

## Oxygen Equilibrium Pressure above the $V_2O_{5-x}$ Oxide System at 600°C ( $x < 0.43$ )

ROMAN DZIEMBAJ\* AND JACEK PIWOWARCZYK

*Institute of Chemistry, Jagiellonian University, Krupnicza 41, 30-060 Kraków, Poland*

Received December 21, 1976; in revised form March 10, 1977

Measurements of equilibrium pressure of oxygen over the  $V_2O_{5-x}$  system performed by mass spectrometry have shown constancy of pressure over a wide range of  $x$ . The effect has been ascribed to thermodynamic equilibrium in the  $V_2O_5-V_6O_{13}-O_2$  system. On cooling of the samples the phase  $V_3O_7$  appears.

### Introduction

Measurements of the oxygen equilibrium pressure have been used for the determination of the enthalpy of partial decomposition of  $V_2O_5$  into a lower oxide and free oxygen. Following the works of Boreskov (1) and Sachtler (2) the value of enthalpy is generally accepted as a measure of the oxygen-binding energy. It has been found (3) that two oxygen forms are released during the temperature-programmed desorption experiments. One of them is given off from the adsorbed layer and another from the lattice anions. The amounts of desorbed loosely bonded oxygen gradually decrease in subsequent runs until they disappear completely.

Owing to these facts one may expect two different types of equilibria between oxygen and  $V_2O_5$ . A "chemisorption" equilibrium appertains to a monolayer chemisorbed on the surface and a "redox" equilibrium corresponds to a subsurface multilayer or to the bulk of the sample.

Earlier (4-6) as well as recent investigations (7-9) reported in the literature are concerned only with a "chemisorption" equilibrium. The aim of the present work is to study the "redox" equilibrium in the  $V_2O_{5-x}$  system. It appears

to us that studies of this equilibrium are more adequate for the determination of the enthalpy of the partial decomposition of  $V_2O_5$  into a lower oxide and free oxygen.

In view of the above considerations great attention should be paid to the pretreatment of the samples, so as to ensure the complete removal of chemisorbed oxygen prior to the measurements of the equilibrium pressure. It has been shown in (3) that for this purpose the sample should be spread in thinner layers and outgassed under more severe conditions than in the works which deal with the "chemisorption" equilibrium. Moreover the present work comprises the measurements carried out over a wide range of  $x$  (degree of reduction).

### Experimental

The intermediate preparation  $V_2O_{5-x}$  was obtained by the thermal decomposition of  $NH_4VO_3$  (Reachim, USSR), with gaseous products being continuously pumped out.  $NH_4VO_3$  (ca. 80 g) was heated at a rate of 2.3°C/min up to 400°C and kept at this temperature for 16 hr. After reaching the maximum value (of about 1 Torr) the pressure decreased at first rapidly and then slowly to  $10^{-4}$  Torr. The mass spectrometric analysis of the gaseous products showed the presence of

\* The author to whom correspondence should be addressed.

$\text{NH}_4^+$ -ion oxidation products even after 16 hr of heating at  $400^\circ\text{C}$ . This intermediate form of  $\text{V}_2\text{O}_{5-x}$  was kept in a desiccator over dried silica gel.

Samples of  $\text{V}_2\text{O}_{5-x}$  of about 1.5 g were spread in a layer about 0.5 mm thick on the flat bottom of the reactor and were heated at  $600^\circ\text{C}$  for 10 hr while being continuously pumped off. The final pressure was as low as  $10^{-7}$  Torr. The mass spectrometric analyses of gases flowing out of the reactor showed that only oxygen was present, indicating thus that all the  $\text{NH}_4^+$  ions were removed from the sample. The composition of  $\text{V}_2\text{O}_{5-x}$  preparations obtained in this way in various runs always corresponded to  $0.41 \leq x \leq 0.43$ .

After preparing the  $\text{V}_2\text{O}_{5-x}$  sample the valve connecting the reactor with the pumping system (Fig. 1) was closed and measurements of pressure with a McLeod-type manometer were begun. The readings of pressure were done with a cathetometer. When the pressure had reached a constant value, the partial pressure of oxygen was determined by mass-analysis of the gaseous phase in the reactor.

A strictly measured amount of oxygen (2.5–250  $\mu\text{mole}$ ) was then introduced into the reactor. As a result the equilibrium was disturbed and the oxygen was absorbed by the sample until a new equilibrium was reached. From the decrease of the partial pressure of oxygen it was possible to calculate the number,  $n$ , of  $\text{O}_2$  moles absorbed by the sample containing  $2N$  moles of vanadium atoms, and

hence the change of  $x$  in the formula  $\text{V}_2\text{O}_{5-x}$

$$\Delta x = x_2 - x_1 = -n/N.$$

The equilibrium pressure of oxygen was measured over a wide range of values of  $x$ .

