Phase Equilibria in the V_2O_3-VO_2 System at High Temperatures

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The phase equilibria in the V_2O_3–VO_2 system were established at 1307 K by varying the oxygen partial pressures from 10^{-4} to 10^{-12} atm. Eight phases, V_2O_3, V_3O_5, V_4O_7, V_5O_9, V_6O_{11}, V_7O_{13}, V_8O_{15}, and VO_2, were observed under these experimental conditions. Vanadium sesquioxide has an extensive range of solid solutions at 1307 K. Also, the phase diagram and isobaric lines of oxygen partial pressure in the V_2O_3 phase were determined from 1307 to 1700 K on the basis of our present and previous studies. Quenching and thermogravimetric methods were applied under a controlled oxygen atmosphere. The oxygen partial pressures were determined by means of a solid electrolyte cell composed of $(ZrO_2)_{0.85}(CaO)_{0.15}$. The standard free energies of the oxidation of V_2O_3 to V_3O_5, of V_3O_5 to V_4O_7, of V_4O_7 to V_5O_9, of V_5O_9 to V_6O_{11}, of V_6O_{11} to V_7O_{13}, of V_7O_{13} to V_8O_{15}, and of V_8O_{15} to VO_2 were determined on the basis of the equilibrium oxygen partial pressure at 1307 K. The enthalpy and entropy data of the oxidations of V_2O_3 to V_3O_5 and of V_3O_5 to V_4O_7 were evaluated from the oxygen partial pressures on the basis of the present results and previous data.

Among early studies,[1-5] Andersson[4,5] investigated a series of compounds formulated by V_nO_{2n-1} (n: integer) at temperatures from 800 to 900 °C, and distinguished such compounds as varied in n value from 2 to 8 Kosuge *et al.*[6] found V_nO_{2n-1} phases in which the n value varied from 2 to 7 at 800 °C. Later, Okinaka *et al.*[7] presented a general-phase diagram of the V_2O_3–VO_2 system up to 1600 K based on their previous data.

In spite of a number of studies of the V_2O_3–VO_2 system at lower temperatures, only a few works have been reported about the thermochemical properties of the V_2O_3–VO_2 system at higher temperatures except for the V_2O_3 and VO_2 phases. Katsura and Hasegawa[8] reconfirmed the phase equilibria studied by Andersson,[4,5] and presented the standard free energies of the compounds which exist in the V_2O_3–VO_2 system at 1600 K. Wakihara and Katsura[9] reported thermodynamic data on the V_2O_3, V_3O_5, and V_4O_7 phases from 1400 to 1700 K. Recently, Anderson and Khan[10] and Okinaka *et al.*[7] studied the V_2O_3–VO_2 system up to 1423 K, and from 600 to 1200 °C, respectively, and reported some thermodynamic data of this system.

The present objectives are: (1) to obtain a detailed phase equilibria of the V_2O_3–VO_2 system at 1307 K in order to establish the phase diagrams at higher temperatures on the basis of both the present and previous studies,[8,9] and also to compare our results with the estimated phase diagrams proposed by several previous investigators; (2) to obtain linear free-energy equations at higher temperatures by determining three thermodynamic functions $\Delta G°$, $\Delta H°$, and $\Delta S°$, and (3) to ascertain the phase transition of V_6O_{11}, which had a different structure at 1600 K from that obtained by Andersson at around 1000 °C.

Experimental

The quenching and thermogravimetric methods were adopted in the present study. Since the details of the procedure have been previously described by Katsura and Muan[11] and by Katsura and Hasegawa,[8] only a brief description of the general procedure will be given here.

In the thermogravimetric method, a pre-reduced vanadium oxide sample was heated at 1307 K in an atmosphere of a CO_2 and H_2 mixture (ratio of 1 : 1). The pellet thus obtained was suspended in a furnace by means of a Pt-40%Rh wire connected to a quick-weighing balance. The oxide had a chemical formula of $VO_{1.500}$ as this oxygen partial pressure and temperature. It was also found that the substantially stoichiometric V_2O_3 phase was stable at lower oxygen partial pressures than 10^{-12} atm. Thus, the weight of $VO_{1.500}$ prepared at an oxygen partial pressure of 10^{-12} atm was chosen as the reference weight standard.

