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Equilibria in the V_2O_3-VO_2 System at 1600°K

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Phase equilibria in the V_2O_3-VO_2 system were established at 1600°K by varying the oxygen partial pressures from 10^{-13} to 10^{-3} atm. The phases of V_2O_3, V_3O_5, V_4O_7, V_5O_9, V_6O_{11}, and VO_2 are stable under these conditions. The only phases of V_2O_3 and V_6O_{11} have extensive ranges of solid solution. The stability ranges of vanadium oxides with respect to the oxygen partial pressure were determined: V_2O_3, from 10^{-13} to $10^{-6.36}$ atm; V_3O_5, from $10^{-6.36}$ to $10^{-4.90}$ atm; V_4O_7, from $10^{-4.90}$ to $10^{-4.20}$ atm; V_5O_9, from $10^{-4.20}$ to $10^{-4.04}$ atm; and V_6O_{11}, from $10^{-4.04}$ to $10^{-3.53}$ atm, while VO_2 is in equilibrium with V_6O_{11} at the oxygen partial pressure of $10^{-3.53}$ atm. The oxygen partial pressures were measured accurately by means of a solid electrolyte cell composed of $(ZrO_2)_{0.85}(CaO)_{0.15}$; these pressures were then compared with the values calculated from the thermochemical data. On the basis of the equilibrium oxygen partial pressures, the standard free energies of oxidation of various vanadium oxides were calculated.

Several studies have been carried out on the V-O system. The method employed in previous studies were all based on the vacuum-sealing technique, used to prepare certain desired compounds of vanadium oxides and to obtain the phase relations among them. Klemm and Grimm(1) studied the phase relations in the V-V_2O_3 system; they found that the VO phase with compositions ranging from $VO_{0.9}$ to $VO_{1.3}$ was stable at high temperatures, while it decomposes to metallic vanadium and a higher oxide at low temperatures. Seybolt and Sumsion(2) also studied the solid solution of vanadium and oxygen in the range from $VO_{0.15}$ to $VO_{0.25}$. Hoschek and Klemm(3) reported that several phases appeared in the V_2O_3-V_2O_5 system, and also recognized that the VO_2 phase with a rutile structure has a wide range in chemical composition, from $VO_{1.8}$ to VO_2. Aebi(4) found a new phase with the composition of $VO_{2.17}$. Lately, Andersson(5) studied in detail the V_2O_3-VO_2 system at temperatures from 800°C to 900°C; he found a series of vanadium oxides represented by the general chemical formula V_nO_{2n-1}, changing the n's from 2 to 8. Kosuge *et al.*(6) recognized the V_2O_3, V_3O_5, V_4O_7, V_5O_9, V_6O_{11}, and V_7O_{13} phases at 800°C. On the other hand, there has been no study of the thermochemical properties of these vanadium oxides except for V_2O_3 and VO_2.(7)

The objectives of the present study are to reveal the detailed phase equilibria in the V_2O_3-VO_2 system at 1600°K by varying the oxygen partial

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1) W. Klemm and L. Grimm, *Z. anorg. u. allgem. Chem.*, **250**, 42 (1942).

2) A. U. Seybolt and H. T. Sumsion, *J. Metals*, **5**, 292 (1953).

3) E. Hoschek and W. Klemm, *Z. anorg. u. allgem. Chem.*, **242**, 63 (1939).

4) F. Aebi, *Helv. Chim. Acta*, **31**, 8 (1948).

5) G. Andersson, *Acta Chem. Scand.*, **8**, 1599 (1954); **10**, 623 (1956).

6) K. Kosuge, T. Takada and Y. Kachi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **83**, 1243 (1962).

7) J. P. Coughlin, Bureau of Mines, Bull. 542, U. S. A. (1954). Also see Ref. 11.

pressure from 10^{-3} to 10^{-13} atm, and to calculate the standard free energies of the oxidations of the vanadium oxides present in the system under consideration. The temperature of 1600°K was adopted for convenience in attaining the equilibrium state for a reasonable period of time.

Experimental

General Procedures. Different experimental methods were used in the present study—quenching and thermogravimetric methods previously described by Katsura and Muan[8] and by Katsura and Kimura.[9]

In the thermogravimetric method, the guaranteed reagent of ammonium meta-vanadate was gently heated at 400°C in globar to obtain V_2O_5; then it was heated at 650°C in an electric furance while passing a mixed gas of $CO_2/H_2=1$ through the heating tube for 12 hr. The oxide thus obtained had a chemical formula of about V_2O_3. This oxide sample was heated at 1600°K in the same mixed gas for 5 hr to make a suitable pellet. This pellet was suspended by a thin platinum-40% rhodium wire from one beam of an analytical balacne, and the weight changes were recorded as a function of the oxygen partial pressure at 1600°K. The data thus obtained were used to locate the oxygen isobars.

