Phase Equilibria in the Tm_2O_3-V_2O_3-V_2O_5 System at 1200 °C

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(Received November 13, 1982)

Phase equilibria in the Tm_2O_3–V_2O_3–V_2O_5 system were established at 1200 °C; the oxygen partial pressure was varied −0.68 (air) to −12.50 atm in terms of log P_{O_2}. In this system, V_nO_{2n-1} (n=2—7), VO_2, Tm_2O_3, $TmVO_3$, $TmVO_4$, $Tm_8V_2O_{17}$ ($4Tm_2O_3 \cdot V_2O_5$), $Tm_7V_3O_{16}$ were stable under the present experimental conditions. The pattern of the phase diagram is different from those of other Ln_2O_3–V_2O_3–V_2O_5 systems (Ln=Sm, Lu, Er, Gd, La, and Nd) that were already established. Compounds $TmVO_3$, $TmVO_4$, $Tm_8V_2O_{17}$, $Tm_7V_3O_{16}$, V_2O_3, and VO_2 have nonstoichiometric compositions. On the basis of the established phase diagram, the Gibbs energies of the reactions,

(1) $2\,Tm_2O_3 + 3\,TmVO_3 + 1/2\,O_2 = Tm_7V_3O_{16}$
(2) $TmVO_3 + 1/2\,O_2 = TmVO_4$
(3) $5/3\,Tm_2O_3 + 2/3\,Tm_7V_3O_{16} + 2/3\,O_2 = Tm_8V_2O_{17}$
(4) $Tm_7V_3O_{16} + O_2 = 5/3\,TmVO_4 + 2/3\,Tm_8V_2O_{17}$

were determined to be −132, −119, −157, and −228 kJ, respectively. The relationship between the ionic radius and ΔG° of the reactions, $LnVO_3 + 1/2\,O_2 = LnVO_4$, is linear, provided that lanthanum and the lanthanoid can be divided into two groups.

Phase equilibria in the Ln_2O_3–V_2O_3–V_2O_5 systems (Ln=Sm, Lu, Er, Gd, La, and Nd) at 1200 °C have been established.[1–6] The oxygen partial pressure was changed from −0.68 to −12.50 or −13.00 atm in terms of log P_{O_2}. We succeeded in obtaining the Gibbs energies of the reactions which appeared in the systems and the crystallographic data of the ternary compounds and the activities of the components in the solid solutions. These established phase diagrams showed the different patterns as a result of the differences of the compounds coexisting under the experimental conditions.

In the present study, Tm_2O_3 was chosen as the Ln_2O_3, because the system might show as interesting a pattern as that of the Lu_2O_3 system.[2] The pyrochlore type compound, $Tm_2V_2O_7$, is well known[7] and its physical properties were studied by many researchers.[7–10]

The Tm_2O_3–V_2O_5 system was studied by Brusset *et al.*[11] in the temperature range from 600 °C to 1500 °C in air. They found two compounds, $4Tm_2O_3 \cdot V_2O_5$ ($Tm_8V_2O_{17}$) and $5Tm_2O_3 \cdot V_2O_5$, besides $TmVO_4$ which is well known. The crystallographic properties of $TmVO_4$ were studied by Brusset *et al.*[11] and Schwarz[12] and those of $Tm_8V_2O_{17}$ by Brusset *et al.*[13] and Ustalova *et al.*[14]

In the Tm_2O_3–V_2O_3 system, only $TmVO_3$ was found; its crystallographic properties were investigated by many researchers.[15–16] But the system has not been completely studied yet on account of the instability of V_2O_3 in air

The objectives of the present study are to (1) make the detailed phase diagram of the Tm_2O_3–V_2O_3–V_2O_5 system at 1200 °C in order to determine the stable compounds under the present experimental conditions, to (2) calculate the Gibbs energies of the reactions found in the established phase diagram, and to (3) ascertain whether or not there is a linear relationship between the Gibbs energies of reactions and the ionic radii of the lanthanoid elements, as found in the Ln–Fe–O system.[17]

Experimental

Analytical grades of Tm_2O_3 (99.9%) and V_2O_5, which was made by heating the guaranteed grade of NH_4VO_3 at 500 °C in air for about 24 h, have been used as the starting materials. Desired Tm_2O_3/V_2O_5 ratios of samples were obtained by mixing the appropriate quantities thoroughly in an agate motar under ethyl alcohol. The mixtures thus obtained were treated by the procedures described in the previous report.[1] The apparatus and procedures for controlling the oxygen partial pressures, keeping a constant temperature, the method of thermogravimetry, the criterion for an equilibrium establishment, the method of the actual oxygen partial pressure measurement, and the method of the chemical analysis are the same as those reported in the previous papers.[1,18–22]

The oxygen partial pressure −12.50 atm in terms of log P_{O_2} was chosen as the reference oxygen partial pressure; that is, the weight of a samples in the atmosphere of $10^{-12.50}$ atm of oxygen partial pressure was chosen as the reference weight thorough the present experiment.

