1820 © 1982 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 55, 1820—1823 (1982) [Vol. 55, No. 6

Phase Equilibria in the Gd_2O_3-V_2O_3-V_2O_5 System at 1200 °C

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(Received September 16, 1981)

The phase equilibria in the Gd_2O_3–V_2O_3–V_2O_5 system are studied at 1200 °C by changing the oxygen partial pressure from −0.68(air) to −12.50 in terms of log P_{O_2}. In this system, Gd_2O_3, $GdVO_4$, $GdVO_3$, $0.81Gd_2O_3 \cdot 0.19V_2O_5$, V_2O_3, V_3O_5, V_4O_7, V_5O_9, V_6O_{11}, V_7O_{13}, and VO_2 are stable. $GdVO_4$ and $0.81Gd_2O_3 \cdot 0.19V_2O_5$ have nonstoichiometric compositions. The crystallographic properties of the latter are determined with reference to the indices of a certain compound, $4Tm_2O_3 \cdot V_2O_5$. On the basis of the phase equilibria, the Gibbs free energy of these two reactions: $31/50\ Gd_2O_3 + 19/50\ GdVO_3 + 19/100\ O_2 = Gd_{1.62}V_{0.38}O_{3.38}$ and: $GdVO_3 + 1/2\ O_2 = GdVO_4$ are determined to be 57.0 and 127.8 kJ respectively.

The phase equilibria in the Ln_2O_3–V_2O_3–V_2O_5 systems (Ln=Sm, Lu, and Er) at 1200 °C have been established.[1–3] In these systems, the existence of V_nO_{2n-1}(n=3—7) was confirmed between V_2O_3 and VO_2. In addition to the above vanadium oxides, in the Sm_2O_3–V_2O_3–V_2O_5 system, $5Sm_2O_3 \cdot V_2O_5$ ($Sm_{10}V_2O_{20}$), $SmVO_3$, and $SmVO_4$; in the Lu_2O_3–V_2O_3–V_2O_5 system, $LuVO_3$, $LuVO_4$, $Lu_7V_3O_{16}$, $Lu_2V_2O_7$, and LuV_4O_8, and in the Er_2O_3–V_2O_3–V_2O_5 system, $ErVO_3$, $ErVO_4$, and $4Er_2O_3 \cdot V_2O_5$ ($Er_8V_2O_{17}$) were stable as the ternary compounds. Different patterns of the phase diagram were obtained as results of differences in the coexisting compounds.

In the present study, Gd_2O_3 was chosen as one of the Ln_2O_3 compounds, because Gd is the first one in the heavy-lanthanoid series from the viewpoint of the electron configuration.

In the Gd_2O_3–V_2O_3 system, only $GdVO_3$ is well known as a double-oxide phase. However, the system has not yet completely been studied because of the instability of V_2O_3 in an atmosphere of air. The crystallographic properties of $GdVO_3$ have been investigated by many researchers.[4–6] It is an orthorhombic system, like the other rare-earth vanadites except $LaVO_3$ and $CeVO_3$.[4,6]

The Gd_2O_3–V_2O_5 system was studied by Brusset *et al.*[7,8] in the temperature range from 600 to 1500 °C. They found two compounds, $4Gd_2O_3 \cdot V_2O_5$ and $5Gd_2O_3 \cdot V_2O_5$, as intermediate phases above 1150 °C in addition to $GdVO_4$. The spacing and relative intensities of the two compounds were also included in one of the reports,[7] but the assignment of the indices was not successful.

