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Phase Equilibria in the Nd_2O_3-V_2O_3-V_2O_5 System at 1200 °C

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Phase equilibria in the Nd_2O_3–V_2O_3–V_2O_5 system were established at 1200 °C by changing the oxygen partial pressures from −0.68 (air) to −12.50 in terms of $\log P_{O_2}$. In this system, V_nO_{2n-1} (n=2—7), VO_2, Nd_2O_3, $NdVO_3$, $NdVO_4$, $0.81Nd_2O_3\cdot0.19V_2O_5$ ($Nd_{1.62}V_{0.38}O_{3.38}$, A), and $3Nd_2O_3\cdot V_2O_5$ (Nd_3VO_7, B) were stable under the present experimental conditions. Compounds with Nd_2O_3/V_2O_5 mole ratios of 6/1 and 2/1 were not found under the present experimental conditions. Compounds A, Nd_3VO_7, $NdVO_3$, and $NdVO_4$ have nonstoichiometric compositions. The pattern of the phase diagram is different from those of other Ln_2O_3–V_2O_3–V_2O_5 systems that have previously been established by us. On the basis of the phase diagram, the Gibbs energies of the reactions:

$$(1)\quad 31/50\,Nd_2O_3 + 19/50\,NdVO_3 + 19/100\,O_2 = Nd_{1.62}V_{0.38}O_{3.38}$$

$$(2)\quad 50/31\,Nd_{1.62}V_{0.38}O_{3.38} + 12/31\,NdVO_3 + 6/31\,O_2 = Nd_3VO_7$$

$$(3)\quad NdVO_3 + 1/2\,O_2 = NdVO_4$$

were determined to be −61.4, −47.4, and −128.9 kJ respectively. In the Nd_2O_3–V_2O_3 system, only $NdVO_3$ is stable under the present experimental conditions.

Phase equilibria in the Ln_2O_3–V_2O_3–V_2O_5 systems (Ln=Sm, Lu, Er, Gd, and La) at 1200 °C have been established.[1–5] In these systems, vanadium oxides V_nO_{2n-1} (n=2—7) and lanthanoid vanadium oxides, $LnVO_3$ and $LnVO_4$, were found to be stable in all systems. In addition to the above vanadium oxides and lanthanoid vanadium oxides, in Sm_2O_3–V_2O_3–V_2O_5 system, $Sm_{10}V_2O_{20}$ ($5Sm_2O_3\cdot V_2O_5$); in the Lu_2O_3–V_2O_3–V_2O_5 system, $Lu_7V_3O_{16}$, $Lu_2V_2O_7$, and LuV_4O_8; in the Er_2O_3–V_2O_3–V_2O_5 system, $Er_8V_2O_{17}$ ($4Er_2O_3\cdot V_2O_5$); in the Gd_2O_3–V_2O_3–V_2O_5 system, $Gd_{1.62}V_{0.38}O_{3.38}$ ($0.81Gd_2O_3\cdot0.19V_2O_5$), and in the La_2O_3–V_2O_3–V_2O_5 system, $La_{1.62}V_{0.38}O_{3.38}$($0.81La_2O_3\cdot0.19V_2O_5$), La_3VO_7 ($3La_2O_3\cdot V_2O_5$), and $La_{1.42}V_{0.58}O_{3.58}$ ($0.71La_2O_3\cdot0.29V_2O_5$) have now been found to be stable under the same experimental conditions as the ternary compounds.

These phase diagrams, therefore, have shown different patterns as a result of the difference in coexisting compounds.

In the present study, Nd_2O_3 was chosen as the Ln_2O_3 because Nd_2O_3–$NdVO_4$ system has compounds with Nd_2O_3/V_2O_5 mole ratios of 6/1, 4/1, and 2/1; thus, we could expect a new type of phase diagram under the same experimental conditions.

