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Phase Equilibria in the Ln_2O_3-V_2O_3-V_2O_5 (Ln=Eu and Yb) Systems at 1200 °C

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Phase equilibria in the systems, Eu_2O_3-V_2O_3-V_2O_5 and Yb_2O_3-V_2O_3-V_2O_5, were established at 1200 °C by changing the oxygen partial pressure from −0.68 (air) to −13.00 atm in terms of log P_{O_2}. In the Eu_2O_3-V_2O_3-V_2O_5 system, $0.81Eu_2O_3\cdot 0.19V_2O_5$ ($Eu_{1.62}V_{0.38}O_{3.38}$) was stable; in the Yb_2O_3-V_2O_3-V_2O_5 system, a new compound $Yb_7V_3O_{16}$ was stable; and in both systems Ln_2O_3, $LnVO_4$, $LnVO_3$, V_nO_{2n-1} (n=2—7), and VO_2 were stable under the present experimental conditions. On the basis of the established phase diagrams, Gibbs energies of these reactions, $31/50\,Eu_2O_3+19/50\,EuVO_3+19/100\,O_2=Eu_{1.62}V_{0.38}O_{3.38}$, $EuVO_3+1/2\,O_2=EuVO_4$, $2\,Yb_2O_3+3\,YbVO_3+1/2\,O_2=Yb_7V_3O_{16}$, $Yb_7V_3O_{16}+O_2=2\,Yb_2O_3+3\,YbVO_4$, and $YbVO_3+1/2\,O_2=YbVO_4$, were determined to be −58.9, −126.0, −134.0, −210.0, and −117.7 kJ respectively. $EuVO_4$, $Eu_{1.62}V_{0.38}O_{3.38}$, $YbVO_4$, $Yb_7V_3O_{16}$, V_2O_3, and VO_2 have nonstoichiometric compositions.

Phase equilibria in the Ln_2O_3–V_2O_3–V_2O_5 systems (Ln=Sm, Lu, Er, Gd, La, Nd, and Tm) at 1200 °C have been established[1-7] by changing the oxygen partial pressure from −0.68 (air) to −12.50 or −13.00 atm[††] in terms of log P_{O_2}. These studies established phase diagrams whose different patterns are a result of the fact that different compounds coexist under the experimental conditions. We also succeeded in obtaining the Gibbs energies of reactions presented in the diagrams, the crystallographic data of the ternary compounds, and the activities of the components in the solid solutions.

In the present studies, Eu_2O_3 and Yb_2O_3 were chosen as the Ln_2O_3. Especially, the system that consists of Yb_2O_3 was expected to form as interesting pattern as that of the Lu_2O_3 system,[2] because the existence of a pyrochlore type compound $Yb_2V_2O_7$ was well known[8] and its physical properties had been studied by many researchers.[8-11]

In the Eu_2O_3–V_2O_3 and Yb_2O_3–V_2O_3 systems, $EuVO_3$ and $YbVO_3$ were well known, but these systems have not yet been completely studied, because of V_2O_3 is unstable in air. The crystallographic properties of $EuVO_3$ and $YbVO_3$ have been investigated by McCarthy *et al.*[12] and Shin-ike *et al.*,[13] and it has been confirmed that these compounds belong to orthorhombic system, like the other lanthanoid vanadites except for $LaVO_3$ and $CeVO_3$.

The Eu_2O_3–V_2O_5 system was studied by Brusset *et al.*[14] and Kiparisov *et al.*[15] Brusset *et al.* studied in the temperature range from 600 °C to 1500 °C in air and found three compounds: $Eu_2O_3\cdot V_2O_5$ ($EuVO_4$), $4Eu_2O_3\cdot V_2O_5$ ($Eu_8V_2O_{17}$), and $5Eu_2O_3\cdot V_2O_5$ ($Eu_{10}V_2O_{20}$), while Kiparisov *et al.* studied in the temperature region 500—1500 °C in air and found $Eu_2O_3\cdot V_2O_5$ and $3Eu_2O_3\cdot V_2O_5$. A discrepancy in two results exists regarding the stable compounds.

The Yb_2O_3–V_2O_5 system was also investigated by Brusset *et al.*[14] in the temperature range from 600 °C to 1500 °C in air; they found $Yb_2O_3\cdot V_2O_5$, $4Yb_2O_3\cdot V_2O_5$, and $5Yb_2O_3\cdot V_2O_5$.

