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Phase Equilibria in Sm_2O_3-V_2O_3-V_2O_5 System at 1200 °C

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The phase equilibria in the Sm_2O_3–V_2O_3–V_2O_5 system was established at 1200 °C. In this system, Sm_2O_3, $Sm_{10}V_2O_{20}$, $SmVO_3$, $SmVO_4$, V_2O_3, V_3O_5, V_4O_7, V_5O_9, V_6O_{11}, and VO_2 were stable and $Sm_{10}V_2O_{20}$, $SmVO_4$, V_2O_3, and VO_2 had the non-stoichiometry. On the basis of the phase equilibria, the Gibbs free energy for the reactions, $SmVO_3+1/2O_2=SmVO_4$ and $4\,Sm_2O_3+2\,SmVO_3+O_2=Sm_{10}V_2O_{20}$, were determined to be -30.4 ± 0.1 and -76.8 ± 0.1 kcal, respectively. Also, standard Gibbs free energies of oxidation of various vanadium oxides were calculated.

$LnVO_4$ has been prepared and its crystallographic,[1,2] fluorescent,[3] and magnetic[4] properties have been investigated. $LnVO_4$ has a tetragonal structure, except for $LaVO_4$. On the other hand, $LnVO_3$ has the crystallographic form of orthorhombic, except for $LaVO_3$ and $CeVO_3$.[5]

Although $LnVO_4$ and $LnVO_3$ had been prepared and their various physical properties studied, as described above, the phase equilibria in the system Ln–V–O had not been determined at high temperature in low oxygen partial pressures.

Many studies have been carried out on the system V–O. Among early studies, Andersson[6] investigated the system VO–V_2O_5 at temperatures between 650—1000 °C, and found a series of vanadium oxides which could be represented with the general formula, V_nO_{2n-1}, changing the *n*'s from 2 to 8.

Kosuge *et al.*[7] also investigated the system V_2O_3–V_2O_5 at 800 °C, and recognized the phases V_nO_{2n-1} of $n=$ 2—7.

Recently, thermochemical studies and phase equilibria in the system V_2O_3–VO_2 at 1600 K,[8] in the system V_2O_3–V_4O_7 at temperatures from 1400 to 1700 K,[9] in the system V_2O_3–VO_2 at 1307 K,[10] in the system V_nO_{2n-1} at temperatures from 1000 to 1200 °C,[11] and in the system V_2O_3–VO_2 at temperatures from 1173 to 1423 K[12] were investigated by means of the quenching and thermogravimetric methods under a controlled oxygen partial pressure by equilibration with CO_2 and H_2 or CO and CO_2. They reported the phases of vanadium oxide and standard free energies of oxidation,[8–12] standard enthalpy,[9,10,12] and entropy change.[9,10,12]

The precise phase equilibria in the system Sm_2O_3–V_2O_3 have not been reported. But the existence of stable phase of $SmVO_3$ is well known, as described above. Recently the phase equilibria in the system Sm_2O_3–V_2O_5 was studied by Brusset *et al.*[13] and Remizov *et al.*[14]

In the report, Brusset *et al.* showed the existence of compounds of $4Sm_2O_3\cdot V_2O_5$ and $5Sm_2O_3\cdot V_2O_5$. On the other hand Remizov *et al.* showed the existence of compounds of $Sm_2O_3\cdot 2V_2O_5$ and $3Sm_2O_3\cdot V_2O_5$. There are sharp differences in the results regarding to the composition.

The objectives of the present study are to establish the detailed phase equilibria in the system Sm_2O_3–V_2O_3–V_2O_5 at 1200 °C by changing the oxygen partial pressures, to calculate the thermochemical values based upon the phase equilibria, and to ascertain, upon completion of the studies of the Ln–V–O system, whether the trend of the linearity of the Gibbs free energy of reaction with rare-earth ionic radii in the system Ln–Fe–O[15] will be observed or not when the iron is changed to vanadium.