In the quenching method, a pellet of oxide sample was heated at 1600°K and at a chosen oxygen partial pressure until equilibrium was attained between the gas and the solid phases. The subsequent quenching technique was similar to that described previously.[9]

The Choice of the Reference State for the Chemical Composition. It was found during preliminary works that the V_2O_3 phase is very stable; *i. e.,* its composition remains constant over a wide range of oxygen partial pressures, from 10^{-9} to 10^{-13} atm. In addition, the chemical analysis of the quenched samples obtained from this range of oxygen partial pressures always had the stoichiometric composition of $VO_{1.500}$, as may be seen in Table 1. On the basis of these facts, we chose the $VO_{1.500}$ prepared under the oxygen partial pressure of about 10^{-11} atm at 1600°K as the reference weight standard.

The Control of the Atmosphere. The atmospheres of the desired oxygen partial pressures were obtained by using pure oxygen, carbon dioxide, and CO_2-H_2 mixtures. The CO_2-H_2 mixtures were prepared by proportioning the two gas components in desired ratios in a gas mixer which is similar in principle to that described by Darken and Gurry.[10] The oxygen partial pressures in the CO_2-H_2 mixtures were calculated from the thermochemical data summarized by Elliott and Gleiser[11] and Coughlin[7]. The fluctuation of the CO_2/H_2 ratio was within ±1% throughout the present study. The actual oxygen partial pressures in gas mixtures of CO_2/H_2 and O_2/CO_2 were measured by means of a solid electrolyte cell, as will be described in the Appendix.

Furnace and Temperature Control. A vertical-tube quench furnace with an 80%Pt20%Rh-wire winding was used for the equilibrium runs. The temperature control system and the accuracy of temperature measurement were similar to those described previously.[9]

The Identification of Phases and the Chemical Analysis. The phases present in the quenched samples were identified by an X-ray diffraction method using CuK_α. Silicon powder was used as the standard in determining the *d*-values.

The V/O ratio in the starting materials and the quenched samples were determined volumetrically by adopting the Zinc-Amalgam method[12] in order to check the thermogravimetric results. Table 1 compares the results of duplicated chemical analyses with the results of the thermogravimetric determination.

TABLE 1. THE WET CHEMICAL ANALYSES OF STABLE VANADIUM COMPOUNDS AND SOME COMPARISONS WITH THOSE OBTAINED FROM THERMOGRAVIMETRY

VO_x by thermogravimetry	VO_x by wet analysis	error in wet analysis
—	1.500	±0.001
1.665	1.664	±0.001
1.750	1.748	±0.002
—	1.799	±0.002
—	1.834	±0.002
—	2.000	±0.0005

The Check of the Equilibrium. The rate of approach to the equilibrium state was studied thermogravimetrically. To ensure the equilibrium, the equilibrated composition was established from both sides of the reaction, that is to say, from $VO_{1.500}$ and from $VO_{2.000}$, according to the following general reaction scheme:

$$VO_{x-y} + {}^{y}/_{2}O_2 \rightarrow VO_x \leftarrow VO_{x+z} - {}^{z}/_{2}O_2$$

where $x-y=1.500$, and $x+z=2.000$. The composition of VO_x represents the equilibrated composition at a fixed oxygen partial pressure. To prepare the VO_2, V_2O_3 was heated at 1600°K for 24 hr in pure carbon dioxide. The equilibrated compositions at the same oxygen partial pressure from both sides of the reaction were identical within the range of analytical error. The approaches toward the final, equilibrated states in the two samples, $VO_{1.500}$ and $VO_{2.000}$ are graphically illustrated in Fig. 1 as an example. It was found in general that the equilibrium was approached quickly in cases of the low oxygen partial pressures, whereas in the cases of the formations of V_4O_7, V_5O_9, V_6O_{11}, and VO_2, the vaporization of these oxides occurred at an appreciable speed in addition to the sluggish reactions. It was, therefore, hard to determine the equilibrated compositions accurately by means of the thermogravimetric method only.

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[8] T. Katsura and A. Muan, *Trans. AIME,* **230**, 77 (1964).

[9] T. Katsura and S. Kimura, This Bulletin, **38**, 1664 (1965).

[10] L. S. Darken and R. W. Gurry, *J. Am. Chem. Soc.,* **67**, 1398 (1945); *ibid.,* **68**, 798 (1946).

[11] J. F. Elliott and M. Gleiser, "Thermochemistry for Steelmaking," Addison-Wesley Publ. Co., Reading, Mass. (1960).

[12] T. Nakazono, *Nippon Kagaku Kaishi (J. Chem. Soc. Japan),* **42**, 761 (1921). See also T. Katsura, "Jikken Kagaku Kōza," XV, Maruzen Co., Tokyo (1959), pp. 272—275; I. Iwasaki, T. Katsura, M. Yoshida and T. Tarutani, *Japan Analyst,* **6**, 211 (1957).

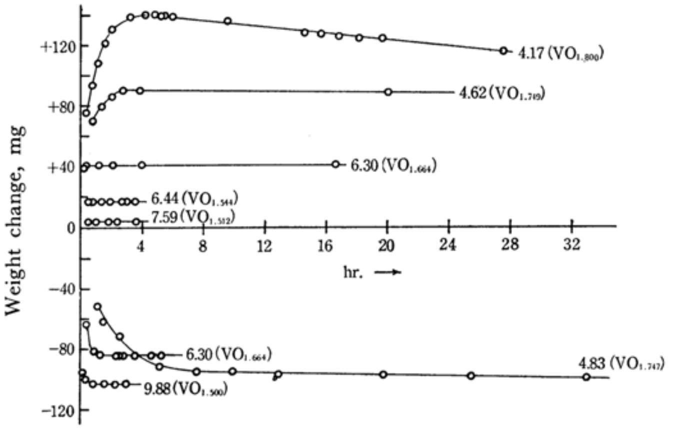

Fig. 1. Curve showing weight changes *vs.* time for a number of reduction-oxidation reactions. The numbers used are the values of $-\log P_{O_2}$. Formula in parentheses is equilibrated composition shown in Table 2 except for $VO_{1.500}$.