The objectives of the present study are: (1) to establish the detailed phase equilibria in the Gd_2O_3–V_2O_3–V_2O_5 system at 1200 °C in order to clarify the stable ternary compounds, (2) to calculate the Gibbs free energy of the reactions of the ternary compounds which were found in the phase diagram, and (3) to ascertain whether or not there exists a linear relationship between the Gibbs free energy of the reactions and the ionic radius of the lanthanoid, as is found in the Ln–Fe–O.[9]

Experimental

Analytical grades of Gd_2O_3 (99.9%) and V_2O_5, which had been obtained by heating guaranteed-grade NH_4VO_3 at 500 °C in air for about 24 h, were used as the starting materials. The desired ratios of Gd_2O_3/V_2O_5 were obtained by mixing the appropriate quantities thoroughly in an agate motar under ethyl alcohol. The mixtures thus made were treated by the procedures described previously.[1] The apparatus and procedures for controlling the oxygen partial pressures, keeping the furnace at a constant temperature, the method of thermogravimetry, the criterion for an equilibrium establishment, the method of identifing solid phases after quenching, the method of lattice-constant measurement, and the method of wet chemical analysis were the same as those described in previous papers.[1,10–13]

The oxygen partial pressure of −12.50 in terms of log P_{O_2} was chosen as the reference oxygen partial pressure, because even samples which contain less than 50% of Gd_2O_3 in mole are stable in composition in this reference atmosphere at 1200 °C.

Results and Discussion

Phase Equilibria. Ten samples with Gd_2O_3/V_2O_5 mole ratios of 86/14, 81/19, 76/24, 7/3, 6/4, 1, 4/6, 2/8, and 1/9 were prepared for use in the thermogravimetric experiment. In Fig. 1, the relationship between the oxygen partial pressure and the weight change, W_{O_2}/W_T, is shown; W_{O_2} is the weight gain of the sample from the reference-state atmosphere of log P_{O_2}=−12.50, and W_T is the total weight gain that the sample would get if the V_2O_3 in the sample changed to V_2O_5. The experimental results for four representative samples, 86/14, 8/2, 7/3, and 2/8, are shown in Fig. 1.

In Table 1, the results of the identification of the phases are shown: the first column shows the compositions of the starting materials; in the second and third are shown the experimental conditions of the oxygen partial pressure in terms of log P_{O_2} and the experimental duration respectively; in the fourth are shown the phases, as identified by means of an X-ray powder diffractometer using Cu $K\alpha$ radiation.

Based upon the above experimental results, a phase diagram of the system at 1200 °C is depicted in Fig. 2. The following phases are present under the present experimental conditions except in the V_2O_3–V_2O_5 system: Gd_2O_3(R), $Gd_{1.62}V_{0.38}O_{3.38}$(A), $GdVO_3$(L), and $GdVO_4$(K). The compounds in the V_2O_3–V_2O_5 system are the same as those in the previous report.[1]

