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Phase Equilibria in the La_2O_3-V_2O_3-V_2O_5 System at 1200 °C

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The phase equilibria in the La_2O_3–V_2O_3–V_2O_5 system were established at 1200 °C by changing oxygen partial pressures from −0.68 (air) to −13.00 in terms of $\log P_{O_2}$. In this system, $0.81La_2O_3\cdot0.19V_2O_5(La_{1.62}V_{0.38}O_{3.38})$, $3La_2O_3\cdot V_2O_5(La_3VO_7)$, $0.71La_2O_3\cdot0.29V_2O_5(La_{1.42}V_{0.58}O_{3.58})$, $LaVO_4$, $LaVO_3$, V_nO_{2n-1} (n=2—7), and VO_2 were stable. $LaVO_3$, $LaVO_4$, $La_{1.62}V_{0.38}O_{3.38}$, La_3VO_7, and $La_{1.42}V_{0.58}O_{3.58}$ have nonstoichiometric compositions. On the basis of the phase equilibria, the Gibbs energies of the reactions:

$$31/50\ La_2O_3 + 19/50\ LaVO_3 + 19/100\ O_2 = La_{1.62}V_{0.38}O_{3.38}$$
$$50/31\ La_{1.62}V_{0.38}O_{3.38} + 12/31\ LaVO_3 + 6/31\ O_2 = La_3VO_7$$
$$21/50\ La_3VO_7 + 4/25\ LaVO_3 + 2/25\ O_2 = La_{1.42}V_{0.58}O_{3.58}$$
$$LaVO_3 + 1/2\ O_2 = LaVO_4$$

were determined to be −64.0, −55.8, −21.6, and −131.5 kJ respectively.

The phase equilibria in the Ln_2O_3–V_2O_3–V_2O_5 system (Ln=Sm, Lu, Er, and Gd) at 1200 °C have been established previously.[1–4] In these systems, the existence of V_nO_{2n-1} (n=2—7), VO_2, $LnVO_3$, and $LnVO_4$ were confirmed. In addition to the above vanadium oxides and lanthanoid vanadium oxides, in the 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, $Er_8V_2O_{17}$ ($4Er_2O_3\cdot V_2O_5$), and in the Gd_2O_3–V_2O_3–V_2O_5 system, $Gd_{1.62}V_{0.38}O_{3.38}$ ($0.81Gd_2O_3\cdot0.19V_2O_5$) were stable as ternary compounds. These diagrams, therefore, have shown different patterns as a result of the different coexisting compounds.

In the present study, we chose La_2O_3 as Ln_2O_3 because lanthanum has the largest ionic radius in the lanthanoid series.

In the La_2O_3–V_2O_3 system, the existence of $LaVO_3$ is well known,[5–8] but the system has not yet been completely studied. The crystallographic properties of $LaVO_3$ has been investigated by many researchers.[5–8] They say that $LaVO_3$, as well as $CeVO_3$, has a tetragonal crystal system, unlike the other orthorhombic $LnVO_3$ substances, although there has been report[8,9] that $CeVO_3$ has a cubic system.

Brusset *et al.*[10] studied the La_2O_3–V_2O_5 system in the temperature range from 600° to 1500 °C; they found that $4La_2O_3\cdot V_2O_5$ was stable between La_2O_3 and $LaVO_4$ in the temperature range. However, their quench products of the composition usually contained three phases: $4La_2O_3\cdot V_2O_5+LaVO_4+La_2O_3$, because of a sluggish reaction. They did not present any crystallographic data for $4La_2O_3\cdot V_2O_5$, except a simple powder diffraction pattern (Fig. 2 in Ref. 10).