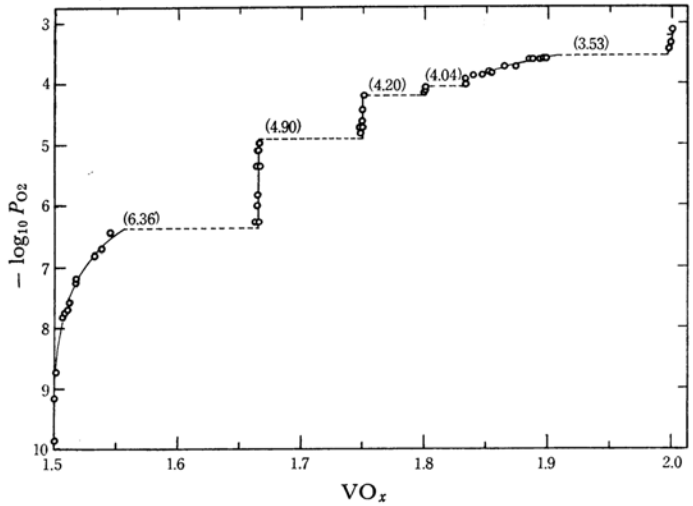

Fig. 2. Graphical representation of equilibrium data at 1600°K. The numbers in parentheses mean the equilibrium oxygen partial pressures in two solid phases equilibria.

Results and Discussion

Phase Equilibrium. The equilibrium data obtained at 1600°K are summarized in Table 2 and are illustrated graphically in Fig. 2.

The following six phases were found to be stable under the present experimental conditions: the V_2O_3 phase: with a variation in the V/O ratio, belonging to the corundum-type structure; V_3O_5: with a monoclinic structure and showing no significant variation in the V/O ratio; V_4O_7 and V_5O_9: with an unknown structure and showing no significant variation in the V/O ratio; V_6O_{11}: with an unknown structure and with a wide range of variation in the V/O ratio, and VO_2: a monoclinic rutile-type structure. The V_7O_{13} and V_8O_{15} phases were also recognized by Andersson⁵⁾ at 800 and 900°C, while Kosuge *et al.*⁶⁾ recognized only the V_7O_{13} phase at 800°C in addition to the oxide phases found in the present study. The phases of V_7O_{13} and V_8O_{15} phases, therefore, seem to be unstable at 1600°K.

In Table 3, several properties of each phase are summarized on the basis of the present study with respect to the range of oxygen partial pressure within which the phase is stable, the range of composition in VO_x, a comparison of the X-ray diffraction pattern with that obtained by Andersson,⁵⁾ and the crystal parameters of each phase when its crystal structure is known.

As is shown in Fig. 2 and summarized in Table 3, the wide ranges in variation in the V/O ratio

Table 2. Results of equilibration experiments at 1600°K at various oxygen partial pressures