Results and Discussion

Phase Equilibria. Tm_2O_3 is stable under the present experimental conditions.[23] Eleven samples with Tm_2O_3/V_2O_5 mole ratios 84/16, 8/2, 77/23, 74/26, 7/3, 65/35, 6/4, 1, 3/7, 2/8, and 1/9 were prepared to be used in the thermogravimetric experiment. The thermogravimetric results of the four samples with mole ratios, 84/16, 74/26, 65/35, and 3/7 are shown in Fig. 1 as representative. In Fig. 1, the ordinate is the oxygen partial pressure (atm) in log P_{O_2} and the abscissa is the composition of the samples represented by 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. Figure 1 shows the different patterns. That is, Fig. 1a had two sudden weight changes at log P_{O_2}=−8.10 and −9.37, Fig. 1b three at log P_{O_2}=−7.70, −8.10, and −9.37, Fig. 1c also three at −7.70, −8.47, and −9.37. Figure 1d shows the same pattern as those of the previous

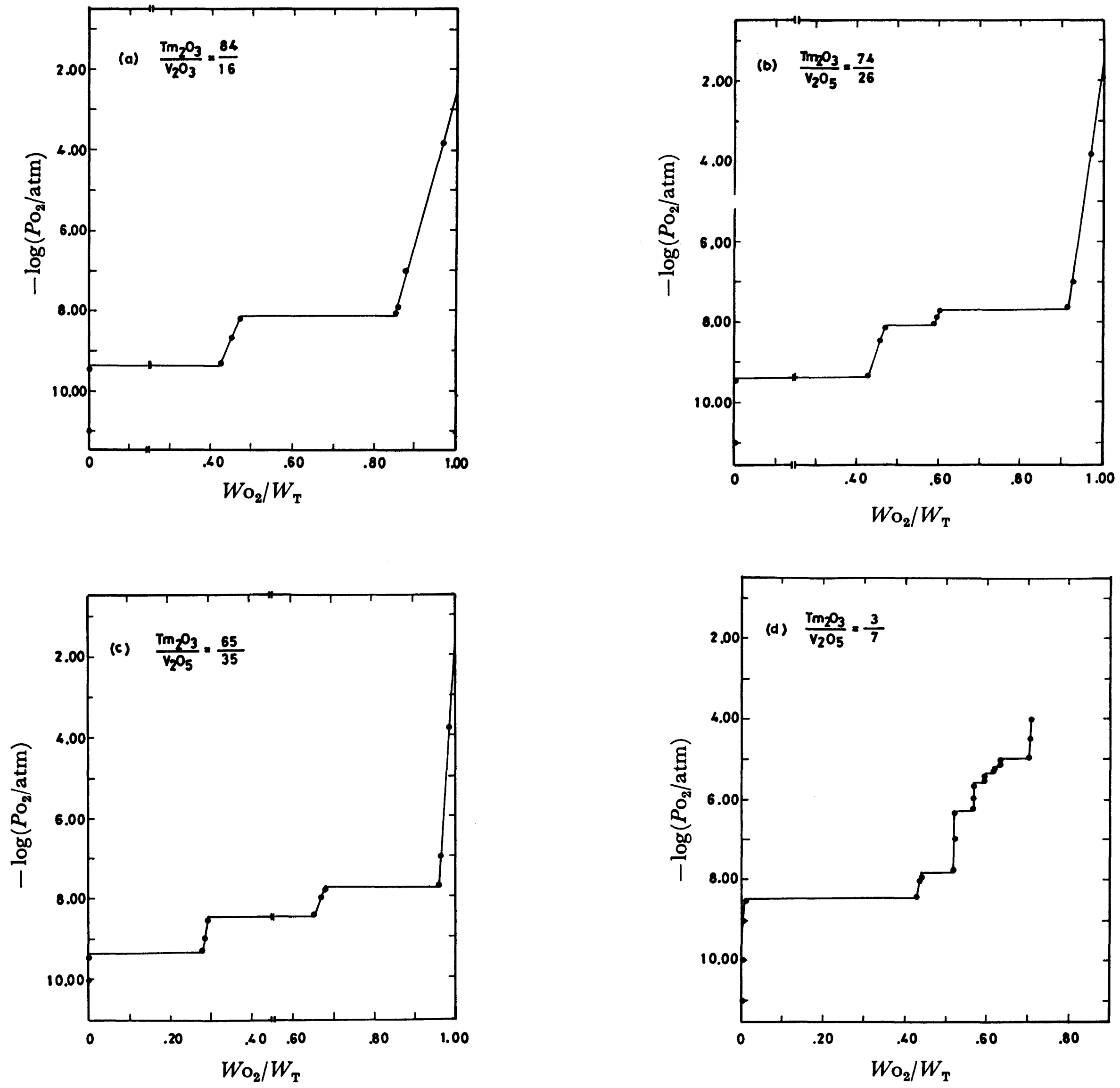

Fig. 1. The relationships between $-\log Po_2$ (atm) and the weight gains, W_{O_2}/W_T, of the samples. (a): $Tm_2O_3/V_2O_5=84/16$, (b): $Tm_2O_3/V_2O_5=74/26$, (c): $Tm_2O_3/V_2O_5=65/35$, (d): $Tm_2O_3/V_2O_5=3/7$.

reports[1,3–6] except one change at the oxygen partial pressure $\log Po_2=-8.47$ that corresponds to the equilibrium oxygen partial pressure of a reaction, $TmVO_3+1/2\,O_2=TmVO_4$. These oxygen partial pressures also correspond to the equilibrium oxygen partial pressures of reactions in the system, as will be shown in Table 5.