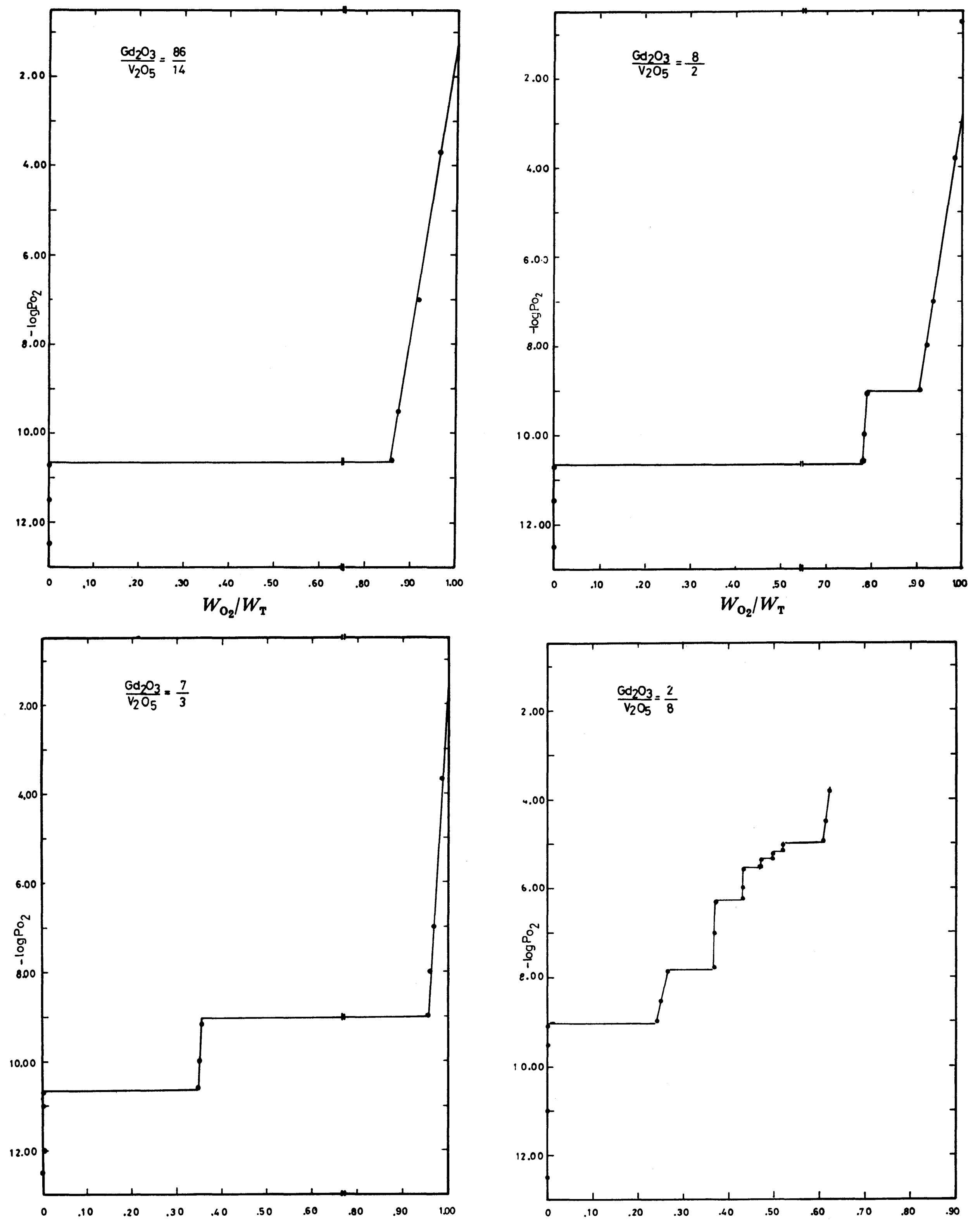

Fig. 1. The relationship between $-\log P_{O_2}$ and the weight gain (W_{O_2}/W_T) of the sample.
(a): $Gd_2O_3/V_2O_5=86/14$, (b): $Gd_2O_3/V_2O_5=8/2$, (c): $Gd_2O_3/V_2O_5=7/3$, (d): $Gd_2O_3/V_2O_5=2/8$.

Compound A has no round mole ratio such as the $4Gd_2O_3 \cdot V_2O_5$ reported by Brusset *et al.*[7,8] A straight line that connects the experimental points tends toward the $0.81Gd_2O_3 \cdot 0.19V_2O_5$ composition point rather than toward $4Gd_2O_3 \cdot V_2O_5$. This result is also supported by the results of the thermogravimetry of the sample 8/2 (Fig. 1-2). That is, the abrupt change occured at -9.06 in $\log P_{O_2}$. In order to support the fact by quenching method, we tried to make two phases quenched samples (A+$GdVO_3$) and (A+$GdVO_4$) at

TABLE 1. IDENTIFICATION OF PHASES

Starting material (mol%)		$-\log P_{O_2}$	Time / h	Phases[a)]
Gd_2O_3	V_2O_5			
86	14	11.00	10.0	$Gd_2O_3+GdVO_3$
		10.50	18.7	Gd_2O_3+A
		8.50	19.4	Gd_2O_3+A
		0.68	23.5	Gd_2O_3+A
70	30	11.00	10.0	$Gd_2O_3+GdVO_3$
		10.50	18.7	$A+GdVO_3$
		8.50	19.4	$A+GdVO_4$
		0.68	23.5	$A+GdVO_4$
20	80	11.00	10.0	$GdVO_3+V_2O_3$
		10.50	18.7	$GdVO_3+V_2O_3$
		8.50	19.4	$GdVO_4+V_2O_3$
		7.00	19.0	$GdVO_4+V_3O_5$
		5.75	28.0	$GdVO_4+V_4O_7$
		5.50	26.0	$GdVO_4+V_5O_9$
		5.30	41.5	$GdVO_4+V_6O_{11}$
		5.10	91.5	$GdVO_4+V_7O_{13}$
		4.50	39.0	$GdVO_4+VO_2$
10	90	11.00	10.0	$GdVO_3+V_2O_3$
		10.50	18.7	$GdVO_3+V_2O_3$
		8.50	19.4	$GdVO_4+V_2O_3$
		7.00	19.0	$GdVO_4+V_3O_5$
		5.75	28.0	$GdVO_4+V_4O_7$
		5.50	26.0	$GdVO_4+V_5O_9$
		5.30	41.5	$GdVO_4+V_6O_{11}$
		5.10	91.5	$GdVO_4+V_7O_{13}$
		4.50	39.0	$GdVO_4+VO_2$