$-\log P_{O_2}$	Sample wt. as V_2O_3, g	Heating time hr	Weight change mg	Formula VO_x	Phase present
12.89	WA (**)	8	—	1.500	[V_2O_3]
9.88	WA (**)	2	—	1.500	[V_2O_3]
12.89	1.7710(*)	2	0	1.500	[V_2O_3]
12.42	1.7710(*)	2	0	1.500	[V_2O_3]
10.81	1.4915(*)	2	0	1.500	[V_2O_3]
9.21	1.7710(*)	2	0	1.500	[V_2O_3]
10.26	1.4915(*)	2	0	1.500	[V_2O_3]
8.73	1.7710(*)	3	0	1.500	[V_2O_3]
7.82	1.7705(*)	2	3.0	1.508	[V_2O_3]
7.74	1.7705(*)	3	3.0	1.508	[V_2O_3]
7.71	0.7284(*)	3	1.5	1.510	[V_2O_3]
7.59	1.7706(*)	2	4.5	1.512	[V_2O_3]
7.23	WA (*)	20	—	1.517	[V_2O_3]
7.23	WA (**)	20	—	1.518	[V_2O_3]
6.81	1.7630(*)	1	11.7	1.531	[V_2O_3]
6.70	WA (*)	20	—	1.538	[V_2O_3]
6.44	1.7630(*)	1	16.6	1.544	[V_2O_3]
6.44	WA (**)	3	—	1.544	[V_2O_3]
6.30	1.1669(**)	17	41.0	1.664	[V_3O_5]
6.30	WA (*)	20	—	1.665	[V_3O_5]
6.00	1.7630(*)	4	62.0	1.664	[V_3O_5]
5.82	1.4036(*)	3	49.4	1.665	[V_3O_5]
5.82	1.3822(**)	14	48.7	1.665	[V_3O_5]
5.37	1.3810(*)	3	48.8	1.666	[V_3O_5]
5.37	WA (*)	20	—	1.664	[V_3O_5]
5.09	1.4535(**)	18	50.8	1.664	[V_3O_5]
5.09	1.2030(*)	5	42.1	1.664	[V_3O_5]
5.09	1.1183(**)	13	39.7	1.666	[V_3O_5]
5.09	WA (*)	4	—	1.664	[V_3O_5]
4.97	1.7610(*)	5	63.0	1.668	[V_3O_5]
4.83	1.7555(**)	33	92.5	1.747	[V_4O_7]
4.72	0.7283(*)	10	38.8	1.750	[V_4O_7]
4.72	WA (*)	26	—	1.746	[V_4O_7]
4.62	1.7283(*)	8	91.9	1.749	[V_4O_7]
4.45	0.9895(**)	30	52.8	1.750	[V_4O_7]
4.21	WA (*)	20	—	1.750	[V_4O_7]
4.19	WA (*)	8	—	1.779	[V_5O_9]
4.19	1.5949(**)	28	102.2	1.800	[V_5O_9]
4.17	1.8941(*)	25	121.2	1.800	[V_5O_9]
4.07	1.3155(**)	22	84.1	1.779	[V_5O_9]
4.01	1.3894(**)	22	99.1	1.834	[V_6O_{11}]
4.01	WA (*)	27	—	1.834	[V_6O_{11}]
3.93	1.3102(*)	17	92.9	1.832	[V_6O_{11}]
3.87	WA (**)	40	—	1.839	[V_6O_{11}]
3.87	1.3101(**)	18	97.1	1.847	[V_6O_{11}]
3.83	WA (**)	40	—	1.853	[V_6O_{11}]
3.78	1.3300(*)	17	99.4	1.850	[V_6O_{11}]
3.72	WA (*)	96	—	1.865	[V_6O_{11}]
3.72	WA (*)	42	—	1.874	[V_6O_{11}]
3.59	WA (**)	24	—	1.893	[V_6O_{11}]
3.59	WA (*)	40	—	1.884	[V_6O_{11}]
3.59	WA (*)	75	—	1.886	[V_6O_{11}]
3.59	1.3224(*)	25	112.0	1.898	[V_6O_{11}]
3.59	1.3125(*)	25	110.2	1.893	[V_6O_{11}]
3.46	WA (**)	75	—	1.996	[VO_2]
3.34	WA (*)	75	—	1.999	[VO_2]
3.13	WA (*)	75	—	2.000	[VO_2]

* The starting material is V_2O_3 prepared at an oxygen partial pressure of 10^{-11} atm.

** The starting material is VO_2 prepared in pure carbon dioxide, and treated at a desired oxygen partial pressure. After equilibration, the oxygen partial pressures were changed to 10^{-11} atm to obtain a stoichiometric $VO_{1.500}$.

WA means for wet analysis.

TABLE 3. SOME PROPERTIES OF PHASES IN THE SYSTEM V_2O_3-VO_2 AT 1600°K

Phase	Range of $-\log_{10} P_{O_2}$ atm	Range of composition (VO_x)	Pattern of X-ray diffraction (comparison with Andersson[5])	Crystal parameter
[V_2O_3]	~6.36	1.500—1.555	identical	rhombohedral: $VO_{1.500}$ $a=5.472$Å $\alpha=53.80°$ $VO_{1.515}$ $a=5.471$Å $\alpha=53.75°$ $VO_{1.541}$ $a=5.464$Å $\alpha=53.74°$
[V_3O_5]	6.36—4.90	1.667 (no variation)	identical	monoclinic: $a=9.993$Å $b=5.063$Å $c=9.872$Å $\beta=138.62°$
[V_4O_7]	4.90—4.20	1.750 (no variation)	identical	unknown
[V_5O_9]	4.20—4.04	1.800 (no variation)	identical	unknown
[V_6O_{11}]	4.04—3.53	1.833—1.905	different*	unknown
[VO_2]	3.53~	2.000~	identical	monoclinic: $a=5.744$Å $b=4.526$Å $c=5.375$Å $\beta=122.55°$

* See Fig. 3.

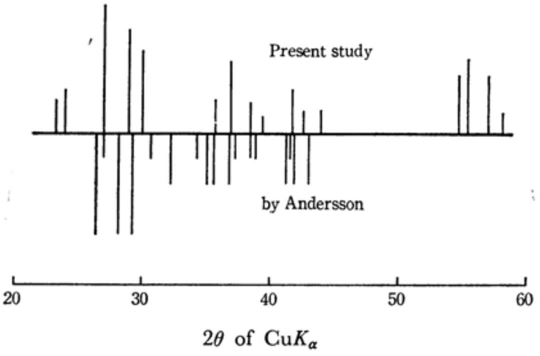

Fig. 3. Comparison of X-ray data obtained by Andersson with those obtained from the present study.

are seen only in the phases of V_2O_3 and V_6O_{11} at 1600°K. Andersson[5] found a narrow range of homogeneity in the V_3O_5 phase at 900°C, but, on the other hand, Kosuge *et al.*[6] estimated fairly wide ranges of variations in the V/O ratio in the phases of V_3O_5 and V_4O_7, together with those in the phases of V_2O_3 and V_6O_{11} at 800 and 900°C, by means of magnetic properties.