The crystallographic system of the $Yb_8V_2O_{17}$ is monoclinic[16,17] but that of $5Yb_2O_3\cdot V_2O_5$ has not been determined, although a rough X-ray powder pattern had been presented by Brusset *et al.*[14] (Fig. 4 in Ref. 14).

The objectives of the present experiment are: (1) to establish the detail phase equilibria in these two systems at 1200 °C in order to confirm which compounds are stable under our experimental conditions, (2) to calculate the Gibbs energies of the reactions which appear in the established phase diagrams, and (3) to ascertain whether or not there exists a linear relationship between the Gibbs energies of the reaction, $LnVO_3+1/2\,O_2=LnVO_4$, and the ionic radii of lanthanoid elements as found in Ln–Fe–O.[18]

Experimental

Analytical grades of Eu_2O_3 (99.9%), of Yb_2O_3 (99.9%), and of V_2O_5, made by heating the guaranteed grade of NH_4VO_3 at 500 °C in air about 24 h, have been used as the starting materials. Desired Eu_2O_3/V_2O_5 and Yb_2O_3/V_2O_5 mole ratios of 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 the previous paper.[1] The apparatus and procedures for controlling the oxygen partial pressures and keeping a constant temperature, the method of the thermogravimetry, the criterion for an equilibrium establishment, and the method of the chemical analysis except for the analysis of vanadium in the presence of europium are the same as those reported in the previous papers.[1,19-23] To obtain the V contents coexisting with Eu, we deduced the weight of Eu_2O_3, which was obtained by the gravimetric method,[1] from the total weight, because Eu^{3+} is reduced to Eu^{2+}, and Eu^{2+} precipitates as $EuSO_4$[24] in the reduction of V^{5+} with Zn–amalgam.

Results and Discussion

Phase Equilibria. *(1) The Eu_2O_3–V_2O_3–V_2O_5 System*: Although europium oxide has several forms, such as Eu_2O_3, EuO, and Eu_3O_4,[25,26] only Eu_2O_3 is stable under the present experimental conditions.[26,27] Nine samples with Eu_2O_3/V_2O_5 mole ratios of 85/15, 82/18, 81/19, 8/2, 7/3, 6/4, 1, 35/65, and 2/8 were prepared to be used in the thermogravimetric experiment. In Fig. 1, the relationships between the

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†† atm = 1.013×10^5 Pa.