Experimental

Analytical grade of Sm_2O_3 (99.9%) and V_2O_5 which was made from the guaranteed grade of NH_4VO_3 by heating at 500 °C in air for 24 h have been employed as starting materials. The desired ratios of Sm_2O_3/V_2O_5 were obtained by mixing throughly in an agate mortar with ethyl alcohol. The mixed samples were heated at 600 °C for 24 h at an oxygen partial pressure of $10^{-10.0}$ atm to reduce V_2O_5 to V_2O_3. The temperature of the furnace was increased to 1200 °C in the same P_{O_2} to solidify the samples. After 6 h, the samples were quenched. Samples thus prepared were crushed to obtain small size pieces (about $2\times3\times3$ mm^3), as described previously.[16]

Mixed gases of CO_2 and H_2 were used to obtain low oxygen partial pressures in the present experiment. The actual oxygen partial pressure of the gas phases was measured by means of a solid electrolytic cell composed of $(ZrO_2)_{0.85}(CaO)_{0.15}$.[8] Phases in quenched samples were identified by the powder X-ray diffraction method with (Ni-filtered) Cu*K*α radiation.

Details of the apparatus, procedures for maintaing constant temperature, methods of thermogravimetry and quenching, and the criterion for equilibrium establishment were the same as those described in previous papers.[8,16,17]

Lattice constants were determined by the powder X-ray diffraction method with Ni-filtered Cu*K*α radiation and with a slow scanning speed of 0.5° per minute. Instrumental errors were calibrated by measuring the diffraction angles of a standard specimen of silicon.

It was found that the V_2O_3 phase was stable: that is, its composition remains constant over a wide range of oxygen partial pressures.[8] During the preliminary work in the present experiments on the V–O system and mixed samples, this fact was ascertained (Fig. 1). On the basis of these preliminary results, an oxygen partial pressure of $10^{-12.00}$ atm was chosen as the reference weight standard. Vanadium contents in the starting materials and quenched samples are determined volumetrically by adopting the zinc–amalgam method[18] in order to check the thermogravimetric results. Samarium contents in the samples are determined by precipitating as samarium oxalate and igniting of the precipitate to samarium sesquioxide.

The results of duplicated wet chemical analysis and the

Table 1. Some comparisons with results obtained from thermogravimetry and by wet chemical analysis of the quenched samples

	$-\log P_{O_2}$	V_t	V_a	Sm_t	Sm_a
$V_2O_{5.000}$[a)]	0.68	56.02	56.0		
$VO_{1.998}$	4.50	61.54	61.5		
$V_2O_{3.065}$	7.90	67.51	67.5		
$V_2O_{3.000}$	11.00	67.98	68.0		
$SmVO_{4.000}$	0.68	19.20	19.1	56.68	56.6
$SmVO_{3.980}$	9.00	19.22	19.2	56.75	56.7
$SmVO_{3.000}$	11.00	20.43	20.4	60.32	60.2

a) Starting material.

results of the thermogravimetric determination are shown in Table 1. Molecular formulas in the first column in Table 1 imply the compositions obtained from the thermogravimetry at each oxygen partial pressure in the second column. V_t and Sm_t are the weight % of the vanadium and samarium calculated from the compositions in the first coumn, whereas V_a and Sm_a are the weight % of the vanadium and samarium of the quenched samples obtained by wet chemical analysis.

Results and Discussion

Phase Equilibrium. Eight samples with Sm_2O_3/V_2O_5 compositions of 0.1111, 0.2500, 0.4286, 1.000, 1.500, 2.333, 5.000, and 5.667 were prepared. In Fig. 1, the relationship between oxygen partial pressures and compositions, VO_x or $Wo_2/W_T \times 100$, are shown, where Wo_2 is the weight gain from the standard state and W_T the total weight gain of the mixed sample as if the reaction, $V_2O_3+O_2=V_2O_5$, were to be completed. Based upon the experimental results of the thermogravimetry and identifications of the sample phases (Table 2), a phase diagram can be depicted. The results of the phase equilibria are illustrated in Fig. 2. The following phases were stable under the present experimental conditions: Sm_2O_3(R), $Sm_{10}V_2O_{20}$(A), $SmVO_4$(B), $SmVO_3$(C), V_2O_3(D), V_3O_5(E), V_4O_7(F), V_5O_9(G), V_6O_{11}(H), V_7O_{13}(I), and VO_2(J). Letters in parentheses are the abbreviations of the compounds. Other Magnéli phases of V–O system could not definitely be detected as a single phase under the experimental conditions.