Brusset *et al.*[6] studied the Nd_2O_3–V_2O_5 system in the temperature range from 600 to 1500 °C in air; they found two compounds, $4Nd_2O_3\cdot V_2O_5$ and $6Nd_2O_3\cdot V_2O_5$, besides $NdVO_4$, which is well known. Remizov *et al.*[7] also studied the same system from 645 to 1560 °C and found another two compounds, $2Nd_2O_3\cdot V_2O_5$ and $Nd_2O_3\cdot 2V_2O_5$. X-ray powder patterns in a simple form were shown for each compounds by both groups. The lattice constants for $NdVO_4$ have been determined by many researchers.[8–10]

In the Nd_2O_3–V_2O_3 system, only $NdVO_3$ was found; its crystallographic properties have been investigated by many researchers,[11–12] but the system has not been completely studied yet because of the instability of V_2O_3 in air.

The objectives of the present study are; (1) to make a detailed phase diagram of the Nd_2O_3–V_2O_3–V_2O_5 system at 1200 °C in order to establish the stable compounds under the present experimental conditions, (2) to calculate Gibbs energies of the reactions found in the established phase diagram, and (3) to ascertain whether or not there exists a linear relationship between the Gibbs energies of reactions and the ionic radius of the lanthanoid, as was found in the Ln–Fe–O system.[18]

Experimental

Analytical grades of Nd_2O_3 (99.9%) and V_2O_5, made by heating guaranteed-grade NH_4VO_3 at 500 °C in air for about 24 h, have been used as the starting materials. Desired Nd_2O_3/V_2O_5 ratios of the samples were obtained by mixing the appropriate quantities thoroughly in an agate mortar under ethyl alcohol. The mixtures thus obtained were treated by the procedures described in a previous report.[1] The apparatus and procedures for controlling the oxygen partial pressures and keeping a constant temperature, the method of thermogravimetry, the criterion for an equilibrium establishment, the method of actual oxygen-partial-pressure measurement, and the method of chemical analysis are the same as those reported in previous papers.[1,13–17]

The oxygen partial pressure of $10^{-12.50}$ was chosen as the reference oxygen partial pressure; that is, the weight of a sample in the atmosphere of $10^{-12.50}$ oxygen partial pressure was chosen as the reference weight throughout the present study.

Results and Discussion

Phase Equilibria. Nd_2O_3 is stable under the present experimental conditions.[18] Nine samples with Nd_2O_3/V_2O_5 mole ratios of 86/14, 80/20, 78/22, 70/30, 65/35, 60/40, 1, 25/75, and 10/90 were prepared to be used in the thermogravimetric experiment. The thermogravimetric results of the five samples with the mole ratios of 86/14, 80/20, 65/35, 1, and 10/90 are shown in Fig. 1 as representative. In Fig. 1 the ordinate is the oxygen partial pressure in $\log P_{O_2}$, while the abscissa is the composition of the samples represented by W_{O_2}/W_T, where W_{O_2} is the weight gain of