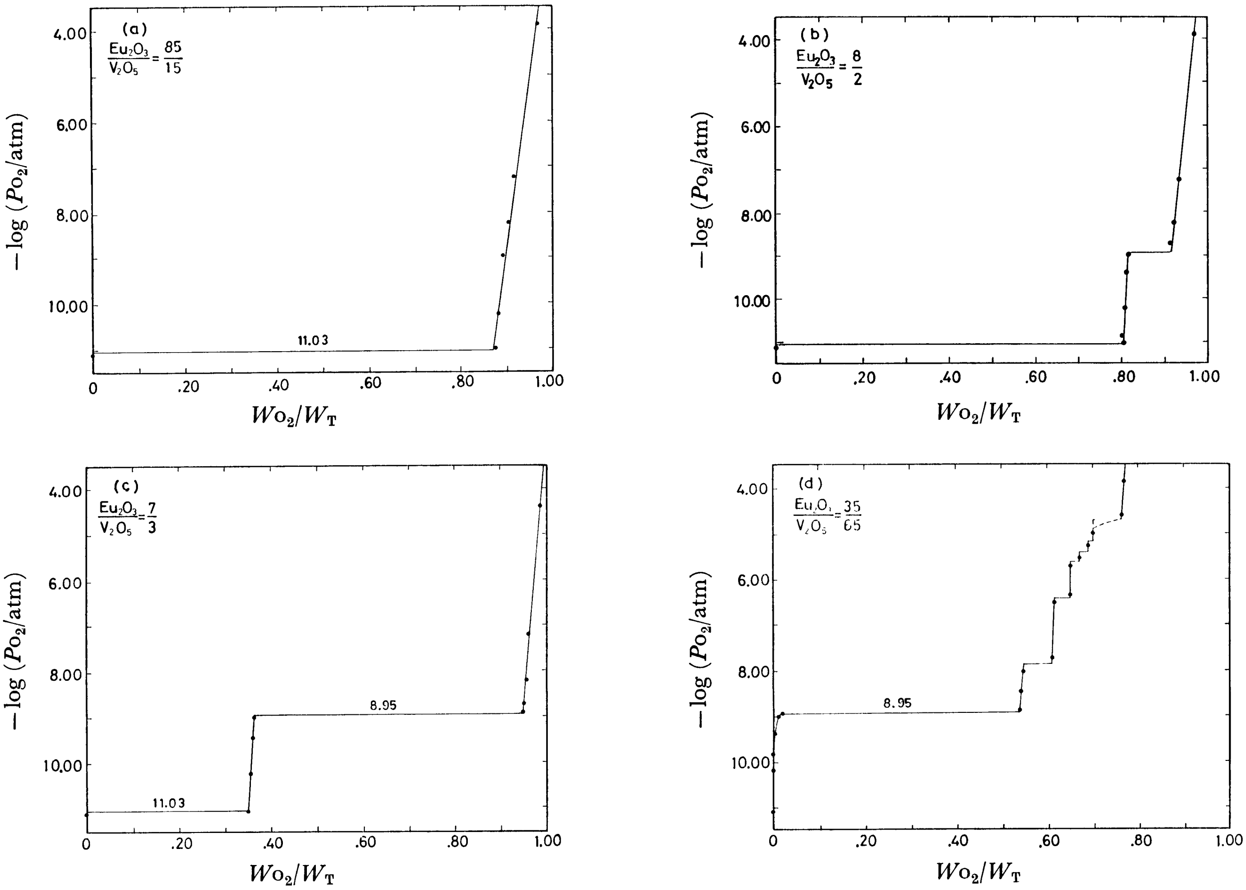

Fig. 1. The relationship between the oxygen partial pressure in $-\log(Po_2/\text{atm})$ and the weight change of the sample in Wo_2/W_T.
(a) $Eu_2O_3/V_2O_5=85/15$, (b) $Eu_2O_3/V_2O_5=8/2$, (c) $Eu_2O_3/V_2O_5=7/3$, (d) $Eu_2O_3/V_2O_5=35/65$.

oxygen partial pressure, atm, on the ordinate and the weight change, Wo_2/W_T, on the abscissa are shown; here Wo_2 is the weight gain of the samples from the reference weight in the atmosphere of $\log Po_2=-13.00$ atm, and W_T is the total weight gain that the samples would get if V_2O_3 in the samples would change to V_2O_5. The experimental results of four samples, 85/15, 8/2, 7/3, and 35/65 are shown in Fig. 1 as representative. From Figs. 1a to 1c, it is apparent that abrupt weight changes occur at two oxygen partial pressures, -11.03 and -8.95 atm in $\log Po_2$. These values correspond to the equilibrium oxygen partial pressures of the reactions described in Table 6. Fig. 1d shows a similar pattern to those of the samples of other systems.[1,3-7] which have the composition of Ln_2O_3/V_2O_5 mole ratios lower than unity. But the value of the oxygen partial pressure, $\log Po_2=-8.95$, that corresponds to the equilibrium oxygen partial pressure of the reaction, $EuVO_3+1/2\,O_2=EuVO_4$, is different.

In Table 1 the results of the identification of phases are shown. In the first column are the compositions of the starting materials in mol%; in the second and third are shown the experimental conditions of the oxygen partial pressures in terms of $\log Po_2$ in atm and the experimental duration in h; and in the fourth are the phases identified by X-ray powder diffractometer using Cu $K\alpha$ radiation.

Based upon the above experimental results, a phase diagram of the system at 1200 °C was drawn; This is shown in Fig. 2. The following phases are present under the present experimental conditions except for six compounds in the V_2O_3–V_2O_5 system; Eu_2O_3(R), $Eu_{1.62}V_{0.38}O_{3.38}$(A), $EuVO_4$(B), and $EuVO_3$(C). Compounds in the V_2O_3–V_2O_5 system are the same as those in the previous report.[1] $5Eu_2O_3\cdot V_2O_5$ reported by Brusset *et al.*[14] and $3Eu_2O_3\cdot V_2O_5$ reported by Kiparisov *et al.*[15] have not been confirmed under the present experimental conditions. The Compound A may correspond to the compound $4Eu_2O_3\cdot V_2O_5$ that Brusset *et al.* have reported. But under the present experimental conditions, this compound has no such round mole ratio as that written above. The straight line drawn by plotting the results of the thermogravimetry usually converges to a composition $0.81Eu_2O_3\cdot 0.19V_2O_5$, even considering the experimental errors. As is shown in Fig. 1b, the sample, $Eu_2O_3/V_2O_5=8/2$, has a pattern similar to that in Fig. 1c which shows the two equilibrium oxygen partial pressures. If compound A had the composition of $Eu_2O_3/V_2O_5=8/2$, the pattern should be the same one as that of Fig. 1a with one equilibrium oxygen partial pressure, $\log Po_2=-11.03$. Compounds with the same $Ln_2O_3/V_2O_5=81/19$ mole ratio were found in other systems.[4,5] Figure 2 has a pattern similar to that of the Gd_2O_3–V_2O_3–V_2O_5 system.[4]