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

$\log P_{O_2}=-10.00$ and in air. However, peaks of $GdVO_3$ and $GdVO_4$ are too weak to identify the phases.

Compounds A and $GdVO_4$ have non-stoichiometric compositions. The relationship between the oxygen partial pressure and the compositions are represented by the following equations: $N_O/N_A=5.83\times10^{-3}\log P_{O_2}+8.83\times10^{-3}$ for Compound A and $N_O/N_K=1.50\times10^{-3}\log P_{O_2}+4.5\times10^{-3}$ for $GdVO_4$. Here, N_O/N_A and N_O/N_K denote the mole fraction ratio of the oxygen to the oxide component, shown by the letters A and K, and the deviation from the stoichiometry. Non-stoichiometry was not found for $GdVO_3$ under those experimental conditions.

In Table 2, the compositions of the compound, as calculated from the results of the thermogravimetry, the symbols of the compounds, the stability ranges of the compounds in terms of the oxygen partial pressure

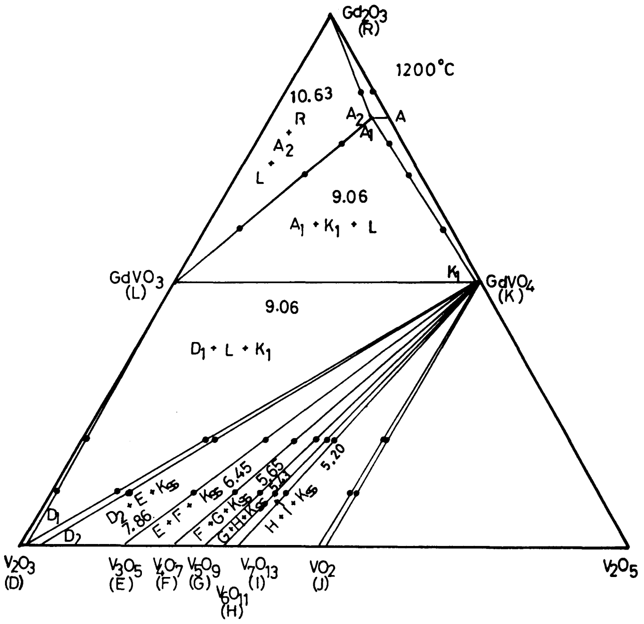

Fig. 2. Phase equilibria in the Gd_2O_3–V_2O_3–V_2O_5 system at 1200 °C. Numerical values in three solid phases regions are the oxygen partial pressure in $-\log P_{O_2}$ in equilibrium. Abbreviations are the same as those in Table 2.

TABLE 3. SPACINGS AND RELATIVE INTENSITIES OF A POWDER SAMPLE OF $Gd_{1.62}V_{0.38}O_{3.38}$ AND PREVIOUS DATA OF $Gd_8V_2O_{17}$

h	k	l	d(obsd)	d(calcd)	I/I_0	$Gd_8V_2O_{17}$	
						d	I/I_0
1	2	3	3.12	3.14	100	3.166	65
2	0	4	2.95	2.97	19	3.129	100
0	3	2	2.70	2.75	45	3.009	55
0	3	3	2.59	2.57	11	2.919	8
0	4	1	2.14	2.17	12	2.690	45
−5	2	2	1.912	1.916	51	1.941	25
−2	4	5	1.766	1.765	18	1.922	10
5	3	2	1.631	1.629	42	1.881	15
						1.870	15
						1.865	20
						1.655	10
						1.639	10
						1.625	10
						1.618	10
						1.589	10
						1.564	7