Much information pertinent to the crystal structure of $LaVO_4$ can be found in the recent literature.[11–14] Almost all lanthanoid vanadium(V) oxides crystallize in the zircon structure with a crystal symmetry of $I4_1$/amd.[15] The only exception is that of the $LaVO_4$ which has been known to have a monoclinic monazite structure with a crystal symmetry of $P2_1/n$.[16]

The objectives of the present study are: (1) to make a detailed phase diagram of the La_2O_3–V_2O_3–V_2O_5 system at 1200 °C in order to ascertain the stable ternary compounds under the present experimental conditions, (2) to calculate the standard Gibbs energy of the reactions found in the phase diagram, and (3) to ascertain whether or not there exists a linear relationship between the standard Gibbs energies of reactions and the ionic radius of the lanthanoid, as found in the Ln–Fe–O system.[17]

Experimental

Analytical-grade quantities of La_2O_3 (99.9%) and V_2O_5, obtained by heating the guaranteed grade of NH_4VO_3 at 500 °C in air for about 24 h, have been employed as the starting materials. The desired ratios of La_2O_3/V_2O_5 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, P_{O_2} (atm), and keeping a constant temperature, the method of thermogravimetry, the criterion for the establishment of an equilibrium, the method of lattice-constant determination, the method of the actual oxygen-partial-pressure measurement, and the method of chemical analysis are the same as those discussed in previous reports.[1,18–22]

The oxygen partial pressure of $10^{-13.00}$ was chosen as the reference oxygen partial pressure; that is, the weight of a sample in the atmosphere of $10^{-13.00}$ oxygen partial pressure was chosen as the reference weight throughout the present study.

Results and Discussion

Phase Equilibria. Eleven samples with La_2O_3/V_2O_5 mole ratios of 17/3, 31/9, 3/1, 29/11, 7/3, 13/7, 3/2, 1, 9/11, 7/13, and 1/4 were prepared to be used in the thermogravimetric experiment. In Fig. 1, the relationships between the oxygen partial pressure and the composition, W_{O_2}/W_T, are shown, where W_{O_2} is the weight gain of the samples from the reference weight at $\log P_{O_2}=-13.00$, while W_T is the total weight gain that the sample would get if the V_2O_3 in the sample had changed to V_2O_5. Thermogravimetric results of the six samples, 17/3, 31/9, 29/11, 7/3, 13/7, and 1/4, are shown as representative in Fig. 1.