Compound A and $EuVO_4$ have nonstoichiometric compositions. The following relationships between the oxygen partial pressure and the composition were found from the results of the thermogravimetry; $N_O/N_A = 8.71\times10^{-3}+5.18\times10^{-3}\log P_{O_2}$ for compound A and $N_O/N_B = 2.24\times10^{-3}+1.62\times10^{-3}\log P_{O_2}$ for $EuVO_4$ (B). Here N_O, N_A, and N_B mean the mole fractions of oxygen and of component A and B. Nonstoichiometry was not found for $EuVO_3$ under the present experimental conditions.

Table 1. Identification of phases

Eu_2O_3 mol%	V_2O_5 mol%	$-\log(P_{O_2}$ /atm)	Time h	Phases
85	15	8.48	20	Eu_2O_3+A[a]
		10.54	48	Eu_2O_3+A
		11.40	22	$Eu_2O_3+EuVO_3$
70	30	8.48	20	$EuVO_4+A$
		10.54	48	$EuVO_3+A$
		11.40	22	$Eu_2O_3+EuVO_3$
60	40	8.48	20	$EuVO_4+A$
		10.54	48	$EuVO_3+A$
		11.40	22	$Eu_2O_3+EuVO_3$
35	65	3.88	42	$EuVO_4+VO_2$
		5.11	70	$EuVO_4+V_7O_{13}$
		5.29	65	$EuVO_4+V_6O_{11}$
		5.43	51	$EuVO_4+V_5O_9$
		6.16	46	$EuVO_4+V_4O_7$
		7.22	23	$EuVO_4+V_3O_5$
		8.48	23	$EuVO_4+V_2O_3$
		9.85	16	$EuVO_3+V_2O_3$
20	80	3.88	42	$EuVO_4+VO_2$
		5.11	70	$EuVO_4+V_7O_{13}$
		5.29	65	$EuVO_4+V_6O_{11}$
		5.50	51	$EuVO_4+V_5O_9$
		6.16	46	$EuVO_4+V_4O_7$
		7.22	23	$EnVO_4+V_3O_5$
		8.48	23	$EuVO_4+V_2O_3$
		9.85	16	$EuVO_3+V_2O_3$

a) A: $Eu_{1.62}V_{0.38}O_{3.38}$.

Table 2 shows compositions of the compounds that were calculated from the results of the thermogravimetry, symbols of the compounds, stability ranges of the compounds in terms of $\log P_{O_2}$, and activities of the components in the solid solutions. Activities of each component in the solid solutions were calculated by using Gibbs-Duhem equation. The detailed method of calculation has been described in the paper of Kimizuka and Katsura.[22]

The lattice constants of the compound A were successfully determined with the aid of the assignment of $4Tm_2O_3\cdot V_2O_5$.[16] Lattice constants of the com-

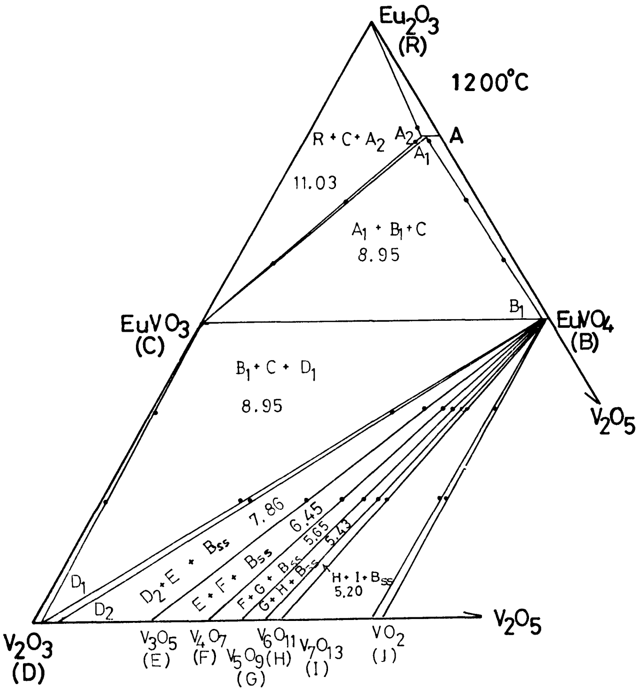

Fig. 2. Phase equilibria in the Eu_2O_3-V_2O_3-V_2O_5 system at 1200 °C. Numerical values in three solid phases regions are the equilibrium oxygen partial pressure in $-\log P_{O_2}$. Abbreviations are the same as those in Table 2.