In Table 1, the results of the identification of phases are shown. In the first column are shown the compositions of the strating materials in mol%, in the second the experimental conditions of the oxygen partial pressure in terms of $\log Po_2$ (atm), in the third the experimental durations in hours, and in the last the phases that are found in the quenched samples by X-ray powder diffractometer using Cu $K\alpha$ radiation.

Based upon the above thermogravimetric results and the results of the identification of phases, a phase diagram of the system was drawn and is shown in Fig. 2. The following phases are stable under the present experimental conditions, omitting compounds in the V_2O_3–V_2O_5 system and Tm_2O_3 : $TmVO_4$, $TmVO_3$, $4Tm_2O_3\cdot V_2O_5$ ($Tm_8V_2O_{17}$, A), and $Tm_7V_3O_{16}$ (L). The compound $5Tm_2O_3\cdot V_2O_5$, which was reported[11] as a stable compound together with $4Tm_2O_3\cdot V_2O_5$ in air in the Tm_2O_3–V_2O_5 system, and the pyrochlore type $Tm_2V_2O_7$ were not found under the present experimental conditions.

The present phase diagram is different from those of the other systems[1–6] on account of the different coexisting compounds. That is, the Sm_2O_3–V_2O_3–V_2O_5 system has a ternary compound, $5Sm_2O_3\cdot V_2O_5$; the Lu_2O_3–V_2O_3–V_2O_5 system contains $Lu_7V_3O_{16}$, $Lu_2V_2O_7$, and LuV_4O_8; the Er_2O_3–V_2O_3–V_2O_5 system $4Er_2O_3\cdot V_2O_5$; the Gd_2O_3–V_2O_3–V_2O_5 system $0.81Gd_2O_3\cdot 0.19V_2O_5$; the La_2O_3–V_2O_3–V_2O_5 system $0.81La_2O_3\cdot 0.19V_2O_5$, $3La_2O_3\cdot V_2O_5$, and $0.71La_2O_3\cdot 0.19V_2O_5$; and the Nd_2O_3–V_2O_3–V_2O_5 system contains $0.81Nd_2O_3\cdot 0.19V_2O_5$ and $3Nd_2O_3\cdot V_2O_5$.