As is shown in Fig. 1a to Fig. 1e, abrupt weight

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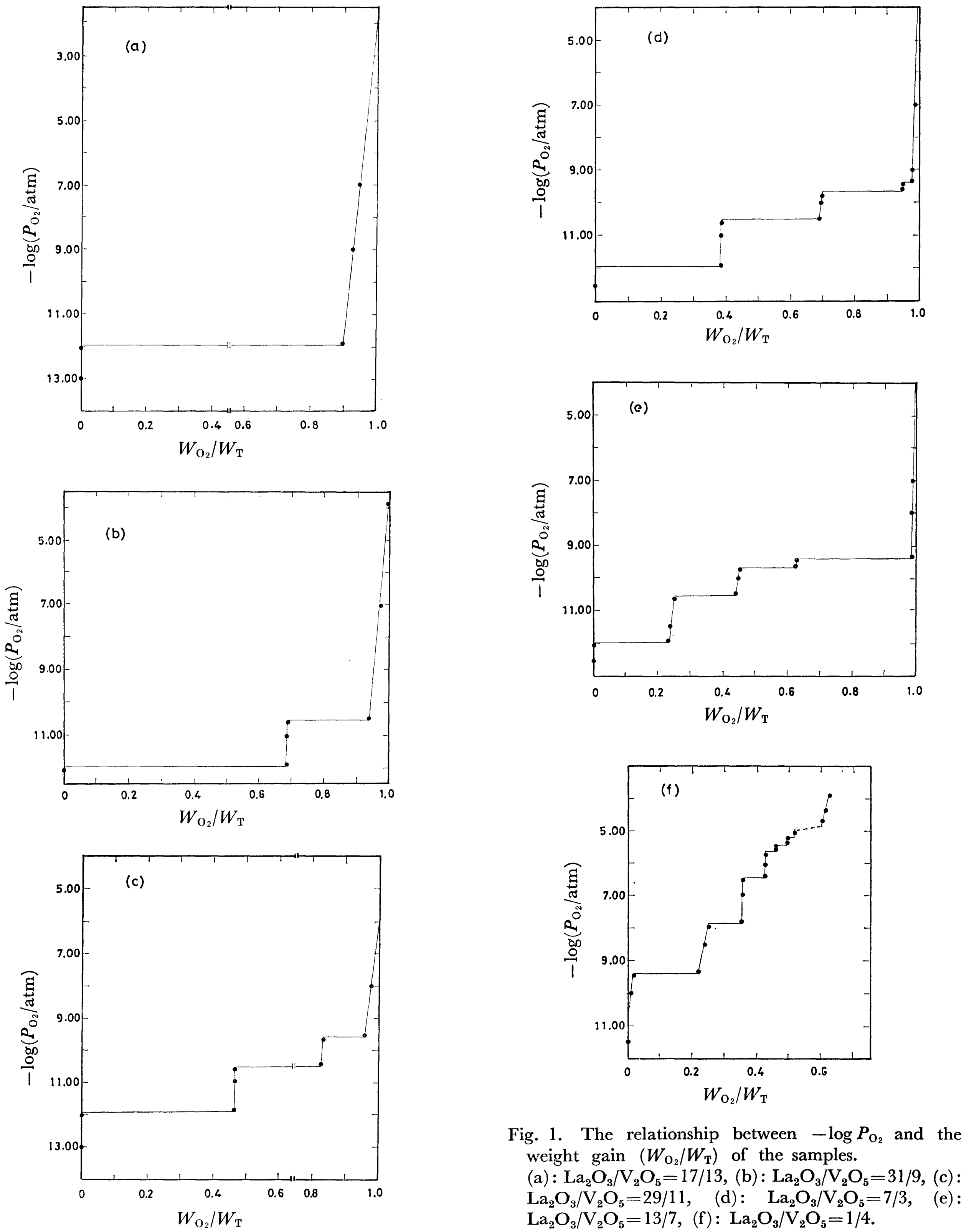

Fig. 1. The relationship between $-\log P_{O_2}$ and the weight gain (W_{O_2}/W_T) of the samples.
(a): $La_2O_3/V_2O_5=17/13$, (b): $La_2O_3/V_2O_5=31/9$, (c): $La_2O_3/V_2O_5=29/11$, (d): $La_2O_3/V_2O_5=7/3$, (e): $La_2O_3/V_2O_5=13/7$, (f): $La_2O_3/V_2O_5=1/4$.

changes occured at 4 oxygen partial pressures, −11.95, −10.51, −9.68, and −9.35, in terms of $\log P_{O_2}$, in the samples in which the mole ratio is larger than unity. These values correspond to the equilibrium oxygen partial pressures of reactions that were found in the system and which are shown in Table 6. The last figure, $\log P_{O_2}=-9.35$, is lower than the value, -9.16 ± 0.05, previously presented by Nakamura *et al.*[6] for the same reaction at 1200 °C.

As is shown in Figs. 1d and 1e, the oxygen-partial-pressure range in which two phases, $LaVO_3$ and C, coexist is very narrow, about 0.3 in $\log P_{O_2}$, compared with the area of the other two phases. As is shown in Fig. 1f, samples with mole ratios lower than unity