The powder X-ray diffraction patterns of seven samples belonging to the V_6O_{11} phase, prepared by quenching at various oxygen partial pressures, showed identical intensities for each peak and *d*-values within the range of experimental error. Andersson[5] reported the X-ray diffraction data of the V_6O_{11} synthesized at 900°C; there was a surprising difference in *d*-values between Andersson's and ours. The differences in 2θ angles and the relative intensities are graphically shown in Fig. 3. If this is true, we could expect a phase transition of V_6O_{11} due to the temperature change. Since we were able to get a single crystal of this phase, a determination of the crystal structure is in progress by Dr. M. Nakahira, The University of Tokyo.[13]

The Standard Free Energies of Oxidations. Of the vanadium oxides which were studied in the present work, the standard free energies of the formations of V_2O_3 and VO_2 have already been compiled by Coughlin[7] and by Elliott and Gleiser[11]. In their calculations, they used the data of the heat of the formations of V_2O_3 and VO_2 by Siemonsen and Ulich,[14] and calculated the standard free energies of formations of these oxides on the basis of the entropy changes compiled by Kelley and King.[15] According to Coughlin,[7] the linear free-energy equations for the reactions below are given as follows:

$$2V(c) + {}^3/{}_2O_2(g) = V_2O_3(c) \qquad (1)$$

$$\Delta G_T^\circ(1) = -291350 + 56.49T \quad (600—2000°K) \qquad (1')$$

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[13] Private communication. A preliminary work given by Nakahira showed the monoclinic structure (1966).

[14] H. Siemonsen and H. Ulich, *Z. Electrochem.*, **46**, 141 (1940).

[15] K. K. Kelley and E. G. King, "Contributions to the Data on Theoretical Metallurgy. X. Heat-Content, Heat-Capacity, and Entropy Data for Inorganic Substances," Bull, 476, Bureau of Mines, U. S. A. (1949).

$$2V(c) + 2O_2(g) = V_2O_4(c) \qquad (2)$$

$$\Delta G^\circ_T(2) = -335000 + 73.24T \qquad (600\text{—}1818°K) \qquad (2')$$

where T is in the absolute temperature. These are the only published data concerning the standard free energies of the formations of the vanadium oxides which we studied.

The standard free energies of oxidations in the following reactions:

$$VO_{5/3} + {}^1/_{24}O_2 = VO_{7/4} \qquad (3)$$

$$VO_{7/4} + {}^1/_{40}O_2 = VO_{9/5} \qquad (4)$$

and

$$VO_{9/5} + {}^1/_{60}O_2 = VO_{11/6} \qquad (5)$$

can readily be calculated on the basis of the present study, since these compounds, $VO_{5/3}$, $VO_{7/4}$, $VO_{9/5}$, and $VO_{11/6}$, have their stoichiometric compositions in their equilibrium states at fixed oxygen partial pressures. Thus the standard free energies of the oxidations of these reactions can be found by the van't Hoff equation:

$$\Delta G^\circ_T = n\boldsymbol{R}T \ln P_{O_2}(\mathrm{eq}) \qquad (6)$$

where n is the number of moles in each equation, and where $P_{O_2}(\mathrm{eq})$ is the equilibrium oxygen partial pressure at which two solid phases are in equilibrium. However, when an extensive solid solution is involved, the situation is somewhat complicated. This is the case with V_2O_3 and V_6O_{11}, in which we found very wide ranges of solid solutions.

Recently, Smiltens[16] calculated the standard free energy of the oxidation of magnetite (Fe_3O_4) to hematite (Fe_2O_3) at temperatures above 1000°C, at which magnetite has an extensive solid solution range. In his paper, he derived a correction term which is related to the formation of a solid solution. This method for calculating the standard free energy of oxidation is directly applicable to the following oxidation reactions in the present study:

$$VO_{3/2} + {}^1/_{12}O_2 = VO_{5/3} \qquad (7)$$

and

$$VO_{11/6} + {}^1/_{12}O_2 = VO_2 \qquad (8)$$

For instance, Eq. (7) may be divided into two parts in respect to its reaction:

$$VO_{3/2} + {}^x/_2O_2 = VO_{3/2+x}$$

(the formation of a solid solution) (7-1)

and

$$VO_{3/2+x} + {}^y/_2O_2 = VO_{5/3}$$

(two-solid-phases equilibrium) (7-2)

where x ranges from 0.000 to 0.055, and where $y=0.167-x$ in the V_2O_3-V_3O_5 system as is shown in Table 3. On the basis of Smiltens' method, the standard free energy due to the reaction expressed by Eq. (7) may be given as:

$$\Delta G^\circ_{1600°\mathrm{K}}(7) = 611.2 \times \log_{10}P_{O_2}(\mathrm{eq}) + 3660\int_{0.000}^{0.055} \log_{10}[P_{O_2}/P_{O_2}(\mathrm{eq})]\mathrm{d}x \qquad (7')$$

where $P_{O_2}(\mathrm{eq})$ is the equilibrium oxygen partial pressure between two solid phases, which was $10^{-6.36}$ atm, and where P_{O_2} represents oxygen partial pressures related to fixed compositions within the solid solution of the V_2O_3 phase. The integral term shown in Fig. 4 was calculated by means of a planimeter.