Table 2. Compositions, symbols, stability ranges in oxygen partial pressures, and activities in solid solution

Component	Composition	Symbol	$-\log(P_{O_2}/\text{atm})$	$\log a_i$
$Eu_{1.62}V_{0.38}O_{3.38}$	$Eu_{1.62}V_{0.38}O_{3.38}$	A	0.68—1.68[a]	0.113
	$Eu_{1.62}V_{0.38}O_{3.34}$	A_1	8.95	0.0448
	$Eu_{1.62}V_{0.38}O_{3.33}$	A_2	11.03	0
$EuVO_4$	$EuVO_{4.00}$	B	0.68—1.38[a]	0.0232
	$EuVO_{3.99}$	B_1	8.95	0
$EuVO_3$	$EuVO_{3.00}$	C	8.95—13.00	0
$Yb_7V_3O_{16}$	$Yb_7V_3O_{16.24}$	A′	9.55	0
	$Yb_7V_3O_{16.40}$	A_1'	8.37	0.116
	$Yb_7V_3O_{16.55}$	A_2'	7.47	0.154
$YbVO_4$	$YbVO_{3.98}$	B_1'	8.37	0
	$YbVO_{3.99}$	B_2'	7.47	0.0077
	$YbVO_{4.00}$	B′	0.68—1.77[a]	0.0279
$YbVO_3$	$YbVO_{3.00}$	C′	8.37—13.00	0

a) These values were obtained by extrapolating the experimental values.

TABLE 3. UNIT CELL DIMENSIONS OF COMPOUNDS TOGETHER WITH THOSE IN PREVIOUS REPORTS

Compound	$-\log(P_{O_2}$ /atm)	a/Å	b/Å	c/Å	β/°	V/Å^3	Ref.
$Eu_{1.62}V_{0.38}O_{3.38}$	0.68	10.77±0.02	8.77±0.02	16.5±0.1	99.2±0.3	1530±10	Present
	10.54	10.77±0.02	8.78±0.02	16.4±0.1	99.2±0.3	1530±10	Present
$EuVO_4$	3.88	7.238±0.001		6.369±0.002		333.6±0.1	Present
		7.2365±0.0002		6.3675±0.0002			29
		7.232±0.002		6.362±0.002			14
		7.239±0.003		6.370±0.003		333.8	28
$EuVO_3$	9.39	5.374±0.004	5.608±0.003	7.657±0.004		230.8±0.2	Present
		5.362±0.002	5.599±0.002	7.651±0.002		229.7±0.05	12
$YbVO_4$	0.68	7.047±0.001		6.250±0.001		310.3±0.1	Present
	7.20	7.047±0.001		6.250±0.001		310.4±0.1	Present
		7.046±0.002		6.233±0.002			14
		7.043±0.003		6.248±0.003		309.9	28
		7.0435		6.2470			30
$YbVO_3$	9.85	5.231±0.001	5.574±0.001	7.542±0.001		219.9±0.1	Present
		5.223±0.002	5.564±0.002	7.534±0.002		219.0±0.05	12

pounds, A, $EuVO_4$, and $EuVO_3$ are tabulated in Table 3, together with those of previous reports.[12,13,27,28] Figures that are shown in the second column of the Table are the oxygen partial pressure used in preparation of samples. We could not discuss about the difference of the unit cell dimensions of two A samples because the experimental errors are too large. Present values for $EuVO_4$ are in good agreement with those of Schwarz,[28] but the values for $EuVO_3$ are slightly larger than those of McCarthy *et al.*[12]

(2) The Yb_2O_3–V_2O_3–V_2O_5 System: Yb_2O_3 is stable under the present experimental conditions.[22] Six samples with Yb_2O_3/V_2O_5 mole ratios of 8/2, 7/3, 6/4, 1, 35/65, and 2/8 were prepared to be used in the thermogravimetric experiments. Relationships between the oxygen partial pressure and the weight change, W_{O_2}/W_T, for three samples: 8/2, 6/4, and 2/8 are shown in Fig. 3 as representative cases. We find three equilibrium oxygen partial pressure: 9.55, 8.37, and 7.47 in $-\log P_{O_2}$ from Figs. 3a and 3b. Figure 3c shows a similar pattern to that in Fig. 1d except for the oxygen partial pressure, $\log P_{O_2}=-8.37$, for the reaction $YbVO_3+1/2\ O_2=YbVO_4$.