Table 1. Identification of Phases

Starting materials (mol%) La_2O_3	V_2O_5	$-\log(P_{O_2}/\text{atm})$	Time / h	Phases[a]
85	15	12.50	6	$La_2O_3+LaVO_3$
		11.00	48	La_2O_3+A
		10.00	43	La_2O_3+A
		0.68	55	La_2O_3+A
80	20	10.00	33	A+B
77.5	22.5	12.50	6	$La_2O_3+LaVO_3$
		11.00	48	$A+LaVO_3$
		10.00	43	A+B
		0.68	55	A+B
72.5	27.5	12.50	6	$La_2O_3+LaVO_3$
		11.00	48	$A+LaVO_3$
		10.00	32	$B+LaVO_3$
		9.50	29	B+C
		0.68	55	B+C
60	40	12.50	6	$La_2O_3+LaVO_3$
		11.00	48	$A+LaVO_3$
		10.00	32	$B+LaVO_3$
		9.50	29	$C+LaVO_3$
		9.00	24	$C+LaVO_4$
		0.68	55	$C+LaVO_4$
35	65	12.00	7	$LaVO_3+V_2O_3$
		9.50	26	$LaVO_3+V_2O_3$
		8.00	27	$LaVO_4+V_2O_3$
		7.00	25	$LaVO_4+V_3O_5$
		5.75	34	$LaVO_4+V_4O_7$
		5.50	34	$LaVO_4+V_5O_9$
		5.30	40	$LaVO_4+V_6O_{11}$
		5.10	44	$LaVO_4+V_7O_{13}$
		4.50	48	$LaVO_4+VO_2$
20	80	12.00	7	$LaVO_3+V_2O_3$
		9.50	26	$LaVO_3+V_2O_3$
		8.00	27	$LaVO_4+V_2O_3$
		7.00	25	$LaVO_4+V_3O_5$
		5.75	34	$LaVO_4+V_4O_7$
		5.50	34	$LaVO_4+V_5O_9$
		5.30	40	$LaVO_4+V_6O_{11}$
		5.10	44	$LaVO_4+V_7O_{13}$
		4.50	48	$LaVO_4+VO_2$

a) A: $0.81La_2O_3\cdot0.19V_2O_5(La_{1.62}V_{0.38}O_{3.38})$, B: $3La_2O_3\cdot V_2O_5(La_3VO_7)$, C: $0.71La_2O_3\cdot0.29V_2O_5(La_{1.42}V_{0.58}O_{3.58})$.

show the similar pattern to those in the other systems[1,3,4] except for the oxygen partial pressure, log $P_{O_2}=-9.35$.

Table 1 shows the results of the identification of phases; in the first column is the composition of the starting materials; in the second, the experimental conditions of the oxygen partial pressure in terms of log P_{O_2}; in the third, the experimental duration, and in the last, the phases that are found in the quenched samples by means of an X-ray diffractometer using Cu $K\alpha$ radiation. The letters in the Phase are the abbreviations of the compounds which are shown in the lower part of the table. The abbreviations are the same as those in Tables 3 and 4 and in Fig. 2.

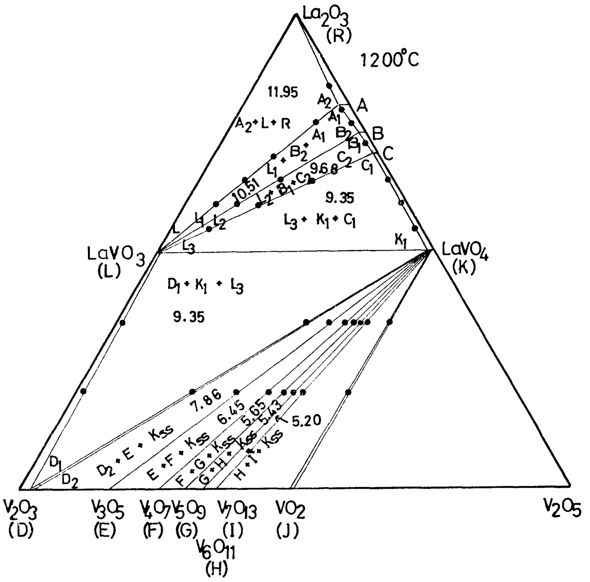

Fig. 2. Phase equilibria in the La_2O_3–V_2O_3–V_2O_5 system at 1200 °C.
Numerical values in the three solid phases regions are the oxygen partial pressures in $-\log P_{O_2}$ in equilibrium.
Abbreviations are the same as those in Tables 1, 2, and 3.