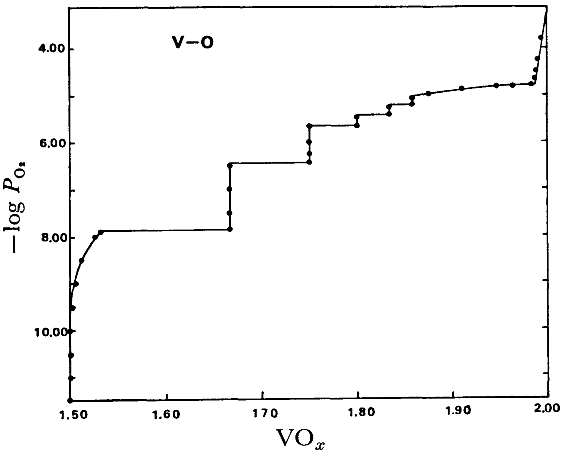

Fig. 1-1. The relationship between $-\log P_{O_2}$ and VO_x at 1200 °C.

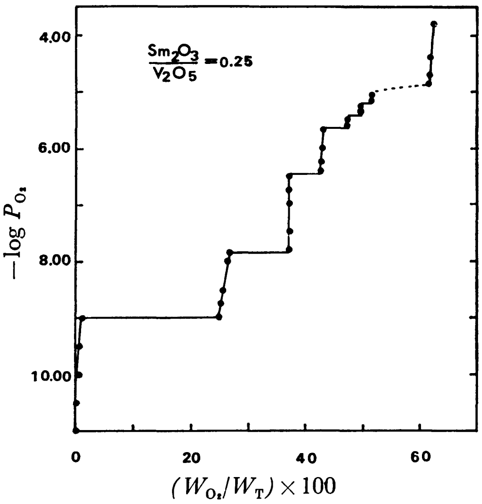

Fig. 1-2. The relationship between $-\log P_{O_2}$ and weight gains of the sample, $Sm_2O_3/V_2O_5=0.25$, at 1200 °C.

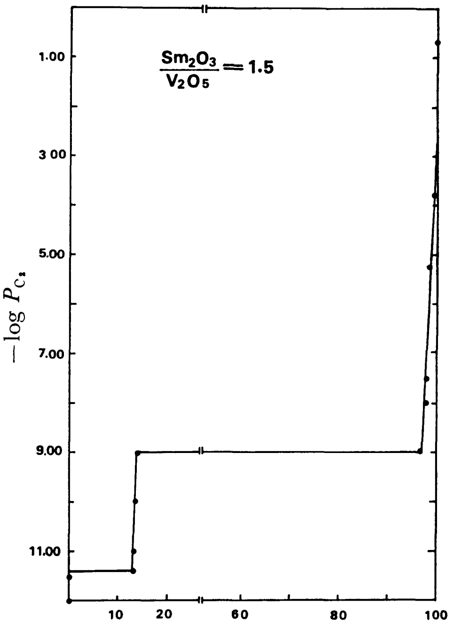

Fig. 1-3. The relationship between $-\log P_{O_2}$ and weight gains of the sample, $Sm_2O_3/V_2O_5=1.5$ at 1200 °C.

Also the compounds of $3Sm_2O_3 \cdot V_2O_5$ and $4Sm_2O_3 \cdot V_2O_5$ did not appear under the experimental conditions.