In Table 4, the results of the identification of phases are shown. Based upon the above experimental results, a phase diagram at 1200 °C was drawn and is shown in Fig. 4. The following phases are present under the present experimental conditions, along with the six compounds in the V_2O_3–V_2O_5 system. Phases are: Yb_2O_3(R′), $Yb_7V_3O_{16}$(A′), $YbVO_4$(B′), and $YbVO_3$(C′). Compounds in the V_2O_3–V_2O_5 system are the same as those in the previous report.[1] The compound $Yb_7V_3O_{16}$ is new although the Ln/V/O mole ratio is identical with those of Lu[2] and Tm[7] systems. Compounds $4Yb_2O_3\cdot V_2O_5$ and $5Yb_2O_3\cdot V_2O_5$ reported by Brusset *et al.*[14,16] and the pyrochlore type $Yb_2V_2O_7$ reported by many authors[8–10] were not found under the present experimental conditions. This phase diagram is a new type.

Compounds $Yb_7V_3O_{16}$ and $YbVO_4$ have nonstoichiometric compositions. The following relationships between the oxygen partial pressure and the composition were obtained from the results of the thermogravimetry: $N_O/N_A'=1.161+0.158\ \log P_{O_2}$ for $Yb_7V_3O_{16}$ (A′) and $N_O/N_B'=4.58\times10^{-3}+2.59\times10^{-3}\ \log P_{O_2}$ for $YbVO_4$ (B′).

TABLE 4. IDENTIFICATION OF PHASES

Yb_2O_3	V_2O_5	$-\log(P_{O_2}$ /atm)	Time/h	Phases
mol%				
80	20	3.88	18	$Yb_2O_3+YbVO_4$
		7.58	45	$Yb_2O_3+Yb_7V_3O_{16}$
		8.90	24	$Yb_2O_3+Yb_7V_3O_{16}$
		10.22	16	$Yb_2O_3+YbVO_3$
70	30	3.88	18	$Yb_2O_3+YbVO_4$
		7.58	45	$Yb_7V_3O_{16}$
		8.90	24	$Yb_7V_3O_{16}$
		10.22	16	$Yb_2O_3+YbVO_3$
60	40	3.88	18	$Yb_2O_3+YbVO_4$
		7.58	45	$Yb_7V_3O_{16}+YbVO_4$
		8.90	24	$Yb_7V_3O_{16}+YbVO_3$
		10.22	16	$Yb_2O_3+YbVO_3$
35	65	3.88	24	$YbVO_4+VO_2$
		5.01	69	$YbVO_4+V_7O_{13}$
		5.25	46	$YbVO_4+V_6O_{11}$
		5.56	21	$YbVO_4+V_5O_9$
		6.16	22	$YbVO_4+V_4O_7$
		7.00	45	$YbVO_4+V_3O_5$
		8.10	21	$YbVO_4+V_2O_3$
		9.00	21	$YbVO_3+V_2O_3$
20	80	3.88	24	$YbVO_4+VO_2$
		5.01	69	$YbVO_4+V_7O_{13}$
		5.25	46	$YbVO_4+V_6O_{11}$
		5.56	21	$YbVO_4+V_5O_9$
		6.16	22	$YbVO_4+V_4O_7$
		7.00	45	$YbVO_4+V_3O_5$
		8.10	21	$YbVO_4+V_2O_3$
		9.00	21	$YbVO_3+V_2O_3$