La_2O_3 is stable under the present experimental conditions, as has already been reported by Kimizuka and Katsura.[22]

Based upon the above experimental results, a phase diagram of the system at 1200 °C was drawn; it is shown in Fig. 2. The following phases are stable under the present experimental conditions, except for six compounds in the V_2O_3–V_2O_5 system, $LaVO_4$, and $LaVO_3$: La_2O_3(R), $La_{1.62}V_{0.38}O_{3.38}$(A), La_3VO_7 (B), and $La_{1.42}V_{0.58}O_{3.58}$(C). Compound A may correspond to the composition, $4La_2O_3\cdot V_2O_5$ that Brusset *et al.*[10] have reported, while Compound C may correspond to $7La_2O_3\cdot3V_2O_5$. Under the present experimental conditions, though these compounds have no round mole ratios such as are written above. The straight lines drawn by plotting the experimental points usually concentrate at the compositions presented above, even considering the experimental errors.

There are two possibilities to account for the deviations from the round mole ratios; one is the nonstoichiometry of the compounds toward the La_2O_3 side, and the other is systematic experimental errors in

Table 2. The relationships between the compositions and the oxygen partial pressures of solid solutions: $N_O/N_X=a\ \log P_{O_2}+b$

X	*a*	*b*
A	7.50×10^{-3}	0.0415
B	5.33×10^{-3}	0.0306
C	4.44×10^{-3}	0.0275
$LaVO_3$	0.0178	0.181
$LaVO_4$	6.64×10^{-3}	0.0325

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

Component	Composition	Symbol	$-\log (P_{O_2}/\text{atm})$	$\log a_i$
$La_{1.62}V_{0.38}O_{3.38}$	$La_{1.62}V_{0.38}O_{3.38}$	A	0.68[a]—5.53[b]	0.0772
	$La_{1.62}V_{0.38}O_{3.34}$	A_1	10.51	0.0308
	$La_{1.62}V_{0.38}O_{3.34}$	A_2	11.95	0
La_3VO_7	$La_3VO_{7.00}$	B	0.68[a]—5.74[b]	0.0303
	$La_3VO_{6.98}$	B_1	9.68	9.63×10^{-3}
	$La_3VO_{6.97}$	B_2	10.51	0
$La_{1.42}V_{0.58}O_{3.58}$	$La_{1.42}V_{0.58}O_{3.58}$	C	0.68[a]—6.19[b]	0.0135
	$La_{1.42}V_{0.58}O_{3.57}$	C_1	9.35	2.43×10^{-3}
	$La_{1.42}V_{0.58}O_{3.57}$	C_2	9.68	0
$LaVO_4$	$LaVO_{4.00}$	K	0.68[a]—4.89[b]	0.033
	$LaVO_{3.97}$	K_1	9.35	0
$LaVO_3$	$LaVO_{3.00}$	L	13.50[c]—10.57[b]	0
	$LaVO_{3.00}$	L_1	10.51	0.0136
	$LaVO_{3.01}$	L_2	9.68	0.0131
	$LaVO_{3.01}$	L_3	9.35	0.0111

a) The stability limit value in $\log P_{O_2}$ may be higher than −0.68 (air). b) These values are obtained by extrapolation using the experimental data. c) The stability-limit value in $\log P_{O_2}$ may be lower than this value.

Table 4. SPACINGS AND RELATIVE INTENSITIES OF COMPOUNDS B AND C

B		C	
d/Å	I/I_0	d/Å	I/I_0
9.596	10	7.629	21
9.017	12	5.700	10
7.658	10	3.8243	10
6.981	10	3.6632	16
4.514	10	3.3457	17
3.765	10	3.2994	67
3.6706	10	3.1935	50
3.3296	80	3.1768	100
3.1931	80	3.1544	52
3.1817	100	3.0717	14
3.0512	16	3.0449	21
2.9833	37	2.8586	17
2.9592	16	2.8256	17
2.8575	37	2.7692	31
2.7551	37	2.0584	19
2.1959	10	2.0059	34
2.1261	15	1.9663	21
2.0151	28	1.9111	10
2.0047	27	1.8554	10
1.9877	18	1.7717	12
1.9527	20		
1.9382	12		
1.9070	16		
1.7838	11		
1.7730	12		
1.7483	14		
1.7438	14		
1.7166	15		
1.7059	16		