In the quenching method, an oxide sample was heated at 1307 K and at a particular oxygen pressure until an equilibrium was attained between the gas and condensed phases. The sample was then quenched rapidly to the temperature of ice by burning away the thin platium wire with an electric current and by allowing the sample to drop into an ice-cooled tube. The sample thus obtained was used for identifying the phases present by means of the powder X-ray diffraction method and for determining the compositions by means of gravimetric analysis.

The atmospheres of the desired oxygen partial pressures were obtained by using mixtures of CO_2 and H_2. In the present study, the ratios of CO_2/H_2 were changed from 1.0 to 4000, and the flow rate in the furnace was set at 0.8 cm/sec. The actual partial pressures of oxygen in the gas mixture were stably and accurately measured by inserting a solid electrolyte cell, $(ZrO_2)_{0.85}$ $(CaO)_{0.15}$, into the furnace tube before a sample was suspended in it. The error of $\log P_{O_2}$ was estimated to be within ±0.01. The details of the procedure have been described in the authors' previous papers.[8,9]

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Results and Discussion

Phase Equilibria. The data obtained at 1307 K are summarized in Table 1 and are graphically illustrated in Fig. 1.

Table 1. Equilibria of the V_nO_{2n-1} phases at 1307K

$-\log P_{O_2}$	CO_2/H_2	Value of x in VO_x	Phase
11.99 (±0.02)	10.0	1.500 (±0.001)	V_2O_3
10.50	40.6	1.503	V_2O_3
10.45	42.9	1.505	V_2O_3
10.38	45.4	1.506	V_2O_3
10.33	47.5	1.506	V_2O_3
10.32	48.3	1.509	V_2O_3
10.24	51.9	1.507	V_2O_3
10.18	54.9	1.510	V_2O_3
10.13	56.4	1.512	V_2O_3
10.04	61.8	1.512	V_2O_3
9.90	68.9	1.520	V_2O_3
9.85 (±0.02)	72	1.667 (±0.008)	V_3O_5
9.73	79	1.667	V_3O_5
8.00	430	1.667	V_3O_5
7.96	450	1.674	V_3O_5
7.93 (±0.02)	470	1.753 (±0.008)	V_4O_7
7.80	540	1.748	V_4O_7
7.42	870	1.747	V_4O_7
7.40	880	1.750	V_4O_7
7.39	910	1.757	V_4O_7
7.31	960	1.756	V_4O^7
7.19	1070	1.760	V_4O_7
7.11 (±0.02)	1130	1.798 (±0.008)	V_5O_9
7.00	1200	1.808	V_5O_9
6.66	1460	1.803	V_5O_9
6.55	1550	1.803	V_5O_9
6.49 (±0.05)	1610	1.830 (±0.008)	V_6O_{11}
6.26	1830	1.830	V_6O_{11}
5.91	2230	1.836	V_6O_{11}
5.80 (±0.06)	2370	1.859 (±0.008)	V_7O_{13}
5.63	2590	1.861	V_7O_{13}
5.57 (±0.06)	2680	1.918 (±0.008)	$V_8O_{15}+VO_2$
5.50	2770	1.901	$V_8O_{15}+VO_2$
5.32 (±0.06)	3100	1.997 (±0.008)	VO_2
4.86	4000	1.997	VO_2

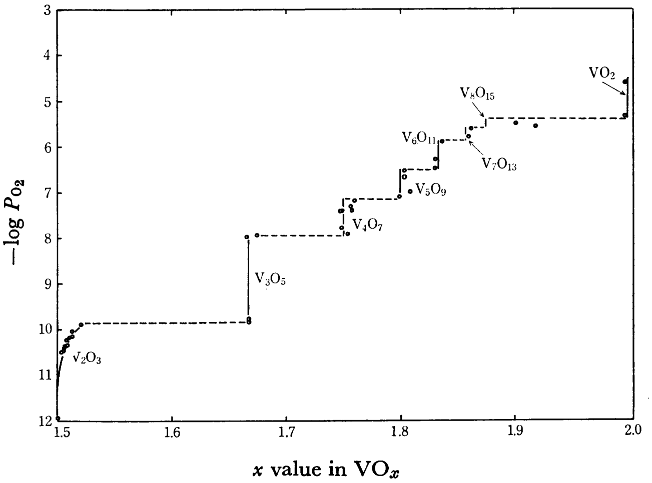

Fig. 1. Relationship between composition of oxide and oxygen partial pressure represented by logarithmic scale on the V_nO_{2n-1} phases at 1307 K.

