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PHASE EQUILIBRIA IN THE V_2O_4-V_2O_5 SYSTEM AT TEMPERATURES FROM 500° TO 651°C

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The standard free energies ($\Delta G°$) for V_2O_4 oxidation according to the following consecutive reaction

$$V_2O_4 \rightarrow V_6O_{13} \rightarrow V_3O_7 \rightarrow V_2O_5$$

have been determined precisely on the basis of equilibrium oxygen pressure at 651°C. The standard free energy change for the reaction

$$2\ V_3O_7 + 1/2\ O_2 = 3\ V_2O_5$$

can be expressed by $\Delta G_R^\circ = -12{,}271 + 2.57\ T$ (500 - 651°C) $\pm$ 1340 cal.

Although the phase equilibrium in the V_2O_3-V_2O_4 system (Magneli phases: V_nO_{2n-1}) has been studied accurately and extensively at high temperatures[1,2], relatively little is known on the system V_2O_4-V_2O_5, and the intermediate phases in it, below 670°C (m.p. of V_2O_5). Iwase et al.[3] measured the oxygen tensions over V_2O_5-V_2O_4 system using Mcleod gauge and gave thermodynamic data for it. The equilibria in the system V_2O_4, V_2O_5, $VOSO_4$, SO_2, and SO_3 were studied by Kleppa et al.[4] and they calculated the oxygen tensions for the reaction $V_2O_5 = V_2O_{4(\text{unknown})} + 1/2\ O_2$. Wasdley et al.[5] found a series of compounds formulated as $V_{2n}O_{5n-2}$ (n: integer). Four phases, V_2O_4, V_6O_{13}, V_3O_7, and V_2O_5, were observed in the phase diagram[6] of V_2O_4-V_2O_5 system in the range of temperature 600 - 900°C. Taniguchi et al.[7] found the phase V_4O_9 with n = 4 in the $V_{2n}O_{5n-2}$ series. Recently, Fotiev et al.[8] have studied the dissociation pressure for the consecutive reaction $V_2O_5 \rightarrow V_3O_7 \rightarrow V_6O_{13} \rightarrow V_2O_4$, and obtained the equilibrium oxygen partial pressures for the transition between V_2O_5 and V_3O_7 phases.

In the present study, it was concluded that the phases V_2O_4, V_6O_{13}, V_3O_7, and V_2O_5 were stable at 651°C and in the range of oxygen partial pressures 10^{-3} - 10^{-7} atm. The thermodynamic data[9] for V_6O_{13}, V_2O_4 as well as V_2O_5 in the V_2O_4-V_2O_5 system could be obtained on the basis of Kleppa's results[4]. Since the gaseous buffering systems e.g. CO_2-CO, CO_2-H_2 etc. can not be used below 680°C due to the difficulties encountered for obtaining the desired oxygen partial pressures (10^{-3} - 10^{-7}), the aim of the present work is (1) to control the oxygen partial pressures from 10^{-3} to 10^{-7} atm in the range of temperature 500 - 651°C, (2) to obtain the detailed informations about the phase equilibrium of the V_2O_4-V_2O_5 system at 651°C, (3) to determine the thermodynamic functions $\Delta G°$ for the consecutive reaction $V_2O_4 \rightarrow V_6O_{13} \rightarrow V_3O_7 \rightarrow V_2O_5$ at 651°C and $\Delta H°$ for the oxidation of V_3O_7 to V_2O_5 at 500 - 651°C, as well as to criticize the enthalpy data for the reaction $V_2O_4 + 1/2\ O_2 = V_2O_5$.

Thermogravimetric method was used in the present study. Finely pulverized vanadium oxide samples were heated in the range of temperatures from 500 to 651°C at the chosen oxygen pressures in an electric furnace. These samples in the platinum-baskets were suspended from one edge of a micro-balance (RMB-50V type, Shimadzu Seisakusho

Ltd.), and weight changes were recorded under each oxygen partial pressure. The oxide samples were heated at the chosen oxygen pressures until equilibria were attained between gas and solid phase. Then, the samples were quenched rapidly to the room temperatures by taking from the furnace. The phases contained in the samples thus obtained were studied by X-ray diffraction method.