Sm_2O_3 was stable in this experimental condition as already described.[19)] $Sm_{10}V_2O_{20}$, $SmVO_4$, V_2O_3, and VO_2 have apparent deviations from the stoichiometric composition, judging by the results of thermogravimetry. As for V_2O_3, many investigators have already pointed out the same phenomena.[6–8)] Deviations from the stoichiometry of VO_2 were recognized by Hoschek and Klemm.[20)] They stated that the VO_2 phase was homogeneous between $VO_{1.8}$ and $VO_{2.0}$. But Andersson pointed out that the homogeneity range of this phase might be very low, arguing from his experimental

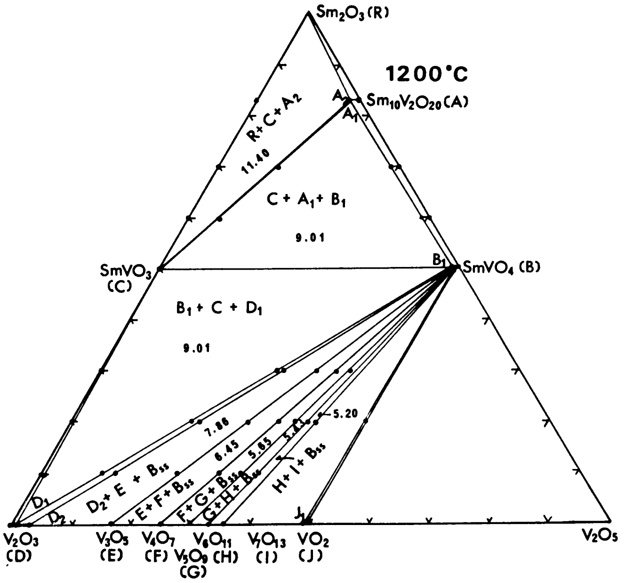

Fig. 2. Phase equilibria in the system Sm_2O_3–V_2O_3–V_2O_5 at 1200 °C. Numerical values in the three solid phases regions are the oxygen partial pressures in $-\log P_{O_2}$ in equilibrium. Abbreviations are the same as those in Table 4.

results of no displacement of the powder lines. The present results showed that the solid solution range is from $VO_{1.988}$ at $\log P_{O_2}=-4.71$ to $VO_{1.995}$ at $\log P_{O_2}=-3.79$ (in CO_2 at 1200 °C).

The deviation from the stoichiometric composition of $Sm_{10}V_2O_{20}$ extended up to $Sm_{10}V_2O_{19.78}$ at $\log P_{O_2}=-11.40$ atm, that of $SmVO_4$ up to $SmVO_{3.980}$ at $\log P_{O_2}=-9.01$, and that of V_2O_3 up to $V_2O_{3.065}$ at $\log P_{O_2}=-7.86$.

The lattice constants of the phases which appear in this system are given in Table 3, together with the data of other authors.[8,21,22,24] The crystal system of $Sm_{10}V_2O_{20}$ could not be determined. Although the relative intensities and *d*-values of $Er_{10}V_2O_{20}$,[26] $Gd_{10}V_2O_{20}$,[26] and $Y_{10}V_2O_{20}$[27] had been reported, their crystal systems have also not yet been determined. *d*-Values and relative intensities of $Sm_{10}V_2O_{20}$ obtained by the powder X-ray method are shown in Table 4. As shown in Table 3, the crystal data of the present samples are in very good agreement with those of the previous authors. Lattice constants of V_2O_3 were determined on the basis of the hexagonal type, and rhombohedral values recalculated from the hexagonal values are shown in parentheses. The lattice constants of $SmVO_4$ and VO_2 solid solutions are constant irrespective of the compositional variations, but those of V_2O_3 decrease with the increasing of the oxygen partial pressures. These phenomena seem to be reflected in the narrow solid solution range of $SmVO_4$ and VO_2, and in the more wide solid solution range of V_2O_3 and in the increasing of the smaller quadrivalent vanadium content.

Calculations of Standard Gibbs Free Energies of Ternary Compounds. On the basis of the phase equilibria, the standard Gibbs free energies of reaction of the $Sm_{10}V_2O_{20}$ and $SmVO_4$ compounds can be calculated by referring to the following equations:

Table 2. Identification of phases

Starting Materials (mol%)		$-\log P_{O_2}$ (atm)	Time (h)	Phases
Sm_2O_3	V_2O_5			
85	15	0.68	48	$Sm_{10}V_2O_{20}+Sm_2O_3$
		8.00	23	$Sm_{10}V_2O_{20}+Sm_2O_3$
		10.00	23	$Sm_{10}V_2O_{20}+Sm_2O_3$
		12.00	23	$SmVO_3 + Sm_2O_3$
70	30	0.68	48	$Sm_{10}V_2O_{20}+SmVO_4$
		8.00	23	$Sm_{10}V_2O_{20}+SmVO_4$
		10.00	23	$Sm_{10}V_2O_{20}+SmVO_3$
		12.00	23	$SmVO_3 + Sm_2O_3$
50	50	0.68	38	$SmVO_4$
		9.00	32	$SmVO_4$
		11.00	24	$SmVO_3$
30	70	4.50	96	$VO_2 + SmVO_4$
		5.10	60	$V_7O_{13} + SmVO_4$
		5.30	51	$V_6O_{11} + SmVO_4$
		5.50	56	$V_5O_9 + SmVO_4$
		5.75	51	$V_4O_7 + SmVO_4$
		7.60	48	$V_3O_5 + SmVO_4$
		8.00	41	$V_2O_3 + SmVO_4$
		10.00	26	$V_2O_3 + SmVO_3$
		12.00	23	$V_2O_3 + SmVO_3$
10	90	4.50	96	$VO_2 + SmVO_4$
		5.10	60	$V_7O_{13} + SmVO_4$
		5.30	51	$V_6O_{11} + SmVO_4$
		5.50	56	$V_5O_9 + SmVO_4$
		5.75	51	$V_4O_7 + SmVO_4$
		7.60	48	$V_3O_5 + SmVO_4$
		8.00	41	$V_2O_3 + SmVO_4$
		10.00	26	$V_2O_3 + SmVO_3$
		12.00	23	$V_2O_3 + SmVO_3$
0	100	4.00	96	VO_2
		5.10	48	V_7O_{13}
		5.30	48	V_6O_{11}
		5.45	48	V_5O_9
		5.75	48	V_4O_7
		7.00	42	V_3O_5
		7.85	48	V_2O_3
		9.00	30	V_2O_3
		11.00	24	V_2O_3

$$SmVO_3 + 1/2O_2 = SmVO_4 \qquad (1)$$

$$4Sm_2O_3 + 2SmVO_3 + O_2 = Sm_{10}V_2O_{20} \qquad (2)$$

The standard Gibbs free energies of both reactions may be calculated directly by adopting the equilibrium oxygen partial pressures corresponding to the Eqs. 1 and 2. Here, the activity of each component, $SmVO_4$ and $Sm_{10}V_2O_{20}$, in each solid solution was set equal to one, the composition $SmVO_{3.980}$ (B_1 in Fig. 2) was in equilibrium with $SmVO_3$, and $Sm_{10}V_2O_{19.78}$ (A_2 in Fig. 2) was in equilibrium with $SmVO_3$ and Sm_2O_3. The standard Gibbs free energies of the reactions (1) and (2) may be determined from the equation: $\Delta G^\circ = -RT\ln K$, where R is the gas constant, T the absolute temperature, and K the equilibrium constant. The values, -30.4 ± 0.1 and -76.8 ± 0.1 kcal, are obtained by referring to reactions

Table 3. Unit cell dimensions of the compounds

Compd.	$-\log P_{O_2}$	a(Å)	b(Å)	c(Å)	α	β	γ	V(Å^3)
$SmVO_4$	0.68	7.263±0.001		6.387±0.001				336.9±0.1
	9.00	7.261±0.001		6.387±0.001				336.7±0.1
		7.2625[21]		6.3894				
$SmVO_3$	11.00	5.398±0.002	5.591±0.002	7.677±0.002				231.7±0.2
		5.393[22]	5.588	7.672				
V_2O_3	11.00	4.950±0.001		13.990±0.002				296.8±0.1
		(5.469)			(53.8)			
	7.88	4.940±0.001		13.964±0.003				295.1±0.1
		(5.459)			(53.8)			
		5.472[8]			53.80			
V_3O_5	7.00	10.00 ±0.04	5.032±0.005	9.86 ±0.04		138.8±0.2		327 ±2
		9.993[8]	5.063	9.872		138.62		
V_4O_7	5.75	5.500±0.004	6.988±0.005	12.242±0.005	95.2±0.1	95.1±0.1	109.2±0.1	439.0±0.4
		5.51[24]	7.01	12.92	96.2	95.2	109.2	
V_5O_9	5.50	5.467±0.006	7.002±0.007	8.71 ±0.01	97.3±0.1	112.4±0.1	109.2±0.1	278.5±0.4
		5.47[24]	6.99	8.72	97.5	112.4	109.0	
V_6O_{11}	5.30	5.439±0.003	6.991±0.002	23.65 ±0.01	98.5±0.1	120.9±0.1	108.9±0.1	674.6±0.5
		5.44[24]	6.99	23.66	98.5	120.9	108.9	
V_7O_{13}	5.10	5.425±0.009	6.991±0.006	15.15 ±0.02	98.9±0.1	125.6±0.1	108.8±0.1	396.4±0.7
		5.43[24]	7.00	15.16	98.9	125.5	108.9	
VO_2	4.00	5.745±0.004	4.519±0.002	5.377±0.004		122.6±0.1		117.6±0.1
	4.60	5.748±0.009	4.519±0.004	5.369±0.008		122.5±0.1		117.6±0.2
		5.744[8]	4.526	5.375		122.55		