TABLE 2. COMPOSITIONS, STABILITY RANGES IN OXYGEN PARTIAL PRESSURES, AND ACTIVITIES IN SOLID SOLUTIONS

Component	Composition	Symbol	$-\log P_{O_2}$	$\log a_i$
$Gd_{1.62}V_{0.38}O_{3.38}$	$Gd_{1.62}V_{0.38}O_{3.38}$	A	1.52[b)]–0.68[a)]	0.121
	$Gd_{1.62}V_{0.38}O_{3.34}$	A_1	9.06	0.0381
	$Gd_{1.62}V_{0.38}O_{3.33}$	A_2	10.63	0
$GdVO_4$	$GdVO_4$	K	3.00[b)]–0.68[a)]	0.0138
	$GdVO_{3.99}$	K_1	9.06	0

a) The stability range in $\log P_{O_2}$ may be higher than −0.68. b) This value was obtained by extrapolation using the experimental values.

TABLE 4. UNIT-CELL DIMENSIONS OF THE COMPOUNDS

Sample	$-\log P_{O_2}$	a/Å	b/Å	c/Å	β/°	V/Å^3	Ref.
$Gd_{1.62}V_{0.38}O_{3.38}$	10.00	10.69±0.06	8.70±0.05	16.4±0.3	99.5±0.7	1504±27	
	0.68	10.70±0.07	8.77±0.08	16.3±0.3	99.6±0.9	1503±35	
$GdVO_3$	12.00	5.341±0.003	5.605±0.003	7.634±0.003		228.5±0.2	
		5.341	5.606	7.630			5
		5.342	5.604	7.637		228.6	6
$GdVO_4$	8.50	7.210±0.001		6.347±0.001		330.0±0.1	
	0.68	7.207±0.001		6.344±0.001		329.5±0.1	
		7.216±0.003		6.351±0.003			8
		7.211		6.350		330.2	15

in $\log P_{O_2}$, and the activities of the components are tabulated. The activities of all the components in the solid solutions are calculated by using the Gibbs-Duhem equation. A detailed method of the calculation has been described in the paper of Kimizuka and Katsura.[13]

The assignment of indices for Compound A was tried with the aid of previous data on $4Tm_2O_3 \cdot V_2O_5$.[14] In Table 3, the results of the assignment of indices, the relative intensities, and the spacings of the sample are tabulated, together with the spacings and relative intensities of $4Gd_2O_3 \cdot V_2O_5$ obtained by Brusset *et al.*[7] There are other weak and broad peaks that are not shown in Table 3. Though Brusset *et al.* did not present the indices, the two substance have similar spacings.

The lattice constants of three samples, A, $GdVO_3$, and $GdVO_4$ are tabulated in Table 4. The figures in second column are the oxygen partial pressure used in preparation of the quenched samples. The present values are in good agreement with those of the previous reports. The experimental errors in the lattice constants of Compound A are, however, still large. Refinement will be done in the near future.

Calculation of Gibbs Free Energy of Reactions. On the basis of the phase equilibria, the Gibbs free energy of reactions, referred to the following equations:

$$31/50Gd_2O_3 + 19/50GdVO_3 + 19/100O_2 = Gd_{1.62}V_{0.38}O_{3.32} \qquad (1)$$

and:

$$GdVO_3 + 1/2O_2 = GdVO_4 \qquad (2)$$

can be calculated from this equation: $\Delta G^\circ = -RT \ln K$, where R is the gas constant; T, the absolute temperature, and K, the equilibrium constant of the reaction. The activities of $Gd_{1.62}V_{0.38}O_{3.38}$ and $GdVO_4$ at the A_2 and K_1 compositions (Table 2) in both solid solutions may be equal to unity. Values of 57.0 and 127.8 kJ were obtained for Reactions 1 and 2 respectively.

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