the thermogravimetry. However, the following facts seem to eliminate both possibilities. For example, if the composition of Compound C were 7/3 in the La_2O_3/V_2O_5 mole ratio, no such sudden weight change would occur at $\log P_{O_2}=-9.35$ as shown in Fig. 1d; rather, it would show the same pattern as that of Fig. 1c. Also, we found compounds with round mole ratios, such as $3La_2O_3\cdot V_2O_5$(B), $4Er_2O_3\cdot V_2O_5$,[4] and $4Ho_2O_3\cdot V_2O_5$, in the Ho_2O_3–V_2O_3–V_2O_5 system in spite of using the same experimental techniques. On the other hand, $0.81Gd_2O_3\cdot 0.19V_2O_5$ was found in the Gd_2O_3–V_2O_3–V_2O_5 system,[4] as has been described above.

Two new compounds, B and C, were found in the La_2O_3–V_2O_5 system. Kiparisov *et al.*[23] reported the existence of $3Er_2O_3\cdot V_2O_5$ at 1300 °C. However, the X-ray powder diffraction pattern of $3Er_2O_3\cdot V_2O_5$ is not similar to that of Compound B. No compound with a Ln_2O_3/V_2O_5 mole ratio of 7/3 or near it has yet been found in the another system.

Ternary compounds, A, B, C, $LaVO_3$, and $LaVO_4$ have nonstoichiometric compositions. The nonstoichiometry of the $LnVO_3$-type compound seems to be very rare, because the other compounds, $SmVO_3$, $LuVO_3$, $ErVO_3$, and $GdVO_3$, are stoichiometric under the same experimental conditions. It is still not clear whether or not $LaVO_3$ is the only special compound with a nonstoichiometric composition at 1200 °C. Nakamura *et al.*[6] pointed out the stoichiometry of $LaVO_3$ at 1000 °C in the oxygen pressure range from $10^{-12.8}$ to $10^{-21.1}$ bar, but they did not write anything about the composition of $LaVO_3$ at 1200 °C.

There are many two- and three-phase areas in Fig. 2. For example, the area that has the equilibrium oxygen partial pressure, −11.95 in $\log P_{O_2}$, has three phases; R, L, and A_2, that is the most reduced end-member of the solid solution A, and the area that has the compositions surrounded by the three points A_2, A, and La_2O_3, have two phases, $A_{ss}+La_2O_3$, in the oxygen partial pressure range from −11.95 to −0.68 in $\log P_{O_2}$. Here, A_{ss} means the solid solution of Compound A; its composition changes from A_2

to A depending upon the oxygen partial pressure.

As is shown in Fig. 2, the pattern of the present phase diagrm is new and different from the patterns of the other systems[1–4] established previously, because of the difference in the coexisting ternary compounds. That is, there are three compounds, A, B, and C, between La_2O_3 and $LaVO_4$ in this system. However, systems which contain Sm_2O_3,[1] Er_2O_3,[3] and Gd_2O_3[4] have one compound, although the compositions of the compounds are different from one another. On the other hand, three compounds were found in the Lu_2O_3-V_2O_3-V_2O_5 system,[2] though they did not appear between Lu_2O_3 and $LuVO_4$. We have not yet been able to find any rule for the appearance of compounds in the series or reasons why all these systems show different patterns.

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 the component X, indicating 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 a and b values for each solid solution were determined to be as shown in Table 2.

In Table 3, the compositions of the compounds, 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 are tabulated. The activity of the components in the solid solutions is calculated with Gibbs-Duhem equations using the N_O/N_X *vs.* $\log P_{O_2}$ relations presented above. A detailed method of the calculation has been discussed in the paper of Kimizuka and Katsura.[21]

The assignment of indices for new compounds did not succeed. The data of relative intensities and spacings obtained by means of an X-ray diffractometer with powder samples are shown in Table 4. Because of the sluggish reactions, the samples used in this measurement were made in air by about 146 h heating at 1200 °C with four intermediate grindings in an agate mortar.