TABLE 1. IDENTIFICATION OF PHASES

Tm_2O_3 (mol %)	V_2O_5 (mol %)	$-\log$ (Po_2/atm)	Time/h	Phases
84	16	10.00	23	$Tm_2O_3 + TmVO_3$
		9.00	27	$Tm_2O_3 + Tm_7V_3O_{16}$
		7.00	30	$Tm_2O_3 + Tm_8V_2O_{17}$
		0.68	38	$Tm_2O_3 + Tm_8V_2O_{17}$
77	23	10.00	23	$Tm_2O_3 + TmVO_3$
		9.00	27	$Tm_2O_3 + Tm_7V_3O_{16}$
		8.00	48	$Tm_8V_2O_{17} + Tm_7V_3O_{16}$
		7.00	30	$Tm_8V_2O_{17} + TmVO_4$
60	40	10.00	23	$Tm_2O_3 + TmVO_3$
		9.00	27	$TmVO_3 + Tm_7V_3O_{16}$
		8.20	42	$TmVO_4 + Tm_7V_3O_{16}$
		7.00	30	$Tm_8V_2O_{17} + TmVO_4$
30	70	9.00	27	$V_2O_3 + TmVO_3$
		8.20	42	$V_2O_3 + TmVO_4$
		7.00	31	$V_3O_5 + TmVO_4$
		6.00	40	$V_4O_7 + TmVO_4$
		5.45	60	$V_5O_9 + TmVO_4$
		5.25	60	$V_6O_{11} + TmVO_4$
		5.05	47	$V_7O_{13} + TmVO_4$
		4.50	38	$VO_2 + TmVO_4$
10	90	8.80	27	$V_2O_3 + TmVO_3$
		7.90	47	$V_2O_3 + TmVO_4$
		7.00	31	$V_3O_5 + TmVO_4$
		6.00	40	$V_4O_7 + TmVO_4$
		5.45	60	$V_5O_9 + TmVO_4$
		5.25	60	$V_6O_{11} + TmVO_4$
		5.05	47	$V_7O_{13} + TmVO_4$
		4.50	38	$VO_2 + TmVO_4$

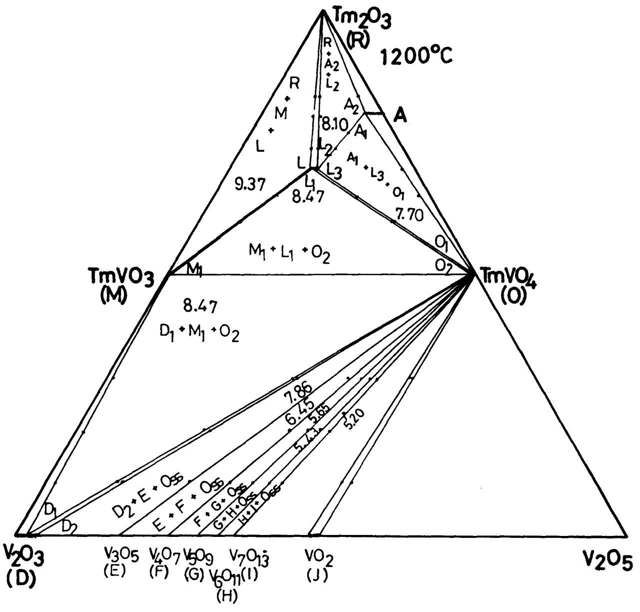

Fig. 2. Phase equilibria in the Tm_2O_3–V_2O_3–V_2O_5 system at 1200 °C. Numerical values in the three solid phases regions are the equilibrium oxygen partial pressure in $-\log P_{O_2}$. Abbreviations are the same as thosein Table 3.

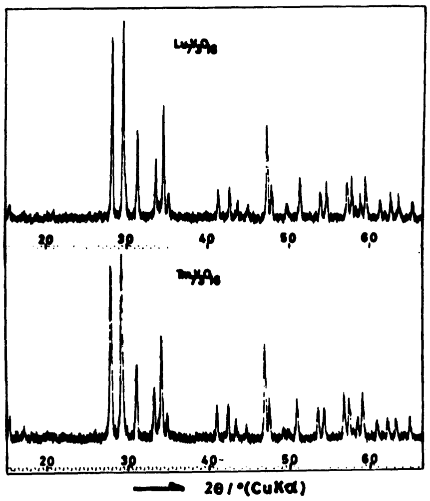

Fig. 3. The X-ray powder pattern of $Tm_7V_3O_{16}$ together with $Lu_7V_3O_{16}$.