The four phases, V_2O_4, V_6O_{13}, V_3O_7, and V_2O_5 were used as the starting materials. The phases V_6O_{13} and V_3O_7 were prepared by heating stoichiometric amounts of V_2O_3 and V_2O_5 to 650°C for 60 days in sealed and evacuated silica tubes. Vanadium dioxide (V_2O_4) was obtained from the reduction of V_2O_5 by SO_2 gas at 500°C for two days.

In order to control the oxygen partial pressures, a method was developed as follows: Nitrogen gas containing trace oxygen ($p_{O_2} \doteqdot 10^{-3.5}$ atm) was dried with $CaCl_2$ and P_2O_5, and deoxygenated with iron nets at about 800°C, then dehydrogenated with cupper oxide at about 200°C. The purified nitrogen gas ($p_{O_2} < 10^{-14}$ atm) was mixed with argon ($p_{O_2} \doteqdot 10^{-4}$ atm) in a calibrated capilary with manometer. The gas mixture was thus similar to that used by Muan$^{10)}$; The oxygen partial pressures in it were independent on temperatures in the range of 750 - 950°C and equal to 10^{-4} - $10^{-5.5}$ atm. In this experiment, it was assumed that the oxygen partial pressures obtained were also independent on the temperature in the range 500 - 651°C. Then a considerably rapid flow rates 15 - 20 cm/s were used to prevent the effect of separation of oxygen gas by thermal diffusion. The error of log p_{O_2} due to the fluctuation of the purified N_2/Ar in the gas mixture was estimated to be within $\pm$ 0.03. The actual oxygen partial pressures in the gases mixtures were measured by using a stabilized zirconia $[(ZrO_2)_{0.85}(CaO)_{0.15}]$.

After setting the starting materials under certain oxygen partial pressure, it was examined with the micro-thermobalance whether they were oxidized or reduced. Then, they were quenched to the room temperatures after the attainment of the equilibria between gas and solid phase. In the present study, no reduction of the starting materials were recognized during 2 days within the experimental error; Oxidations leading to unknown compositions of the samples were detected from the weight gain, from which the compositions of the oxidized samples could be evaluated.

In the thermogravimetric method, the system is regarded to be in the equilibrium state between gas and solid phase when the weight of the sample indicated a constant value at any oxygen atmosphere within the experimental error. Although the strict check of the equilibrium between two solid phases was lacking because the reductions of starting materials (dissociation of the oxides) could not be detected within the 2 days due to the quite low reaction velocity, it will be approximately adequate to estimate the equilibrium oxygen partial pressures in this way, because the oxidation reactions between gas and solid phase were apparrently rapid. Thus, in the quenching method$^{11)}$, the check of the equilibria in the V_2O_4-V_2O_5 system was carried out by using SO_2-N_2 gas mixture at 651°C, within the experimental error for log p_{O_2} with $\pm$ 0.03.

The equilibrium data obtained at 651°C are cited in Table 1. The products obtained by the quenching method were indicated by [red.]. In Table 1, the equilibrium data of the system V_3O_7 - V_2O_5 - O_2 at 500, 532, 600, and 651°C are cited. The oxygen partial pressures at which any two phases can coexist can be estimated by the interpolation method. Thus, the standard free energies of the following oxidation reactions can be calculated by means of the van't Hoff equation.

$$3\ V_2O_4 + 1/2\ O_2 = V_6O_{13} \qquad (1)$$

$$V_6O_{13} + 1/2\ C_2 = 2\ V_3O_7 \qquad (2)$$

and

$$2\ V_3O_7 + 1/2\ O_2 = 3\ V_2O_5 \qquad (3)$$

From the calculated standard free energies for the above reactions in Table 2, and by applying the least square method, the enthalpy and the entropy of reaction (3) can be calculated and are equal to be - 12.27 ± 1.34 Kcal and - 2.57 ± 1.09 e.u. in the temperature range 500 - 651°C ,respectively. The general equation for estimating the standard free energy in the range of temperature 500 - 651°C is given in Table 2.