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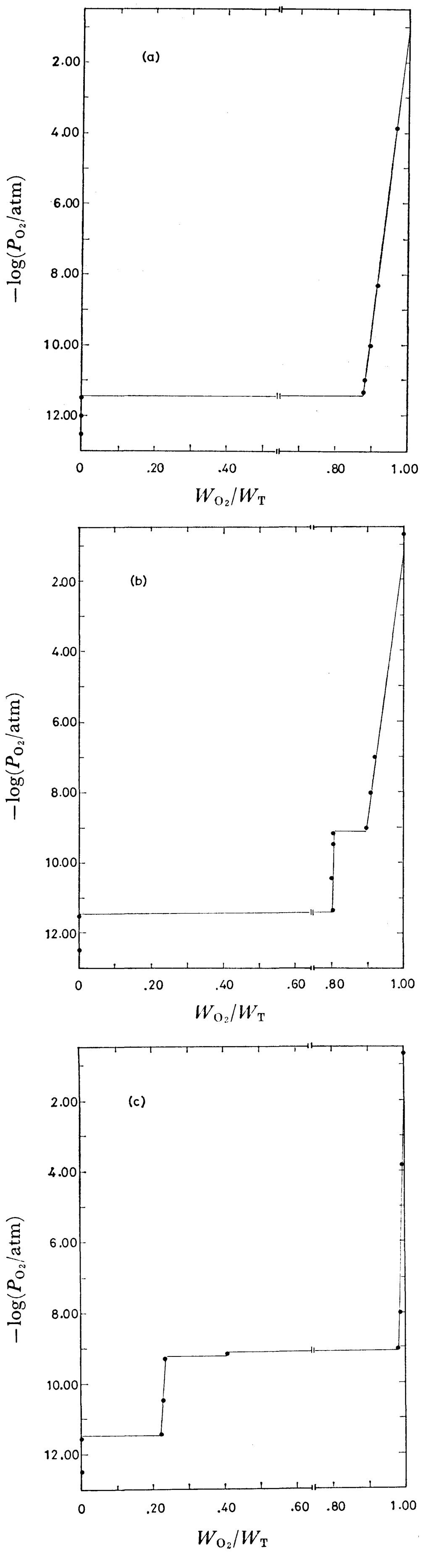

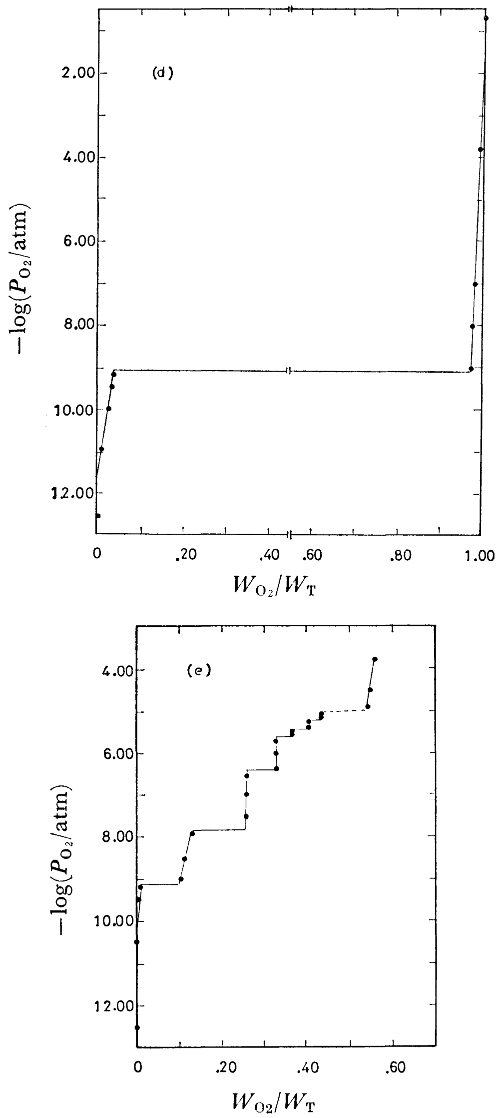

Fig. 1. The relationship between the oxygen partial pressure in $-\log P_{O_2}$ and the weight change of the samples in W_{O_2}/W_T, where W_{O_2} is the weight gain of the samples from the reference weight at $-\log P_{O_2}=12.50$ and W_T is the total weight gain that the samples would get if V_2O_3 in the samples had changed to V_2O_5.
(a): $Nd_2O_3/V_2O_5=86/14$, (b): $Nd_2O_3/V_2O_5=80/20$, (c): $Nd_2O_3/V_2O_5=65/35$, (d): $Nd_2O_3/V_2O_5=1$, (e): $Nd_2O_3/V_2O_5=10/90$.

the samples from the reference weight at $\log P_{O_2}=-12.50$, and where W_T is the total weight gain that the samples would get if V_2O_3 in the samples had been changed to V_2O_5.