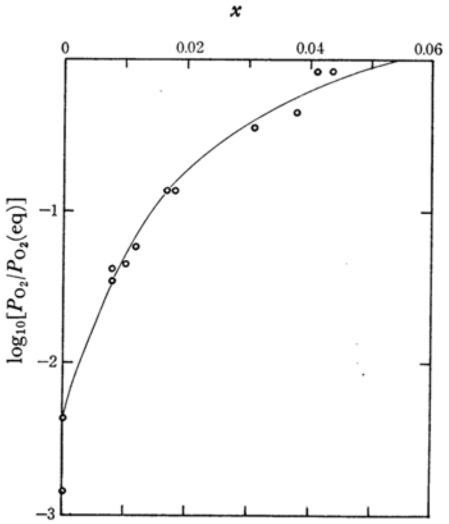

Fig. 4. The $\log_{10}[P_{O_2}/P_{O_2}(\mathrm{eq})]$ *vs.* x curve at 1600°K for the V_2O_3 solid solution.

The standard free energy of the oxidation of $VO_{11/6}$ to VO_2 may be obtained by the same method as above; for the reaction expressed in Eq. (8), we will get the following equation:

$$\Delta G^\circ_{1600°\mathrm{K}}(8) = 611.2 \times \log_{10}P_{O_2}(\mathrm{eq}) + 3660\int_{0.000}^{0.072} \log_{10}[P_{O2}/P_{O_2}(\mathrm{eq})]\mathrm{d}x \qquad (8')$$

where $P_{O_2}(\mathrm{eq})$ indicates the equilibrium oxygen partial pressure between the two solid phases, which was $10^{-3.53}$ atm, and where P_{O_2} is the oxygen partial pressure of the system with a fixed composition within the range of the solid solution of the $VO_{11/6}$ phase. The integral term shown in Fig. 5 was calculated by means of a planimeter.

In Table 4, the standard free energies of the oxidations of vanadium oxides expressed in Eqs. (7), (3), (4), (5), and (8) are listed. The maximum errors introduced in the experiments and in the calculations may be estimated to be ±100 cal in the cases of the Eqs. (7) and (8), and ±50 cal in Eqs. (3), (4), and (5). The last line in Table IV shows the sum of these standard free energies of oxidations, which is related to the equation:

$$VO_{3/2} + {}^1/_4O_2 = VO_2 \qquad (9)$$

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[16] J. Smiltens, *J. Am. Chem. Soc.*, **79**, 4877 (1957).

TABLE 4. STANDARD FREE ENERGIES OF OXIDATION AT 1600°K

Oxidation reaction	$\log P_{O_2}$	Correction term, cal	$\Delta G^\circ_{1600^\circ K}$ cal
$VO_{3/2} + {}^1/_{12}O_2 = VO_{5/3}$	-6.36	-140	-4030 ± 100
$VO_{5/3} + {}^1/_{24}O_2 = VO_{7/4}$	-4.90	0	-1490 ± 50
$VO_{7/4} + {}^1/_{40}O_2 = VO_{9/5}$	-4.20	0	-770 ± 50
$VO_{9/5} + {}^1/_{60}O_2 = VO_{11/6}$	-4.04	0	-490 ± 50
$VO_{11/6} + {}^1/_{12}O_2 = VO_2$	-3.53	-40	-2200 ± 100
$VO_{3/2} + {}^1/_4O_2 = VO_2$			-8980 ± 200

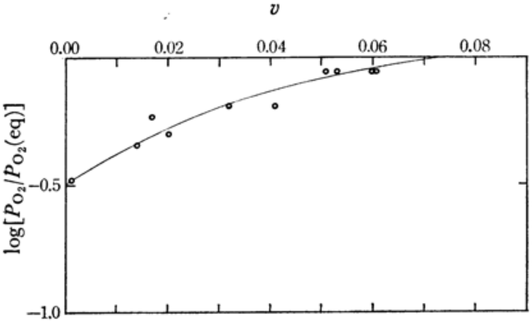

Fig. 5. The $\log_{10}[P_{O_2}/P_{O_2}(eq)]$ *vs.* x curve at 1600°K for the V_6O_{11} solution.

We can also calculate the standard free energy of the oxidation of $VO_{3/2}$ to VO_2 on the basis of the approximate free energy equations for the reactions (1), and (2) compiled by Coughlin.⁷⁾ From the values of $1/2[\Delta G^\circ(2)-\Delta G^\circ(1)]$ at 1600°K, we obtained the following value for the oxidation reaction, Eq. (9):

$$\Delta G^\circ_{1600^\circ K}(9) = -43650 + 16.75T$$
$$= -8425 \text{ (cal)} \qquad (9')$$

The agreement with the present value(-8980 cal) is fairly good.