TABLE 2. SPACINGS AND RELATIVE INTENSITIES OF THE COMPOUND, $Tm_7V_3O_{16}$

d/Å	I/I_0	d/Å	I/I_0
5.78	12	1.8536	7
3.20	98	1.7968	27
3.05	100	1.7121	20
2.878	44	1.6923	22
2.695	33	1.6229	29
2.624	58	1.6068	24
2.576	16	1.5799	11
2.206	21	1.5651	27
2.136	18	1.5237	12
2.092	12	1.4941	13
1.9380	59	1.4727	13
1.9175	23	1.4384	13

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

Component	Composition	Symbol	$-\log$ (Po_2/atm)	$\log a_i$
$TmVO_4$	$TmVO_{4.00}$	O	0.68—7.70[a)]	≈0
	$TmVO_{3.987}$	O_1	7.70	≈0
	$TmVO_{3.985}$	O_2	8.47	0
$TmVO_3$	$TmVO_{3.00}$	M	12.50—9.37	≈0
	$TmVO_{3.00}$	M_1	8.47	0
$Tm_8V_2O_{17}$	$Tm_8V_2O_{17.0}$	A	0.68—1.83[a)]	0.02
	$Tm_8V_2O_{16.72}$	A_1	7.70	0.06
	$Tm_8V_2O_{16.68}$	A_2	8.10	0
$Tm_7V_3O_{16}$	$Tm_7V_3O_{16.3}$	L	9.37	0
	$Tm_7V_3O_{16.4}$	L_1	8.47	−0.152
	$Tm_7V_3O_{16.7}$	L_2	8.10	−0.235
	$Tm_7V_3O_{16.6}$	L_3	7.70	−0.329

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

The compound $Tm_7V_3O_{16}$ is a new compound, although the atomic ratio is analogous to the compound $Lu_7V_3O_{16}$ that was found by us thorough the study of the Lu_2O_3–V_2O_3–V_2O_5 system.[2)] Both compounds, $Tm_7V_3O_{16}$ and $Lu_7V_3O_{16}$, have a similar powder X-ray diffraction pattern, as shown in Fig. 3, but we could not yet determine the crystallographic system. The spacing and relative intensities which were obtained

TABLE 4. UNIT CELL DIMENSIONS OF THE COMPOUNDS

Sample	$-\log (P_{O_2}/\text{atm})$	$\frac{a}{\text{A}}$	$\frac{b}{\text{A}}$	$\frac{c}{\text{A}}$	$\frac{\beta}{°}$	$\frac{V}{\text{A}^3}$	Ref.
$TmVO_4$	0.68	7.071 ± 0.001		6.260 ± 0.001		313.0 ± 0.1	Present
		7.071 ± 0.003		6.263 ± 0.003		313.1	12
		7.062 ± 0.002		6.252 ± 0.003			11
$TmVO_3$	12.00	5.243 ± 0.001	5.581 ± 0.001	7.551 ± 0.001		220.9 ± 0.	Present
		5.237	5.573	7.545		220.2	15
		5.248	5.575	7.548		220.8	16
$Tm_8V_2O_{17}$	7.00	10.42 ± 0.02	8.30 ± 0.02	16.07 ± 0.06	98.1 ± 0.2	137.7 ± 6	Present
		10.440 ± 0.003	8.328 ± 0.003	16.069 ± 0.010	98.23 ± 0.03		13

TABLE 5. GIBBS ENERGIES OF REACTIONS

Reaction	$-\log (P_{O_2}/\text{atm})$	$\frac{-\Delta G°}{\text{kJ}}$
(1) $2\,Tm_2O_3 + 3\,TmVO_3 + 1/2\,O_2 = Tm_7V_3O_{16}$	9.37 ± 0.05	132 ± 1
(2) $TmVO_3 + 1/2\,O_2 = TmVO_4$	8.47 ± 0.05	119 ± 1
(3) $5/3\,Tm_2O_3 + 2/3\,Tm_7V_3O_{16} + 2/3\,O_2 = Tm_8V_2O_{17}$	8.10 ± 0.07	157 ± 2
(4) $Tm_7V_3O_{16} + O_2 = 5/3\,TmVO_4 + 2/3\,Tm_8V_2O_{17}$	7.70 ± 0.07	228 ± 2

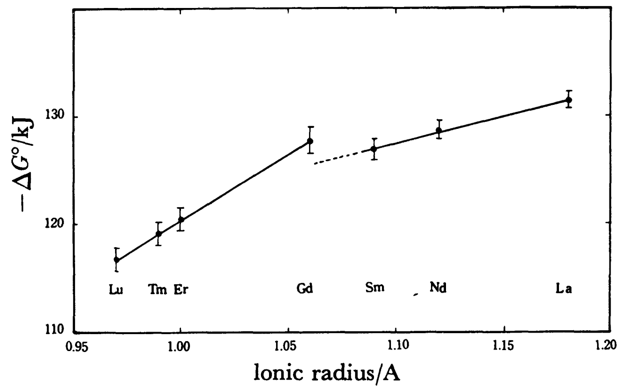

Fig. 4. The relationship between the ionic radius in 8 coordination number and the Gibbs energy of reaction, $LnVO_3 + 1/2\,O_2 = LnVO_4$.

by the X-ray powder diffractometer are shown in Table 2.