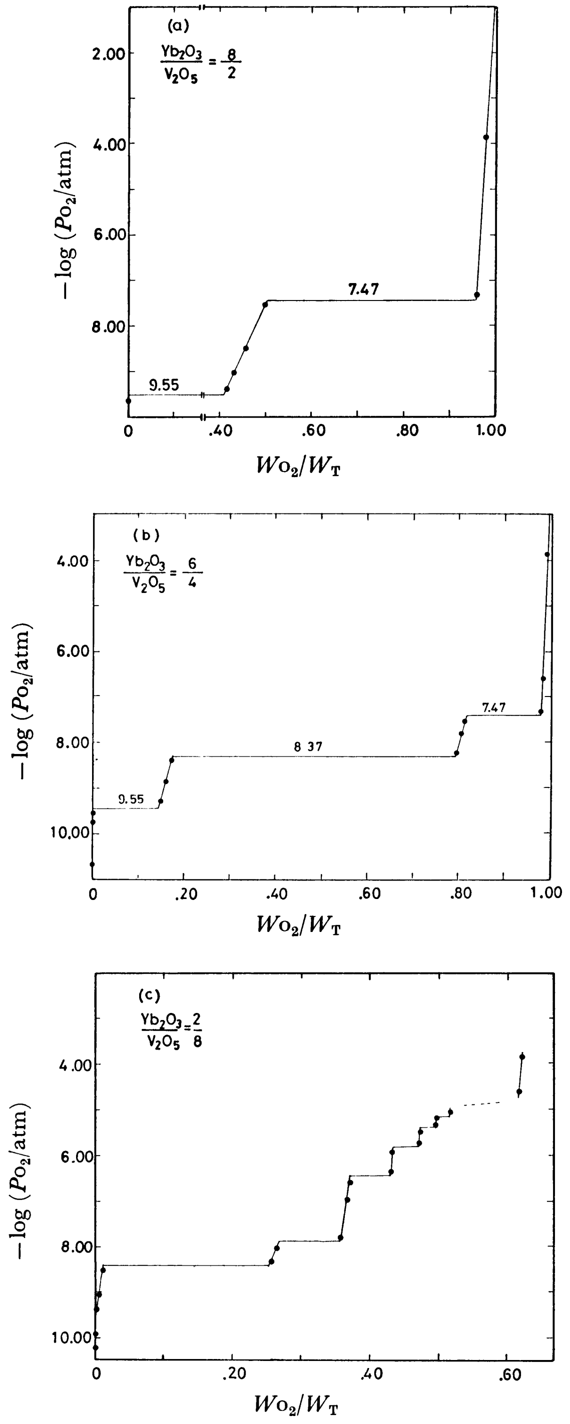

Fig. 3. The relationship between the oxygen partial pressure in $-\log(Po_2/\text{atm})$ and the weight change of the sample in Wo_2/W_T.
(a) $Yb_2O_3/V_2O_5=8/2$, (b) $Yb_2O_3/V_2O_5=6/4$, (c) $Yb_2O_3/V_2O_5=2/8$.

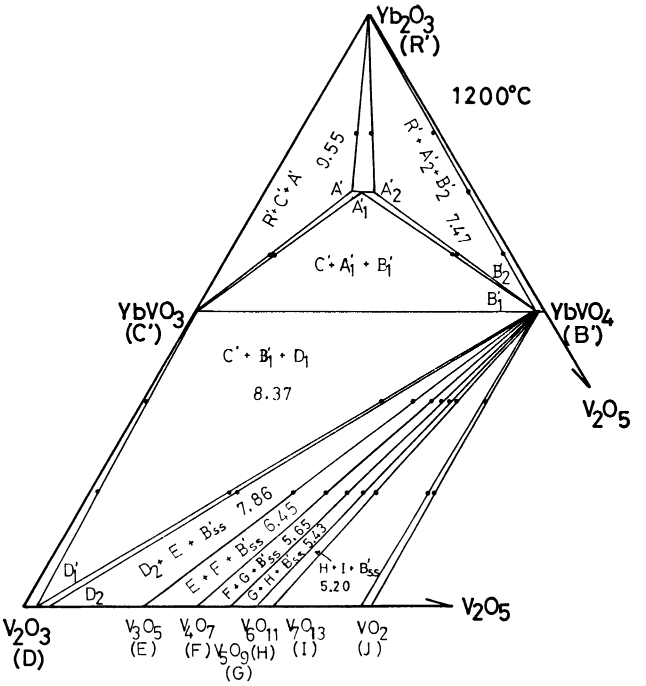

Fig. 4. Phase equilibria in the Yb_2O_3-V_2O_3-V_2O_5 system at 1200 °C. Numerical values in three solid phases regions are the equilibrium oxygen partial pressure in $-\log Po_2$. Abbreviations are the same as those in Table 2.

Table 5. The spacings and relative intensities of $Yb_7V_3O_{16}$

d/Å	I/I_0	d/Å	I/I_0
5.73	11	1.7881	24
3.176	98	1.7070	20
3.033	100	1.6839	19
2.863	48	1.6150	24
2.680	33	1.5993	21
2.608	59	1.5722	11
2.560	16	1.5580	25
2.193	17	1.5161	11
2.126	17	1.4869	12
2.080	10	1.4659	11
1.9282	57	1.4317	12
1.9076	22		

In Table 2, the compositions of the compounds at various oxygen partial pressures, stability ranges of the compounds in terms of $\log Po_2$, the symbols of the compounds, and the activities of the components in the solid solutions are also tabulated.