Conclusions

On the basis of the foregoing experimental results at 1600°K, we obtain the following conclusions; 1) the V_2O_3, V_3O_5, V_4O_7, V_5O_9, V_6O_{11}, and VO_2 phases exist under various oxygen partial pressures, ranging from 10^{-13} to $10^{-3.1}$ atm; 2) in these oxide phases, the V_2O_3 and V_6O_{11} phases have extensive ranges of solid solutions, but the others have very narrow ranges of solid solutions, almost equal to their stoichiometric compositions; 3) there is no evidence of the presence of the V_7O_{13} and V_8O_{15} phases which were recognized by Andersson⁵⁾ and Kosuge *et al.*⁶⁾ at 900 and 800°C respectively, and the V_6O_{11} phase is equilibrated with the VO_2 phase at the oxygen partial pressure of $10^{-3.53}$ atm; and 4) the standard free energy of the oxidation of each vanadium oxide has been calculated on the basis of the present study, and the standard free energy of the oxidation of $VO_{3/2}$ to VO_2 has been compared with that compiled by Coughlin.⁷⁾

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Appendix

Determination of Actual Oxygen Partial Pressures by Means of a Solid Electrolyte. In the present study, we used a solid electrolyte cell composed of $(ZrO_2)_{0.85}(CaO)_{0.15}$ which was prepared at 1800°C by courtesy of the Hitachi Electric Co., Ltd., under the supervision of Mr. K. Hirota, Tokyo Institute of Technology. The principles of this electrolyte for the determination of the oxygen partial pressure and the design for general utility have been published,¹⁷⁾ and some precise results have been reported.¹⁸⁾ The $(ZrO_2)_{0.85}(CaO)_{0.15}$ solid electrolyte devised for the present study will be briefly described here.

A mixed powder of ZrO_2 and CaO was pressed into a rod 15 mm in diameter and 300 mm long, and then heated at 1300°C for a long time to make a loosely sintered rod. The rod thus prepared was holed by a diamond lathe, and again heated at 1800°C for 5 hr. The tube, which was sealed at one end, has a wall-width of 2 mm. The bottom portion was coated both inside and outside with a porous platinum film. Platinum electrical leads 0.5 mm in diameter connect the

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17) C. Wagner, *Naturwissenschaften*, **23/24**, 265 (1943); F. Hund, *Z. phys. Chem.*, **199**, 142 (1952); E. Bauer and H. Preis, *Z. Elektrochem.*, **43**, 727 (1937); J. Weissbart and R. Ruka, *J. Electrochem. Soc.*, **109**, 723 (1962); J. Weissbart and R. Ruka, *Rev. Sci. Instr.*, **32**, 593 (1961).

18) K. Kiukkola and C. Wagner, *J. Electrochem. Soc.*, **104**, 379 (1957); H. A. Johansen and J. G. Cleary, *ibid.*, **111**, 100 (1964); W. D. Kingery, J. Pappis, M. E. Dotty, and D. C. Hill, *J. Am. Ceram. Soc.*, **42**, 393 (1959).

platinum electrods of the cell to a potentiometer which measures the cell emf. A calibrated thermocouple was also brought into contact with the bottom wall of the cell, and the temperature was measured. Inside the tube pure oxygen was circulated at one atmosphere during the period of measurement.

At a high temperature in a galvanic cell of the Pt, $O_2(P_1)$/solid oxide/$O_2(P_2)$, Pt type, the emf is a function of the oxygen partial pressures at the oxygen/Pt electrode, and the maximum electrical energy, $4\boldsymbol{EF}$, is given by:

TABLE 5a. OXYGEN PARTIAL PRESSURES IN MIXED GASES MEASURED BY SOLID ELECTROLYTE CELL AND COMPARISON WITH THE DATA CALCULATED FROM THERMOCHEMICAL DATA

$[CO_2/H_2]_i$	emf, mV observed	$-\log P_{O_2}$	
		$-\log P_1$ from emf (Eq. (2A))	$-\log P_1'$ from (Eq. (3A))
0.054	1020	12.89	12.89
0.102	986	12.42	12.42
0.452	858	10.81	10.81
0.726	814	10.26	10.26
1.00	784	9.88	9.88
1.76	731	9.21	9.21
2.75	693	8.73	8.73
6.73	620	7.82	7.83
7.39	612	7.74	7.74
7.70	609	7.71	7.71
8.66	601	7.59	7.59
12.6	572	7.23	7.24
20.0	540	6.81	6.82
22.4	530	6.70	6.72
30.0	510	6.44	6.46
35.0	499	6.30	6.32
50.0	474	6.00	6.01
60.0	460	5.82	5.85
100.0	425	5.37	5.40
132	405	5.09	5.16
150	394	4.97	5.05
180	382	4.83	4.89
193	374	4.72	4.82
217	366	4.62	4.72
255	353	4.45	4.58
328	334	4.21	4.36
335	333	4.19	4.34
337	332	4.18	4.34
341	332	4.17	4.33
379	323	4.07	4.23
406	318	4.01	4.18
439	312	3.93	4.11
465	307	3.87	4.06
481	304	3.83	4.03
512	300	3.78	3.98
550	295	3.72	3.91
650	285	3.59	3.77
906	274	3.46	3.48
1540	265	3.34	3.02

TABLE 5b.