Table 1 Equilibrium data

- log p_{O_2} (atm)	phase
at 651°C	
3.90(± 0.03)	V_2O_5(red.)
4.15	V_2O_5
4.24	V_3O_7
4.33	V_3O_7
4.51	V_3O_7
4.60	V_3O_7
4.62	V_3O_7
4.87	V_6O_{13}
4.92	V_6O_{13}(red.)
5.05	V_6O_{13}
5.08	V_6O_{13}(red.)
5.14	V_6O_{13}
5.20	V_6O_{13}(red.)
5.23	V_6O_{13}
5.41	V_2O_4
5.42	V_2O_4(red.)
5.50	V_2O_4
5.59	V_2O_4
5.80	V_2O_4(red.)
at 600°C	
4.15(± 0.03)	V_2O_5
4.33	V_2O_5
4.51	V_2O_5
4.69	V_3O_7
4.74	V_3O_7
4.79	V_3O_7
4.87	V_3O_7
4.95	V_3O_7
at 532°C	
4.69(± 0.03)	V_2O_5
4.90	V_2O_5
5.08	V_3O_7
5.17	V_3O_7
5.17	V_3O_7
5.35	V_3O_7
at 500°C	
4.33(± 0.03)	V_2O_5
4.87	V_2O_5
4.96	V_2O_5
5.05	V_2O_5
5.14	V_2O_5
5.23	V_2O_5
5.32	V_3O_7
5.41	V_3O_7

The thermodynamic data[3,4] for the reactions

$$V_2O_5 = V_2O_{4(\text{unknown})} + 1/2\ O_2 \qquad (4)$$

and

$$V_2O_5 = V_2O_4 + 1/2\ O_2 \qquad (5)$$

are graphically represented in Fig. 1. Due to the discovery of new intermediate phases such as V_3O_7[12], V_6O_{13}[13], VOx[14], and V_4O_9[7] in the V_2O_4-V_2O_5 system, it seems that the equation (4) already suggested by Kleppa et al.[4] might be in the following form

$$V_6O_{13} = 6\ VOx + (\ 13 - 6X\ )/2\ O_2 \qquad (6)$$

and the equation (5) suggested by Iwase et al.[3] might be $3\ V_2O_5 = 2\ V_3O_7 + 1/2\ O_2$ (7).

In the present study, though the V_4O_9 phase was not found, if the lower oxygen partial pressures were exactly controled at lower temperatures, this phase may be found under the fixed oxygen partial pressures. Also, Kleppa et al.[15] have studied the thermochemistry of some vanadium oxides using a developed high temperature combusion calorimeter. They obtained

Table 2 Thermodynamic data in the V_2O_4-V_2O_5 system

		ΔG° (cal)
at 651°C		
	$3V_2O_4 + 1/2\ O_2 = V_6O_{13}$	- 11247 ± 203
	$V_6O_{13} + 1/2\ O_2 = 2V_3O_7$	- 10021 ± 265
	$2V_3O_7 + 1/2\ O_2 = 3V_2O_5$	- 8879 ± 116
at 600°C		
	$2V_3O_7 + 1/2\ O_2 = 3V_2O_5$	- 9188 ± 191
at 532°C		
	$2V_3O_7 + 1/2\ O_2 = 3V_2O_5$	- 9191 ± 177
at 500°C		
	$2V_3O_7 + 1/2\ O_2 = 3V_2O_5$	- 9338 ± 83

from 500° to 651°C	ΔH°(Kcal)	ΔS°(e.u.)
$2V_3O_7 + 1/2\ O_2 = 3V_2O_5$	-12.27±1.34,	-2.57±1.09

General equation:

$$\Delta G^\circ = - 12{,}271 + 2.57\ T\ (\text{ cal })$$

the enthalpy of V_6O_{13} when the powdered V_6O_{13} was exposed to oxygen atmosphere at 600-650°C. Using this advantage, the thermodynamic data of the V_3O_7 and V_4O_9 phases in V_2O_4-V_2O_5 system will also be obtained.