The following eight phases were found to be stable under the present experimental conditions: V_2O_3, with a corundum-type structure and various V/O ratios; V_3O_5, with a monoclinic structure showing no significant variation in the V/O ratio; V_4O_7, V_5O_9, V_6O_{11}, V_7O_{13}, and V_8O_{15}, showing no significant variations in the V/O ratio, and VO_2, with a monoclinic rutil-type structure.

According to the previous paper,[8] the V_6O_{11} phase had a wide range of composition, from $VO_{1.833}$ to $VO_{1.905}$, and $VO_{1.905}$ was in equilibrium with the stoichimoetric VO_2. In addition, it is significant that the structural powder X-ray patterns of $VO_{1.834}$, $VO_{1.853}$, and $VO_{1.898}$ obtained at 1600 K, all of which compositions belong to the V_6O_{11} phase, were identical with each other, but definitely different from that of the V_6O_{11} phase obtained by Andersson[4] at around 1000 °C. Under the present experimental conditions, the stoichiometric V_6O_{11} phase was in equilibrium with the stoichiometric V_7O_{13} phase at the oxygen partial pressure of $10^{-5.91}$ atm. Also, the structural powder X-ray pattern of the present V_6O_{11} phase was identical with that obtained by Andersson.[4] This leads to the conclusion that the transition point must be located at a temperature between 1307 and 1600 K.

The compositions of $VO_{1.901}$ and $VO_{1.918}$ in Table 1 correspond to a mixture of the V_8O_{15} and VO_2 phases. The single phase of V_8O_{15} could not be obtained under the present conditions, because the stable range of oxygen partial pressure to the V_8O_{15} phase was too narrow for us to obtain an equilibrated single phase of V_8O_{15} at the present temperature; therefore, no exact composition range of the V_8O_{15} phase was determined.

As is shown in Fig. 2, the homogeneous region and

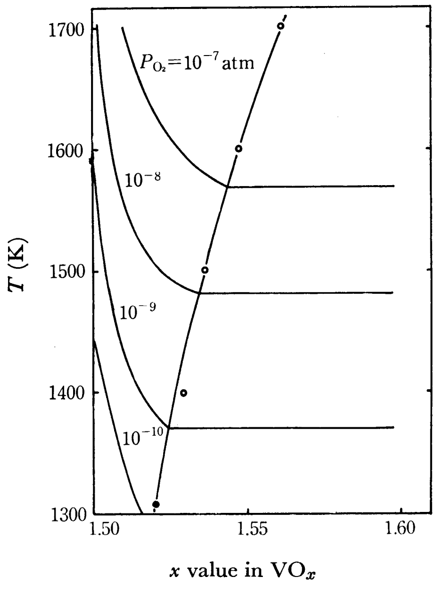

Fig. 2. Isobaric lines of oxygen partial pressure and the homogeneous range in the V_2O_3 solid solution at temperatures from 1300 to 1700 K.

the isobaric lines of the oxygen pressure relating to the change in composition and temperature in the V_2O_3 phase were determined from 1300 to 1700 K on the basis of the present study and previous results.[8,9] The compositions of the V_2O_3 phase were determined by applying the thermogravimetric method, while the compositions from V_3O_5 to VO_2 phase were obtained using the quenching method, because of the appreciable amounts of sublimation in these samples.

Andersson[4] pointed out a narrow homogeneity range in the V_3O_5 phase at 900 °C. On the other hand, Kosuge *et al.*[6,7] suggested a fairly wide range of variations in the V/O ratio in the phases of V_3O_5, V_4O_7, and V_6O_{11}, as well as that in the phase of V_2O_3 over a wide range of temperature. However, a wide homogeneous range was seen only in the phase of V_2O_3 at 1307 K. The results in the present study may be reliable because the samples were quenched in an equilibrium state. Also, in a preliminary experiment, no change in the composition was found in any phase between before and after quenching. By way of summarizing both the present and previous results,[8,9] the phase diagram of the V_2O_3–VO_2 system at higher temperatures is briefly given in Fig. 3; this diagram is somewhat different from that of Okinaka *et al.*[7]