As is shown in Figs. 1a to 1d, sudden weight changes occurred at 3 oxygen partial pressures, −11.45, −9.23, and −9.10, in $\log P_{O_2}$ in samples with Nd_2O_3/V_2O_5 mole ratios equal to unity and larger than unity. These figures correspond to the equilibrium oxygen partial pressures of reactions in the system shown in Table 5.

As is shown in Fig. 1c, the range of oxygen partial pressure in which $NdVO_3$ and Nd_3VO_7 coexist is very

TABLE 1. IDENTIFICATION OF PHASES IN QUENCHED SAMPLES

Nd_2O_3 (mol%)	V_2O_5 (mol%)	$-\log(P_{O_2}/\text{atm})$	Time / h	Phases[a)]
86	14	12.00	24	$Nd_2O_3+NdVO_3$
		10.00	24	Nd_2O_3+A
		9.00	28	Nd_2O_3+A
		0.68	30	Nd_2O_3+A
78	22	9.00	24	$A+B$
		0.68	24	$A+B$
70	30	12.00	24	$Nd_2O_3+NdVO_3$
		10.00	24	$A+NdVO_3$
		9.15	56	$B+NdVO_3$
		9.00	28	$B+NdVO_4$
		0.68	48	$B+NdVO_4$
60	40	12.00	24	$Nd_2O_3+NdVO_3$
		10.00	24	$A+NdVO_3$
		9.15	32	$B+NdVO_3$
		9.00	28	$B+NdVO_4$
		0.68	48	$B+NdVO_4$
25	75	11.00	8	$V_2O_3+NdVO_3$
		9.50	29	$V_2O_3+NdVO_3$
		8.50	25	$V_2O_3+NdVO_4$
		7.00	24	$V_3O_5+NdVO_4$
		6.00	43	$V_4O_7+NdVO_4$
		5.45	56	$V_5O_9+NdVO_4$
		5.25	50	$V_6O_{11}+NdVO_4$
		5.05	48	$V_7O_{13}+NdVO_4$
		4.50	40	VO_2+NdVO_4
10	90	11.00	8	$V_2O_3+NdVO_3$
		9.50	29	$V_2O_3+NdVO_3$
		8.50	25	$V_2O_3+NdVO_4$
		7.00	24	$V_3O_5+NdVO_4$
		6.00	43	$V_4O_7+NdVO_4$
		5.45	56	$V_5O_9+NdVO_4$
		5.25	50	$V_6O_{11}+NdVO_4$
		5.05	48	$V_7O_{13}+NdVO_4$
		4.50	40	VO_2+NVO_4

a) A: $Nd_{1.62}V_{0.38}O_{3.38}$, B: Nd_3VO_7.

narrow. This range is, indeed, too small for us to find Nd_3VO_7 in the early period of the thermogravimetric experiment. Throughout the experiment aimed at the identification of phases in the quenched samples, Compound Nd_3VO_7 was found as an unexpected phase.

As is shown in Fig. 1e, samples with mole ratios lower than unity showed patterns similar to those of the other systems[1,3-5)] except for the oxygen partial pressure of $\log P_{O_2}=-9.10$, which correspond to the equilibrium oxygen partial pressure of the $NdVO_3+1/2\ O_2=NdVO_4$ reaction.

In Table 1, the results of the identification of phases are shown. In the first column is the composition of the starting materials in mol%; in the second, the experimental conditions of the oxygen partial pressure in terms of $\log P_{O_2}$; in the third, the experimental duration in hours, and in the last, phases that are found in the quenched samples by means of an X-ray powder diffractometer using Cu $K\alpha$ radiation. The letters in the phases are abbreviations of the compounds shown in the lower part of the table. The abbreviations are the same as those of the other tables and figures in the present report.