Table 4. d-Values and relative intensities of $Sm_{10}V_2O_{20}$

d(Å)	I/I_0	d(Å)	I/I_0
8.89	13	1.783	11
3.22	14	1.695	6
3.198	11	1.646	34
3.152	100	1.6186	7
3.009	10	1.5761	13
2.972	17	1.4935	6
2.730	41	1.4402	8
2.611	10	1.3649	6
2.162	11	1.2528	11
1.930	45	1.2208	8
1.886	9	1.2093	6
1.867	6	1.1145	8
1.810	7		

(1) and (2) respectively.

The activities of the $Sm_{10}V_2O_{20}$ and $SmVO_4$ components in stoichiometric composition, that is, A and B in Fig. 2, were readily calculated by means of the Gibbs-Duhem equation on the basis of the experimental results. The relationships, $\log P_{O_2}$ - N_O/N_{SmVO_4} and $\log P_{O_2}$ - $N_{O_2}/N_{Sm_{10}V_2O_{20}}$, are determined to be $N_O/N_{SmVO_4}=3.77\times10^{-3}\log P_{O_2}+0.01377$ and $N_O/N_{Sm_{10}V_2O_{20}}=0.0227\log P_{O_2}+0.0388$ from the thermogravimetric results. Here N_{O_2}/N_{SmVO_4} and $N_O/N_{Sm_{10}V_2O_{20}}$ are the fraction rations of oxygen to $SmVO_4$, and to $Sm_{10}V_2O_{20}$, indicating the deviation from the stoichiometry. A detailed calculation method has been described in the paper of Kimizuka and Katsura.[28] The calculated activity values and stability ranges of the oxygen partial pressures of the compounds which appeared are summarized in Table 5.

Table 5. Compositions, stability ranges in oxygen partial pressures, and activities in solid solutions

Component	Composition	Symbol	$-\log P_{O_2}$ (atm)	$\log a_i$
$Sm_{10}V_2O_{20}$	$Sm_{10}V_2O_{20.00}$	A	0.68[a] — 1.59[b]	0.533
	$Sm_{10}V_2O_{19.81}$	A_1	9.01	0.231
	$Sm_{10}V_2O_{19.78}$	A_2	11.40	0.0
$SmVO_4$	$SmVO_{4.000}$	B	0.68[a] — 3.70[b]	0.0264
	$SmVO_{3.980}$	B_1	9.01	0.0
$SmVO_3$	$SmVO_{3.000}$	C	9.01 —12.00[c]	0.0
V_2O_3	$V_2O_{3.000}$	D	9.98 —12.00[c]	
	$V_2O_{3.012}$	D_1	9.01	
	$V_2O_{3.065}$	D_2	7.86	
V_3O_5	$V_3O_{5.000}$	E	6.45 — 7.86	
V_4O_7	$V_4O_{7.000}$	F	5.65 — 6.45	
V_5O_9	$V_5O_{9.000}$	G	5.43 — 5.65	
V_6O_{11}	$V_6O_{11.00}$	H	5.20 — 5.43	
V_7O_{13}	$V_7O_{13.00}$	I	5.05 — 5.20	
VO_2	$VO_{2.000}$	J	3.07[b]	0.0046
	$VO_{1.988}$	J_1	4.71	0.0

a) Stability range in $\log P_{O_2}$ may be higher than −0.68. b) These values were obtained by extrapolations by using the experimental values. c) Stability range in $\log P_{O_2}$ may be lower than −12.00.