Compounds $Tm_8V_2O_{17}$, $Tm_7V_3O_{16}$, $TmVO_3$, $TmVO_4$, V_2O_3, and VO_2 have nonstoichiometric compositions. The relationship between a composition, N_O/N_Y, and the oxygen partial pressure of the solid solution, Y that means an arbitary component, were determined using the thermogravimetric results. Here, N_O and N_Y are the mole fractions of oxygen and of the component Y. Using the method of the least squares with a linear equation, $N_O/N_Y = a \log P_{O_2} + b$, the constants a and b for each solid solution were determined as follows: for $Tm_8V_2O_{17}$ 0.10 and 0.49 and for $Tm_7V_3O_{16}$ 0.17 and 0.186. As for the solid solutions $TmVO_4$ and $TmVO_3$, the composition ranges are too narrow to obtain such equations. Especially, the nonstoichiometric ranges of $TmVO_3$ are very small, although the width of ranges is a little exaggerated in Fig. 2. V_2O_3 and VO_2 were already discussed in the previous report.[1]

In Table 3, the compositions of the compounds at various oxygen partial pressures, stability ranges of the compounds in terms of $\log P_{O_2}$, the symbol of the compounds, and the activities of the component in the solid solutions at distinct oxygen partial pressures are tabulated. The activities of the components in the solid solutions were calculated with the Gibbs-Duhem equation using the thermogravimetric results of the N_O/N_Y *vs.* $\log P_{O_2}$ relations described above. A detailed method of the calculation has been discussed in the paper of Kimizuka and Katsura.[21] Since solid solution ranges of $TmVO_4$ and $TmVO_3$ were too small to get the general equations of N_O/N_Y *vs.* $\log P_{O_2}$, we took the activities of components $TmVO_4$ and $TmVO_3$ as unity over the whole range of compositions.

Lattice constants of the compounds $TmVO_4$, $TmVO_3$, and $Tm_8V_2O_{17}$ are tabulated in Table 4. Our values are in good agreement with those quoted in the Table.

Calculation of Gibbs Energies of Reactions. On the basis of the present phase diagram, Gibbs energies of the reactions represented in the system, except those in the partial system V_2O_3–V_2O_5, can be calculated by the equation $\Delta G° = -RT \ln K$, where R is the gas constant, T the absolute temperature, and K the equilibrium constant of each reaction. Chemical reactions, the equilibrium oxygen partial pressure for each reaction, and $\Delta G°$ values calculated are shown in Table 5. Activities of each component of the solid solutions, which are necessary for the calculations, are tabulated in Table 3.

The relationship between $\Delta G°$ and Ionic Radius. In the series of the Ln_2O_3–V_2O_3–V_2O_5 system, the common reaction $LnVO_3 + 1/2\,O_2 = LnVO_4$ appear in all the systems. So it is very interesting to correlate the $\Delta G°$ with some properties of this lanthanoid element. As mentioned above, we reported a linear relation between the $\Delta G°$ values of the formation of perovskite from Ln_2O_3, iron, and oxygen and the tolerance factor. In Fig. 4, is shown the relationship between the ionic radius of the lanthanoid element with coordination number 8[24] of $LnVO_4$ and $\Delta G°$ values. Unlike the case of Ln–Fe–O system, it seems to seperate to two groups:

the so-called heavy lanthanoid series and the so-called light one and they show a linear relationship with a rule that ΔG° values decrease with increasing the atomic radius. This pattern is similar even if the abscissa is changed to the radius of coordination number 12[25] of $LnVO_3$ or to the tolerance factor. As is well known, $LaVO_3$ has a tetragonal crystal system and $LaVO_4$ has a monoclinic system. The linear relation fits well even for La, in spite of the difference of crystal system. This means that the difference of the crystal system does not affect the energies of such a reaction.

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