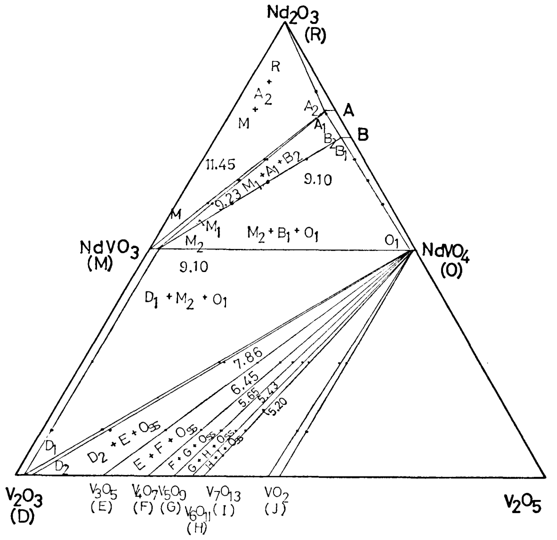

Fig. 2. Phase equilibria in the Nd_2O_3–V_2O_3–V_2O_5 system at 1200 °C. Numerical values in the three solid phases regions are the oxygen partial pressures in $-\log P_{O_2}$ in equilibrium. Abbreviations are the same as those in Tables 1 and 3. ss means the solid solution.

Based upon the above experimental results, a phase diagram of the system at 1200 °C is shown in Fig. 2. The following phases are stable under the present experimental conditions, except for compounds in the V_2O_3–V_2O_5 system, $NdVO_3$, $NdVO_4$, and Nd_2O_3. The phases are: $Nd_{1.62}V_{0.38}O_{3.38}$ ($0.81Nd_2O_3\cdot0.19V_2O_5$, A) and Nd_3VO_7 ($3Nd_2O_3\cdot V_2O_5$, B). Compounds with Nd_2O_3/V_2O_5 mole ratios of 6/1 and 2/1 were not found under the present experimental conditions. Compound A might have the composition, $4Nd_2O_3\cdot V_2O_5$, that Brusset *et al.*[6)] and Remizov *et al.*[7)] reported. However, under the present experimental conditions it has no round number of the mole ratio. The straight line drawn in Fig. 2 by plotting the experimental points is used to concentrate to the composition described above, even considering the experimental errors.

There are two possible explanations of why the deviation from the round number of the mole ratio occurred; one is the nonstoichiometry of the compound

TABLE 2. THE RELATIONSHIP BETWEEN THE OXYGEN PARTIAL PRESSURE AND THE COMPOSITION OF THE SOLID SOLUTIONS

N_O/N_X indicates the mole fraction ratio of oxygen to component X.

X	*a*	*b*
$Nd_{1.62}V_{0.38}O_{3.38}$	4.73×10^{-3}	4.16×10^{-3}
Nd_3VO_7	4.76×10^{-3}	8.10×10^{-3}
$NdVO_4$	2.67×10^{-3}	2.30×10^{-3}
$NdVO_3$	1.60×10^{-2}	0.183

$N_O/N_X=a\log P_{O_2}+b$.

TABLE 3. COMPOSITIONS, SYMBOLS, STABILITY RANGES IN OXYGEN PARTIAL PRESSURES, AND ACTIVITIES IN SOLID SOLUTIONS

Component	Composition	Symbol	$-\log(P_{O_2}/\text{atm})$	$\log a_i$
$Nd_{1.62}V_{0.38}O_{3.38}$	$Nd_{1.62}V_{0.38}O_{3.38}$	A	0.88[a)]—0.68	0.132
$Nd_{1.62}V_{0.38}O_{3.88}$	$Nd_{1.62}V_{0.38}O_{3.34}$	A_1	9.23	0.0705
	$Nd_{1.62}V_{0.38}O_{3.33}$	A_2	11.45	0
Nd_3VO_7	$Nd_3VO_{7.00}$	B	1.70[a)]—0.68	0.0674
	$Nd_3VO_{6.96}$	B_1	9.10	0.0023
	$Nd_3VO_{6.95}$	B_2	9.23	0
$NdVO_4$	$NdVO_{4.00}$	C	0.86[a)]—0.68	0.0453
	$NdVO_{3.98}$	C_1	9.10	0
$NdVO_3$	$NdVO_{3.00}$	M	11.45[a)]—12.50	0
	$NdVO_{3.035}$	M_1	9.23	−0.0203
	$NdVO_{3.037}$	M_2	9.10	−0.0221

a) These values were obtained by extrapolations using the experimental values.