The lattice constants of the compounds A, $LaVO_3$ and $LaVO_4$, are tabulated in Table 5. The lattice constants of Sample A were successfully determined with the aid of the assignment of the indices of $4Tm_2O_3 \cdot V_2O_5$.[24]

Differences in the unit-cell dimensions are found in the two $LaVO_3$ samples quenched under different conditions of the oxygen partial pressure. Our values of the samples, made in the atmosphere of −9.45 in $\log P_{O_2}$, are in good agreement with all those of authors previously cited except for one.[7]

As for the cell dimensions of $LaVO_4$, no differences are found in the two quenched samples. Three previous data are shown in Table 5, together with ours.

Calculation of the Standard Gibbs Energies of Reactions. On the basis of the present phase diagram, the standard Gibbs energies of reactions appearing in the 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 equations of reactions, the equilibrium oxygen partial pressures for each reaction, and the ΔG° values obtained are shown in Table 6. The activities of each component in the solid solutions which are necessary for the calculation are listed in Table 3. The ΔG° value, −128.9 kJ, presented by

TABLE 5. UNIT-CELL DIMENSIONS OF COMPOUNDS

Compound	$-\log(P_{O_2}/\text{atm})$	a / Å	b / Å	c / Å	β / °	V / Å^3	Ref.
$La_{1.62}V_{0.38}O_{3.38}$	0.68	11.18±0.08	9.12 ±0.07	17.0 ±0.4	99.4±0.8	1709±39	Present
	11.50	11.20±0.08	9.07 ±0.06	16.9 ±0.5	99.2±0.5	1700±49	Present
$LaVO_4$	0.68	7.043±0.008	7.344±0.010	6.694±0.012	104.9±0.1	334.6±0.8	Present
	9.00	7.043±0.007	7.345±0.009	6.694±0.011	104.9±0.1	334.5±0.7	Present
		7.07	7.29	6.77	105		13
		7.03 ±0.03	7.34 ±0.03	6.69 ±0.03	105±0.5		24
		7.047	7.286	6.725	104.85		14
$LaVO_3$	(in H_2)	5.517±0.001		7.852±0.002		242.0±0.1	Present
	9.45	5.545±0.001		7.843±0.002		241.1±0.1	Present
		5.544		7.848			5
		5.547±0.002		7.840±0.003			6
		5.535		7.830		239.9	7
		5.546±0.005		7.827±0.005		240.7±0.1	9

TABLE 6. GIBBS FREE ENERGIES OF REACTIONS

	Reaction	$-\log(P_{O_2}/\text{atm})$	$-\Delta G^\circ$ / kJ
(1)	$31/50\ La_2O_3 + 19/50\ LaVO_3 + 19/100\ O_2 = La_{1.62}V_{0.38}O_{3.38}$	11.95	64.0
(2)	$50/31\ La_{1.62}V_{0.38}O_{3.38} + 12/31\ LaVO_3 + 6/31\ O_2 = La_3VO_7$	10.51	55.8
(3)	$21/50\ La_3VO_7 + 4/25\ LaVO_3 + 2/25\ O_2 = La_{1.42}V_{0.58}O_{3.58}$	9.68	21.6
(4)	$LaVO_3 + 1/2\ O_2 = LaVO_4$	9.35	131.5

Nakamura *et al.*[6] for reaction (4) is in fairly good agreement with ours, −131.5 kJ.

The $LnVO_3+1/2\ O_2=LnVO_4$ reaction is common in all the systems, and the ΔG° values for the reactions related to La, Sm,[1] Gd,[4] Er,[3] and Lu[2] were obtained as −131.5, −127.2, −127.7, −121.0, and −116.3 kJ respectively. Judging from the values obtained, the values seem to increase gradually as the atomic numbers increase from La to Lu, although the values for Sm and Gd are almost the same.

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