The Standard Gibbs Free Energies of Oxidation of Vanadium Oxides. On the basis of the phase equilibria of the V–O system, the standard Gibbs free energies of oxidation of vanadium oxides which appeared in the present experimental conditions can be calculated. Although the details of the method were already described by Katsura and Hasegawa[8] at 1600 K and by Smiltens,[29] we will briefly describe them below.

In the cases of the following reactions:

$$VO_{5/3} + 1/24O_2 = VO_{7/4}, \quad (3)$$

$$VO_{7/4} + 1/40O_2 = VO_{9/5}, \quad (4)$$

$$VO_{9/5} + 1/16O_2 = VO_{11/6}, \quad (5)$$

$$VO_{11/6} + 1/84O_2 = VO_{13/7}, \quad (6)$$

which are concerned with the stoichiometric compounds in equilibrium states at fixed oxygen partial pressures, the standard Gibbs free energies of the oxidations can be readily calculated. For example, in the case of reaction (3), $\Delta G° = -RT \ln K = 1/24\ RT \ln P_{O_2}(eq)$ is applicable, where $P_{O_2}(eq)$ is the equilibrium oxygen partial pressure at which two solid phases are in equilibrium.

In the case of the following reactions, which involve solid solutions:

$$VO_{3/2} + 1/12O_2 = VO_{5/3}, \quad (7)$$

$$VO_{13/7} + 1/14O_2 = VO_2, \quad (8)$$

the method of the calculation of the standard Gibbs free energy of oxidation is more complicated. We assume from the results of the phase diagram that $VO_{13/7}$ has a solid solution, although the phase diagram between $VO_{13/7}$ and VO_2 is not so exactly determined because of the slow reaction rate.

On the basis of Smiltens's method, the standard free energies referring to reactions (7) and (8) may be given as follows:

$$\Delta G°_{1473}(7) = RT/12 \ln P_{O_2}(eq) + RT/2\int_{0\ 000}^{0.0320} \ln [P_{O_2}/P_{O_2}(eq)]dx_1,$$

$$\Delta G°_{1473}(8) = RT/14 \ln P_{O_2}(eq) + RT/2\int_{0.000}^{0.1301} \ln [P_{O_2}/P_{O_2}(eq)]dx_2,$$

where x_1 and x_2 are defined as $VO_{3/2}+x_1/2O_2=VO_{3/2+x_1}$ and $VO_{13/7}+x_2/2O_2=VO_{13/7+x_2}$, respectively.

The second term of the right side of the above equations is named by Smiltens as the correction term. We obtained the values by adopting the graphical integration method. The relationships, $\log [P_{O_2}/P_{O_2}(eq)]$ - x_1 and $\log [P_{O_2}/P_{O_2}(eq)]$ - x_2, are shown in Fig. 3-1 and 3-2. The results of the standard Gibbs free energies of the oxidation of vanadium oxides are summarized in Table 6 together with the values calculated from equations presented by Okinaka *et al.*[11] The present values are in good agreement with those of Okinaka *et al.*

The standard Gibbs free energy of the reaction,

$$VO_{3/2} + 1/4O_2 = VO_2 \quad (9)$$

can be calculated as the summation of the values of the respective reactions, and is also shown in Table 6.