toward the Nd_2O_3 side, and the other is experimental errors in the thermogravimetry. However, as shown in Fig. 1b, in which the results for $Nd_2O_3/V_2O_5=4/1$ are shown, a sudden change in the weight occurred at the oxygen partial pressure, −9.23 in $\log P_{O_2}$. Besides, this result has a good reproducibility. If the composition of Compound A was 4/1 in the Nd_2O_3/V_2O_5 mole ratio, such a weight change would not occur and there were be the same pattern as in Fig. 1a. Some might point out a systematic shift in the experimental points. To answer this, it is enough to show the existence of $3Nd_2O_3\cdot V_2O_5$. As has been described above, a compound with the same composition of A was found in the systems of both Gd and La.

A compound with a Ln_2O_3/V_2O_5 mole ratio of 3/1 was also found in the systems of La_2O_3,[5)] Eu_2O_3,[19)] and Sm_2O_3.[7)]

Ternary compounds, A, Nd_3VO_7, $NdVO_3$, and $NdVO_4$ have nonstoichiometric compositions. The nonstoichiometry of the $LnVO_3$-type compound seems to be very rare. In this series, only $LaVO_3$[5)] had a nonstoichiometric composition like $NdVO_3$. Judging from these two instances, the ionic radius seems to be effective. As is well known, La and Nd have ionic radii rather larger than the others in the lanthanoid series, although the crystal structure of $LaVO_3$ is different from that of $NdVO_3$. On the other hand, $SmVO_3$ is stoichiometric.[1)]

There are many two-and three-phase areas in Fig. 2. For example, the area that has the equilibrium oxygen partial pressure of −9.10 in $\log P_{O_2}$ has three phases, B_1, M_2, and O_1; here, B_1 has the composition of the B solid solution at $\log P_{O_2}=-9.10$ and M_2 is the most oxidized end member of the solid solution M, while, on the other hand, O_1 is the most reduced end member of the solid solution O. The square area that is surrounded by points, B, B_1, O_1, and O, is a two-phase area, $B_{ss}+O_{ss}$, where ss indicates the solid solution.

As is shown in Fig. 2, the pattern of the present phase diagram is of a new type and is different from those of the previously reported systems because of the difference in the coexisting ternary compounds.

TABLE 4. COMPARISON OF SPACINGS AND RELATIVE INTENSITIES OF Nd_3VO_7 WITH THOSE OF La_3VO_7 AND $3Eu_2O_3\cdot V_2O_5$

Nd_3VO_7		La_3VO_7		$3Eu_2O_3\cdot V_2O_5$		
d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0	$h\ k\ l$
3.266	88	3.330	80			
3.144	80	3.193	80	3.11	60	1 1 1
3.111	100	3.182	100	2.70	100	0 0 2
		3.051	16	1.93	30	2 2 0
2.919	35	2.983	37	1.799	30	0 0 3
		2.959	16	1.727	15	1 0 3
2.788	36	2.858	37	1.622	25	1 1 3
2.709	47	2.755	37			
		2.126	15			
1.970	37	2.015	28			
		2.005	27			
1.916	28	1.988	18			
1.867	20	1.953	20			

The relationship between the composition, N_O/N_X, and the oxygen partial pressure of the solid solution, X, were determined using the thermogravimetric results. Here, N_O/N_X is the mole fraction ratio of oxygen to a component X at a certain oxygen partial pressure; it indicates the deviation from the component composition. Using the method of the least squares with a linear equation, $N_O/N_X=a\log P_{O_2}+b$, the constants, a and b, for each solid solution were determined; they are shown in Table 2.

