difference in the concentration ratio $V_O^{\cdot}/V_O^{\cdot\cdot}$. The value of slope of the straight line in the plot of the partial molar entropies of oxygen against log x in $NbO_{2.5-x}$ in Fig. 6 is about 23 ($=5R \times 2.3$). This value is directly derived from the value of the slope for the plots of log x against log P_{O_2} shown in Fig. 7, since log P_{O_2} is considered to be proportional to $\Delta\bar{S}_{O_2}$ when the value of $\Delta\bar{H}_{O_2}$ is nearly constant against composition (x).

The slope for the plots of log x against log P_{O_2} for phase V is about $-1/3$ in the temperature range from 1123 to 1223 K as shown in Fig. 7, which corresponds to the value of the slope ($3R \times 2.3$) of the straight line in the plot of the partial molar entropy of oxygen against log x in phase V in Fig. 6. This slope $-1/3$ is different from the values $-1/7.8$ to $-1/4.7$ which were determined from the slopes for the plots of log σ vs log P_{O_2} for phase V (σ: electrical conductivity) in the temperature range from 1283 to 1573 K (*2*). The complex defect consisting of a $Nb_{25}O_{62}$-type Wadsley defect and singly ionized oxygen vacancy has been proposed to explain the oxygen partial pressure dependence of the electrical conductivity for phase V (*2*). A defect structure consisting of oxygen vacancies, quasi-free electrons, and tetravalent niobium ions has been proposed for phases X, Y, and Nb_2O_{5-x} by Kikuchi and Goto (*14*) and for phase IV by Marucco (*15*). To interpret the oxygen partial pressure dependence of both log σ and log x for phase V without contradiction, a similar defect model involving neutral oxygen vacancies, neutral and singly ionized $Nb_{25}O_{62}$-type Wadsley defects (V_{wad} and $V_{\mathrm{wad}}^{\cdot}$), quasi-free electrons, and tetravalent niobium ions is assumed. The defect equations are written as

$$\mathrm{O_0} = V_0 + \tfrac{1}{2}\mathrm{O_2}, \tag{3}$$

$$K_1 = [V_0] \cdot P_{\mathrm{O_2}}^{1/2}, \tag{4}$$

$$25\mathrm{Nb_{28}O_{70}} = 28\mathrm{Nb_{25}O_{62}} + 7\mathrm{O_2}, \tag{5}$$

or

$$\tfrac{25}{28}\mathrm{Nb_{28}O_{70}} = V_{\mathrm{wad}} + \tfrac{1}{4}\mathrm{O_2}, \tag{5'}$$

$$K_2 = [V_{\mathrm{wad}}] \cdot P_{\mathrm{O_2}}^{1/4}, \tag{6}$$

$$V_{\mathrm{wad}} = V^{\cdot}_{\mathrm{wad}} + e, \tag{7}$$

$$\begin{aligned} K_3 &= [V^{\cdot}_{\mathrm{wad}}] \cdot [e]/[V_{\mathrm{wad}}] \\ &= \{[V^{\cdot}_{\mathrm{wad}}] \cdot [e] \cdot P_{\mathrm{O_2}}^{1/4}\}/K_2, \end{aligned} \tag{8}$$

where K_1 and K_2 are equilibrium constants. By assuming that some of the quasi-free electrons liberated from the singly ionized Wadsley defect ($V^{\cdot}_{\mathrm{wad}}$) can be retrapped in the valence band of some Nb^{5+} ions on the normal lattice site, the following defect equations are given

$$e + \mathrm{Nb_{Nb}} = \mathrm{Nb}'_{\mathrm{Nb}}, \tag{9}$$

$$K_4 = [\mathrm{Nb}'_{\mathrm{Nb}}]/[e]. \tag{10}$$

From the condition of electroneutrality,

$$[e] + [\mathrm{Nb}'_{\mathrm{Nb}}] = [V^{\cdot}_{\mathrm{wad}}]. \tag{11}$$

Thus, compositional change x is considered to be proportional to $P_{\mathrm{O_2}}^{-1/2}$—$P_{\mathrm{O_2}}^{-1/8}$ depending on the concentration ratios of $[V_0]$, $[V_{\mathrm{wad}}]$, and $[V^{\cdot}_{\mathrm{wad}}]$ from the equations

$$\begin{aligned} x &\propto [V_0] + 2[V_{\mathrm{wad}}]_{\mathrm{total}} \\ &= [V_0] + 2([V_{\mathrm{wad}}] + [V^{\cdot}_{\mathrm{wad}}]) \\ &= K_1 P_{\mathrm{O_2}}^{-1/2} + 2[K_2 \cdot P_{\mathrm{O_2}}^{-1/4} \\ &\quad + \{K_2 K_3 (1 + K_4)\}^{1/2} \cdot P_{\mathrm{O_2}}^{-1/8}]. \end{aligned} \tag{12}$$

On the other hand, the electrical conductivity σ is found to be proportional to $P_{\mathrm{O_2}}^{-1/8}$ from the equations

$$\begin{aligned} \sigma \propto [e] &= \frac{[V^{\cdot}_{\mathrm{wad}}]}{1 + K_4} \\ &= \left(\frac{K_2 K_3}{1 + K_4}\right)^{1/2} \cdot P_{\mathrm{O_2}}^{-1/8}. \end{aligned} \tag{13}$$

The oxygen partial pressure dependence of log σ obtained experimentally at 1283 K ($\sigma \propto P_{\mathrm{O_2}}^{-1/7.8}$) is consistent with the dependence given by Eq. (13) and the experimental dependence of log x ($x \propto P_{\mathrm{O_2}}^{-1/3}$) is given by Eq. (12), assuming $[V_0] \simeq [V_{\mathrm{wad}}] \geqq [V^{\cdot}_{\mathrm{wad}}]$.

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