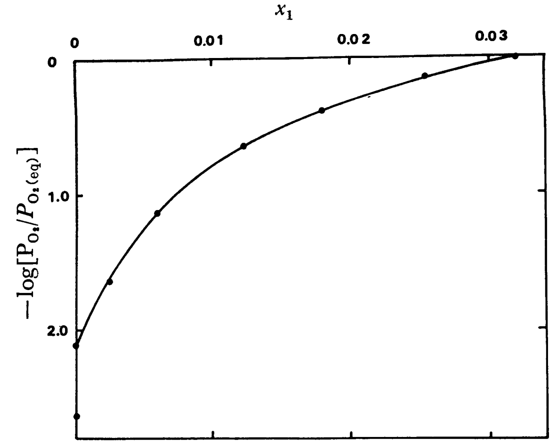

Fig. 3-1. The log $[P_{O_2}/P_{O_2}(eq)]$ *versus* x_1 curve for V_2O_3 solid solution at 1200 °C.

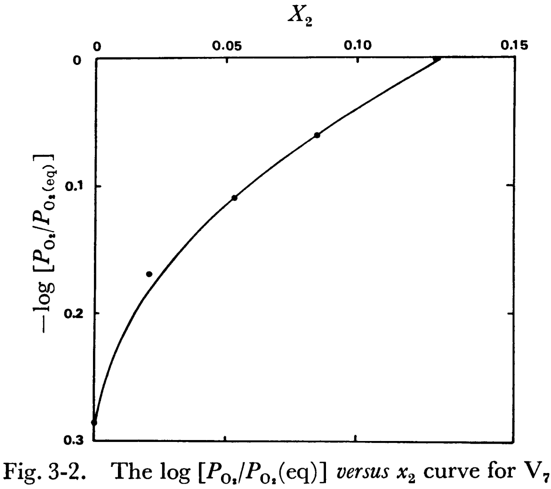

Fig. 3-2. The log $[P_{O_2}/P_{O_2}(eq)]$ *versus* x_2 curve for V_7O_{13} solid solution at 1200 °C.

Allen *et al.*[30] obtained the free energy equation, $\Delta G° = 102800 - 33.5\ T$ (calcd, 1020—1180 K, ±5 kcal), for the reaction $4VO_2=2V_2O_3+O_2$ and Anderson *et al.*[12] −26.9 at 1173, −24.77 at 1273, and −21.24 kcal at 1473 K for the reaction $V_2O_3+1/2O_2=2\ VO_2$. Althoguh this equation and values are not adequate for 1200 °C, we obtained the values −13360 and −10070 cal for reaction (9) at 1200 °C by extrapolation.

According to Coughlin,[31] Mah and Kelly,[32] and Okinaka *et al.*,[11] the standard free energy of the reaction $V_2O_3+1/2O_2=2VO_2$ was given as $\Delta G° = -43650+$

Table 6. Standrad free energies of oxidation at 1200 °C

Oxidation Reaction	$-\log P_{O_2}(eq)$ (atm)	Correction term (cal)	$-\Delta G°$ (calcd)	
			Present	Okinaka *et al.*
$VO_{3/2} + 1/12\ O_2 = VO_{5/3}$	7.86	−70	4490±100	4370
$VO_{5/3} + 1/24\ O_2 = VO_{7/4}$	6.45	0	1810± 50	1710
$VO_{7/4} + 1/40\ O_2 = VO_{9/5}$	5.65	0	950± 50	910
$VO_{9/5} + 1/60\ O_2 = VO_{11/6}$	5.43	0	610± 50	550
$VO_{11/6} + 1/84\ O_2 = VO_{13/7}$	5.20	0	420± 50	390
$VO_{13/7} + 1/14\ O_2 = VO_2$	4.71	−40	2310±100	2400
$VO_{3/2} + 1/4\ O_2 = VO_2$			10590±400	10330

16.75 T (calcd, 500—1800 K, ±2000 cal), $\Delta G°=-42200+13.0\ T$ (calcd, 800—1600 K, ±400 cal), and $\Delta G°=-48860+19.14\ T$ (calcd, above 1120 K, ±200 cal), respectively. Values calculated by using these equations at 1200 °C are −9490, −11530, and −10330 cal, respectively. The present value (−10590 cal) is in good agreement with the value of Okinaka *et al.*

The relationship between N_O/N_{VO_2} and log P_{O_2} in the VO_2 solid solution is obtained to be $N_O/N_{VO_2}=6.85\times10^{-3}\log P_{O_2}+0.0210$. The activity of the stoichiometric VO_2 was also determined and is shown in Table 6.

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