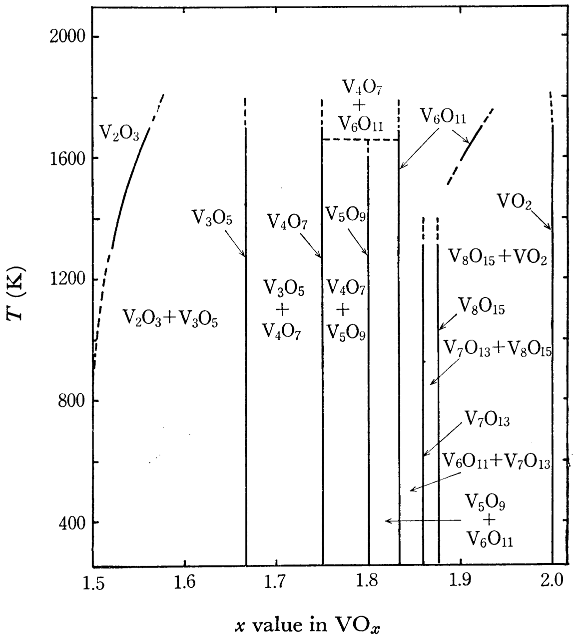

Fig. 3. Phase diagram of the V_2O_3–VO_2 system based on the present and previous data.[8,9]

Thermodynamic Properties of Oxidation. Since the oxygen partial pressure at which two oxide phases coexist had been determined, the standard free energy of the oxidation of each oxide could readily be estimated by means of the van't Hoff equation except for Reaction (1), as is shown in Table 2. It may be necessary for Reaction (1) to use a correction term because of the existence of homogeneity in the V_2O_3 phase. The method of calculating the standard free energy of the formation of a solid solution has been derived from the expansion of the Gibbs-Duhem equation described in previous papers.[8,9] In the present study, the correction term for the standard free energy was estimated to be about 21 cal. Since the establishment of a discrete oxygen partial pressure for the V_8O_{15} phase was impossible, the proper oxygen partial pressure for the stoichiometric V_8O_{15} phase was estimated (Table 2) on the basis of the powder X-ray pattern. The standard free energies of the oxidation of Reactions (1) to (7) are summarized in Table 2.

TABLE 2. OXIDATION REACTIONS AND CORRESPONDING FREE ENERGIES AT 1307K

Reaction	$-\log P_{O_2}$	Free energy $\Delta G°$ (cal)
$VO_{3/2}+1/12\ O_2=VO_{5/3}(1)$	9.88 ± 0.05	$-4955\pm\ 50$
$VO_{5/3}+1/24\ O_2=VO_{7/4}(2)$	7.95 ± 0.05	$-1981\pm\ 30$
$VO_{7/4}+1/40\ O_2=VO_{9/5}(3)$	7.15 ± 0.07	$-1069\pm\ 10$
$VO_{9/5}+1/60\ O_2=VO_{11/6}(4)$	6.52 ± 0.05	$-\ 650\pm\ 5$
$VO_{11/6}+1/84\ O_2=VO_{13/7}(5)$	5.86 ± 0.12	$-\ 417\pm\ 10$
$VO_{13/7}+1/112\ O_2=VO_{15/8}(6)$	5.60 ± 0.09	$-\ 299\pm\ 5$
$VO_{15/8}+1/16\ O_2=VO_2(7)$	5.41 ± 0.17	$-2022\pm\ 60$
$VO_{3/2}+1/4\ O_2=VO_2(8)$		$-11393\pm\ 170$
[Mah *et al.*[12]		$-12604\pm\ 200$]
[Coughlin[13]		-10879 ± 1000]
[Okinaka *et al.*[7]		$-11922\pm\ 100$]

The summation of these reactions gives Reaction (8) and the corresponding free energy, shown in Table 2. The value thus obtained is compared with those obtained by Mah *et al.*,[12] by Coughlin[13] and by Okinaka *et al.*[7] in the same table.