$[O_2/CO_2]_i$	emf, mV observed (±0.2)	$-\log P_{O_2}$	
		$-\log P_1$ from emf (Eq. (2A))	$-\log P_1'$ from Smiltens*
0.000768	236.4	2.98	2.88
0.00135	223.1	2.81	2.74
0.00386	212.3	2.67	2.63
0.00270	200.5	2.53	2.52
0.00405	188.6	2.38	2.36
0.00592	174.3	2.20	2.21
0.00849	163.1	2.05	2.06
0.01185	151.8	1.91	1.92
pure O_2	0.0	0.00	0.0

* J. Smiltens, *J. Am. Chem. Soc.*, **79**, 4877 (1957).

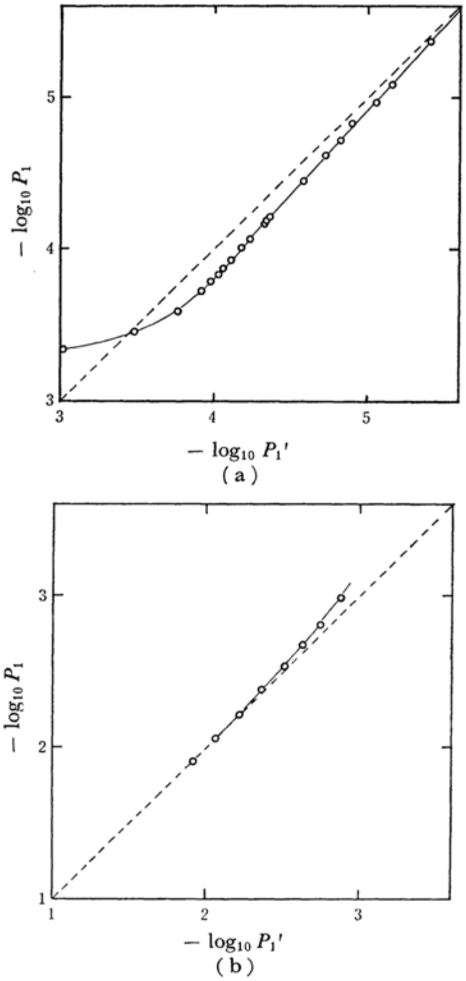

Fig. 6. Relationship between thermochemically calculated oxygen partial pressure and measured oxygen partial pressure based on the emf of solid electrolyte. 6-a is for mixtures of CO_2-H_2, and 6-b is for mixtures of O_2-CO_2. P_1 is oxygen partial pressure based on the emf measurement (Eq. (2A)), and P_1' is thermochemically calculated oxygen partial pressure.

$$4E\boldsymbol{F} = -\Delta G = -\boldsymbol{R}T \ln P_1/P_2 \tag{1A}$$

where E is the emf at a fixed temperature, $\boldsymbol{F}$, the Faraday constant; P_1, an oxygen partial pressure of a mixed gas at that temperature, and P_2, the reference oxygen pressure, which was kept constant at one atmosphere in the present study. When we insert the cell into a furnace tube heated to a desired temperature, an oxygen partial pressure in the mixed gas passing through the furnace tube can be readily measured by reading the emf. At 1600°K, the measured oxygen partial pressure based on Eq. (1A) is expressed as:

$$\log_{10}P'_1 = -E/79.37 \tag{2A}$$

where E is in milli-volts.

On the other hand, the calculated oxygen partial pressure, based on the CO_2/H_2 ratio by using the thermochemical data, may be expressed as follows at 1600°K:

$$\left.\begin{aligned} \log_{10}P'_1 &= \log_{10}K_2 + 2\log_{10}[(a-1) \\ &\quad + \sqrt{(a-1)^2 + 4a/K_1}] \\ &= -4.697 + 2\log_{10}[(a-1) \\ &\quad + \sqrt{(a-1)^2 + 1.279a}] \end{aligned}\right\} \tag{3A}$$

where K_1 is the equilibrium constant for the reaction, $CO_2+H_2=CO+H_2O$ (3.083 at 1600°K), where K_2 is for the reaction, $CO_2=CO+{}^1/_2\,O_2$ (2.009×10^{-5} at 1600°K), and where a is the initial ratio of CO_2/H_2 mixed at room temperature. The standard free energies of the formation of CO_2, CO, and H_2O were selected from Coughlin's compilation in order to calculate the values of K_1 and K_2. We also used a mixed gas, O_2-CO_2, to obtain higher oxygen parital pressures around 10^{-3} atm. The calculation of the oxygen partial pressures in mixtures of O_2 and CO_2 has been described by Smiltens.16) Calculated oxygen partial pressures from Eqs. (2A) and (3A) are compared in Table 5 and illustrated in Fig. 6 (a and b) in order to emphasize the deviation in the oxygen partial pressures calculated by Eq. (3A) from those calculated by Eq. (2A) at certain intervals of oxygen partial pressures.

As is shown in Table 5, when the ratios of the two gas species are moderate, P_1' is almost the same as the P_1 calculated from the emf. However, when the ratios of the gas mixture become large or small, the discrepancy between P_1 and P_1' is appreciable. In the present study, the oxygen partial pressures obtained by measuring the emf values according to Eq. (2A) were adopted as the actual oxygen partial pressures at 1600°K.