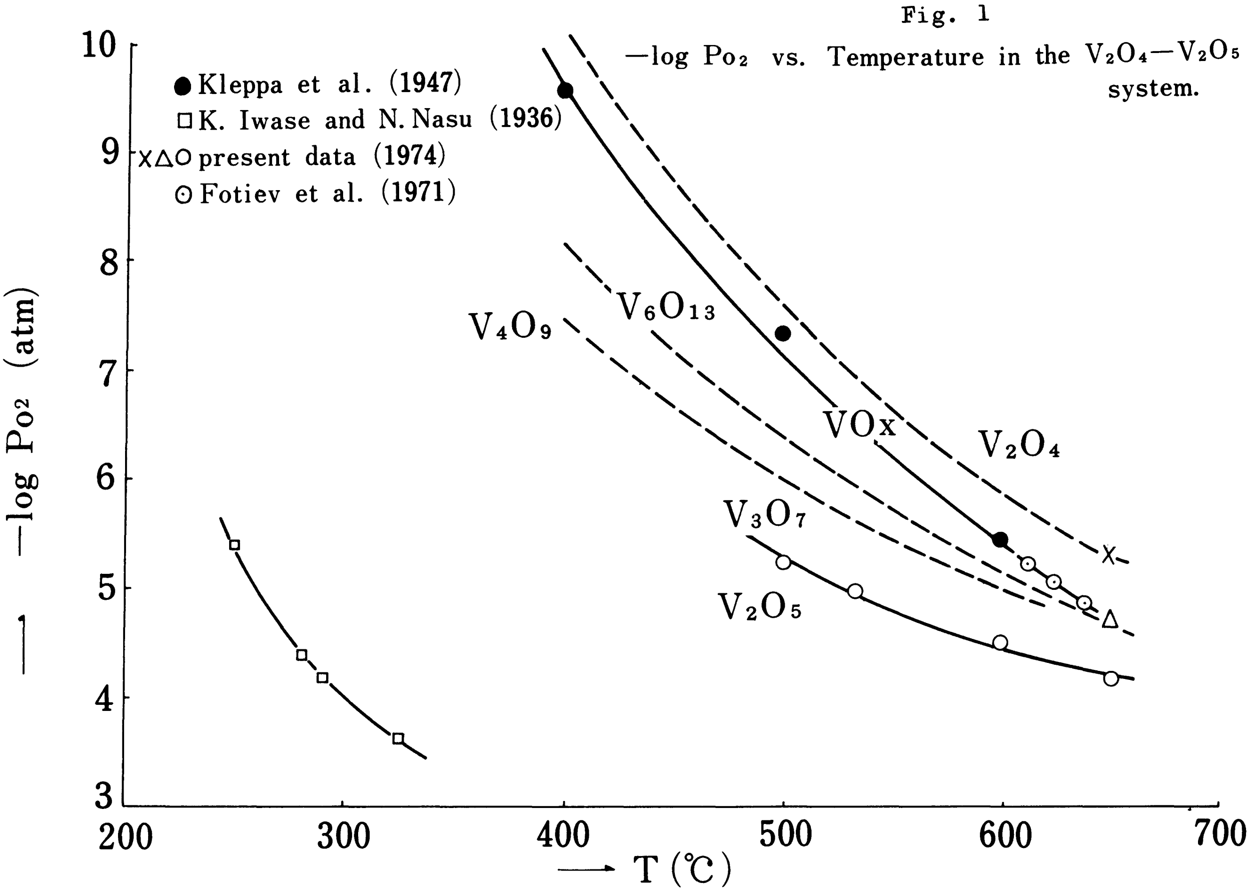

Fig. 1 —log P_{O_2} vs. Temperature in the V_2O_4—V_2O_5 system.

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