In Table 3, the compositions of the compounds at various oxygen partial pressures, the stability ranges of the compounds in terms of $\log P_{O_2}$, the symbols of the compounds, and the activities of the components in the solid solutions were calculated with Gibbs-Duhem equation using the N_O/N_X *vs.* $\log P_{O_2}$ relations described above. The method of the calculation has been discussed in detail in the paper of Kimizuka and Katsura.[16)]

The attempted assignment of Miller indices for new compound was not successful. However, the values of the relative intensities and spacings that were obtained by means of an X-ray diffractometer with powder samples are shown in Table 4, together with $3Eu_2O_3\cdot V_2O_5$[19)] and $3La_2O_3\cdot V_2O_5$.[5)] The weak peaks

Table 5. Unit-cell dimensions of compounds, together with those in previous reports

Compound	$-\log(P_{O_2}/\text{atm})$	a/Å	b/Å	c/Å	β/°	V/Å^3	Ref.
$NaVO_4$	0.68	7.337±0.001		6.644±0.002		346.8±0.2	
	9.00	7.320±0.005		6.414±0.006		343.6±0.6	
		7.335		6.434			9
		7.3290		6.4355			10
		7.326		6.426			8
$NdVO_3$	12.00	5.443±0.005	5.566±0.003	7.736±0.004		234.4±0.3	
		5.451	5.575	7.740		235.2	11
		5.466	5.569	7.735		235.5	12
A	0.68	10.97±0.04	8.82 ±0.03	16.5±0.2	99.2±0.4	1570±17	
	11.30	10.94±0.04	8.79 ±0.03	16.3±0.2	99.2±0.4	1550±17	

Table 6. Gibbs free energies of reactions

Reaction	$-\log(P_{O_2}/\text{atm})$	$\frac{-\Delta G^\circ}{\text{kJ}}$
(1) $\frac{31}{50}Nd_2O_3 + \frac{19}{50}NdVO_3 + \frac{19}{100}O_2 = Nd_{1.62}V_{0.38}O_{3.38}$	11.45±0.07	61.4
(2) $\frac{50}{31}Nd_{1.62}V_{0.38}O_{3.38} + \frac{12}{31}NdVO_3 + \frac{6}{31}O_2 = Nd_3VO_7$	9.23±0.03	47.4
(3) $NdVO_3 + \frac{1}{2}O_2 = NdVO_4$	9.10±0.03	128.9

of Nd_3VO_7 and La_3VO_7 were omitted from the table. The pattern of Nd_3VO_7 is very similar to that of La_3VO_7, though its *d*-values are a little smaller than those of La_3VO_7, while the pattern of Eu_3VO_7 is different from those of Nd_3VO_7 and La_3VO_7.

The lattice constants of the A, $NdVO_3$ and $NdVO_4$ compounds are tabulated in Table 5. The lattice constants of Compound A were successfully determined with the aid of the assignment of indices of $4Tm_2O_3 \cdot V_2O_5$.[20] It is apparent from the table that the values of the lattice constants of $NdVO_4$ depend upon the oxygen partial pressures, and that those quoted in the table are intermediate in nature. The values of $NdVO_3$ are smaller than those of McCarthy *et al.*[11]

Calculation of Gibbs Energies of Reactions. On the basis of the present phase diagram, the Gibbs energies all of the reactions appearing in the system except those in the V_2O_3–V_2O_5 system can be calculated by means of this equation; $\Delta G^\circ = -RT \ln K$, where R is the gas constant; T, the absolute temperature, and K, the equilibrium constant of each reaction. The equation of the reactions, the equilibrium oxygen partial pressures for each reaction, and the ΔG° values calculated are shown in Table 6. The activities of each component in the solid solutions which are necessary for calculation are listed in Table 3.

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