The assignment of Miller's indices for the new compound, $Yb_7V_3O_{16}$, did not succeed. Relative intensities and spacings that were obtained by X-ray diffractometer with the powder sample are shown in Table 5, several weak peaks being omitted.

Lattice constants of the compounds, $YbVO_4$ and $YbVO_3$, are tabulated in Table 3, together with those of previous reports.[12,14,28,29] The lattice constants of $YbVO_4$, made in air, are in good agreement with those prepared at $\log Po_2 = -7.20$ and with those of the previous reports. Present values of $YbVO_3$ are larger than those obtained by McCarthy *et al.*[12]

Calculation of Gibbs Energies of Reactions. On the basis of the established phase diagrams, Gibbs energies of reactions appearing in the systems, except for the reactions in the V_2O_3–V_2O_5 system, can be calculated by an equation, $\Delta G° = -RT \ln K$, where the R is the

TABLE 6. GIBBS ENERGIES OF REACTIONS

Reaction	$-\log(P_{O_2}/\mathrm{atm})$	$-\Delta G^\circ/\mathrm{kJ}$
$19/50\ \mathrm{EuVO_3} + 31/50\ \mathrm{Eu_2O_3} + 19/100\ \mathrm{O_2} = \mathrm{Eu_{1.62}V_{0.38}O_{3.38}}$	11.03 ± 0.06	58.9 ± 0.2
$\mathrm{EuVO_3} + 1/2\ \mathrm{O_2} = \mathrm{EuVO_4}$	8.95 ± 0.02	126.0 ± 0.3
$2\ \mathrm{Yb_2O_3} + 3\ \mathrm{YbVO_3} + 1/2\ \mathrm{O_2} = \mathrm{Yb_7V_3O_{16}}$	9.55 ± 0.05	134.0 ± 0.7
$\mathrm{Yb_7V_3O_{16}} + \mathrm{O_2} = 2\ \mathrm{Yb_2O_3} + 3\ \mathrm{YbVO_4}$	7.47 ± 0.03	210.0 ± 0.7
$\mathrm{YbVO_3} + 1/2\ \mathrm{O_2} = \mathrm{YbVO_4}$	8.37 ± 0.03	117.7 ± 0.4

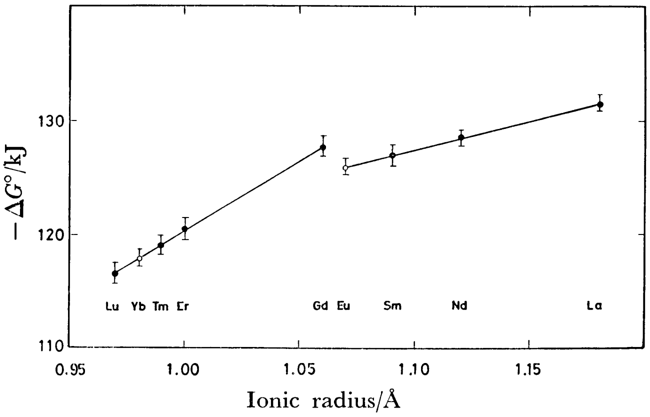

Fig. 5. The relationship between the ionic radius in 8 coordination number and the Gibbs energies of reaction, $\mathrm{LnVO_3} + 1/2\ \mathrm{O_2} = \mathrm{LnVO_4}$. The solid circles are the previous values and the open circles present values.

gas constant, the T the absolute temperature, and the K the equilibrium constant of each reaction. Reactions and the ΔG° values obtained are shown in Table 6, together with the equilibrium oxygen partial pressures. Activities of each component in the solid solutions whose activity is necessary for the calculations are listed in Table 2.

The Relationship between ΔG° and Ionic Radius. In the previous report,$^{7)}$ the relationship between ΔG° values for the reaction $\mathrm{LnVO_3} + 1/2\ \mathrm{O_2} = \mathrm{LnVO_4}$ and the 8 coordinated ionic radius of lanthanoid elements was graphically shown. The series divided into two groups and the relationship is linear within each of the groups. The experimental results of the present systems are plotted in Fig. 5 with open circles together with the previous data shown as solid circles. Both open circles fit well on the lines which were drawn using the data of the previous experiments.

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