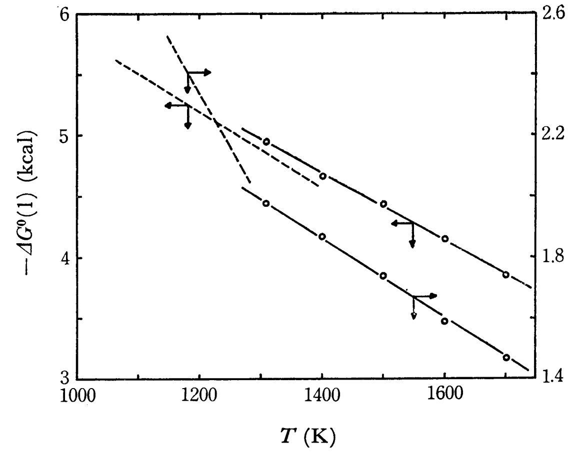

Fig. 4. Free energy change *vs.* temperature of reactions (1) and (2). Solid lines indicate our data, while dashed lines are derived from the data of Okinaka *et al.*[7]

The values of $\Delta G°(1)$ and $\Delta G°(2)$ are plotted against the temperatures from 1307 to 1700 K in Fig. 4, on the basis of the present and our previous data,[9] together with the relationships of Okinaka *et al.*[7] It may be expected from Fig. 4 that the linear free-energy equations for Reaction (1) are in pretty good agreement with each other, but for Reaction (2) there is a slight difference in slope. The standard entropy changes in Reactions (1) and (2) were evaluated from the slope

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12) A. D. Mah and K. K. Kelley, *U. S. Bur. Mines Rept. Invest.*, (1961), p. 5858.

13) J. P. Coughlin, *U. S. Bur. Mines, Bulletin*, **542**, (1954).

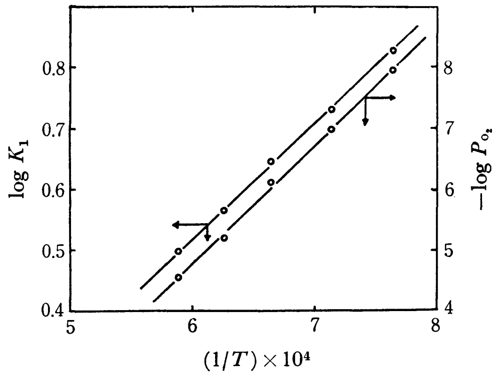

Fig. 5. log K_1 corresponding to Eq. (1) and equilibrium oxygen partial pressure in Eq. (2) *vs.* reciprocal absolute temperature, $1/T$.

in Fig. 4. The least-squares method was used to estimate the standard entropy changes of the two reactions. Also, the entropy changes of Reactions (1) and (2) were evaluated by means of the van't Hoff equation. The logarithmical equilibrium constant of Reaction (1) was calculated from the following equation:

$$\log K_1 = \log \frac{P_{O_2}(1)}{a_{V_2O_3}} = -\frac{\Delta G^\circ(1)}{RT}$$

The relationship between log K_1 and $1/T$ was substantially linear, as is illustrated in Fig. 5. Hence, the following equation may be deduced from the above equation:

$$\frac{\mathrm{d}\log K_1}{\mathrm{d}(1/T)} = -\frac{\Delta H^\circ(1)}{2.303R}$$

where $\Delta H^\circ(1)$ and R are the heat of Reaction (1) and the gas constant respectively. The heat of Reaction (2), $\Delta H^\circ(2)$, may be estimated from this reaction:

$$\frac{\mathrm{d}(-\log P_{O_2}(2))}{\mathrm{d}(1/T)} = -\frac{\Delta H^\circ(2)}{2.303R}$$

The equilibrium constant of Reaction (2), K_2, is equal to the equilibrium oxygen partial pressure ($P_{O_2}(2)$).

Table 3. Estimated respective thermodynamic functions at temperatures from 1300 to 1700 K

$\Delta H^\circ(1) = -8310$	(± 230)	(cal)
$\Delta H^\circ(2) = -3716$	(± 250)	(cal)
$\Delta S^\circ(1) = -2.73$	(± 0.30)	(e.u.)
$\Delta S^\circ(2) = -1.32$	(± 0.13)	(e.u.)
$\Delta G^\circ(1) = -8310 + 2.73T$	(± 630)	(cal)
$\Delta G^\circ(2) = -3716 + 1.32T$	(± 430)	(cal)

The respective entropy and enthalpy data are shown in Table 3. The linear equations of the standard free energies of Reactions (1) and (2) were estimated by using the entropy and enthalpy data obtained above over the temperature range from 1307 to 1700 K. The equations are also listed in the last two lines of Table 3.