In order to check whether the measured partial pressure of oxygen corresponds to a real thermodynamic equilibrium, the following tests were carried out. About 0.2  $\mu\text{mole}$  of  $\text{O}_2$  was removed from the reactor and, as a result, the induced transfer of oxygen from the  $\text{V}_2\text{O}_{5-x}$  sample to the gaseous phase was observed. After this operation was carried out twice, 0.5  $\mu\text{mole}$  of  $\text{O}_2$  was introduced into the reactor and absorbed by the sample. It was finally shown that even for tests lasting over 100 hr the partial pressure of oxygen reached the same constant value, under isothermal conditions, regardless of the direction of transition.

It should be noticed that after introduction of several portions of oxygen, the gas over the sample always contained a certain amount of  $\text{N}_2$  and also traces of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and Ar. They were introduced into the reactor together with oxygen as impurities in very small quantities. However, when the oxygen was absorbed by the sample and its total pressure was decreased about  $10^3$  times, the partial pressure of impurities became comparable with that of  $\text{O}_2$  or even greater. It should be noted that these gases were removed from the reactor after several mass-analyses, as is illustrated by the data given in Table I.

The chemical composition of the samples was determined at the end of the measurements. The amount of vanadium with an oxidation state lower than +5 was determined by manganometric titration (10). The numerical value of  $x$  in  $\text{V}_2\text{O}_{5-x}$  was calculated from the formula

$$x = 181.81/(2m/n_e + 16.00),$$

where  $n_e$  is the known amount of  $\text{KMnO}_4$  gram-equivalents used for the complete oxidation of vanadium atoms contained in  $m$  grams of sample. The changes of  $x$  calculated on the basis of chemical analysis were in agreement, within experimental error, with those calculated from the changes in the partial pressure

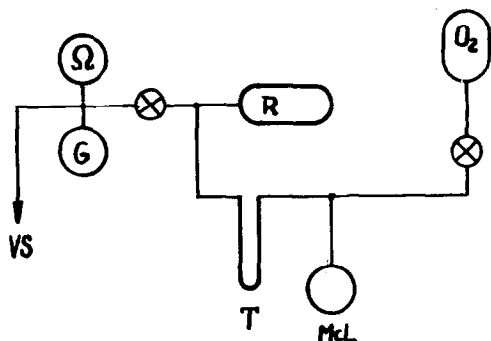


FIG. 1. The apparatus schema. R: reactor,  $\Omega$ : mass-spectrometric head, G: ionization gauge head, McL: McLeod-type manometer, T: liquid nitrogen trap, VS: high-vacuum system,  $\text{O}_2$ : oxygen-dosage system.

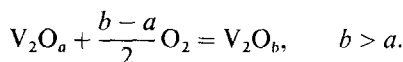
TABLE I  
THE CHANGE OF GASEOUS COMPOSITION DURING THE EXPERIMENTS

Stages of the experiment	Partial pressure (Torr)				
	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	Ar
Injection of pure oxygen	$6 \times 10^{-1}$	$1.5 \times 10^{-3}$	$\sim 10^{-5}$	$\sim 10^{-5}$	$\sim 10^{-5}$
After oxygen absorption	$6 \times 10^{-4}$	$1.5 \times 10^{-3}$	$1 \times 10^{-5}$	$1 \times 10^{-5}$	$2 \times 10^{-5}$
Equilibrium state	$6 \times 10^{-4}$	$< 10^{-6}$	—	—	—

of oxygen caused by its absorption by the sample.

at first disturbs the equilibrium, but the system in which two solid oxide phases coexist soon gains it back. This process is described by the equation

**Results and Discussion**



The changes of the equilibrium pressure of oxygen above  $V_2O_{5-x}$  at 600°C are shown in Fig. 2 as a function of chemical composition. The fact that the equilibrium pressure is constant in a wide range of  $x$  ( $0.02 < x < 0.43$ ) permits one to conclude on the basis of the Gibbs phase rule that the system studied contains three phases remaining in equilibrium:  $V_2O_a$ ,  $V_2O_b$ , and gaseous oxygen.

Since this equation imposes constraints on the system the number of independent components is reduced to two; the system is univariant and under isothermal conditions zerovariant. Hence the changes of oxygen pressure imposed on the system are spontaneously compensated by the system and constant equilibrium pressure of oxygen is restored.

The introduction of a new portion of oxygen

With an increasing amount of oxygen ab-

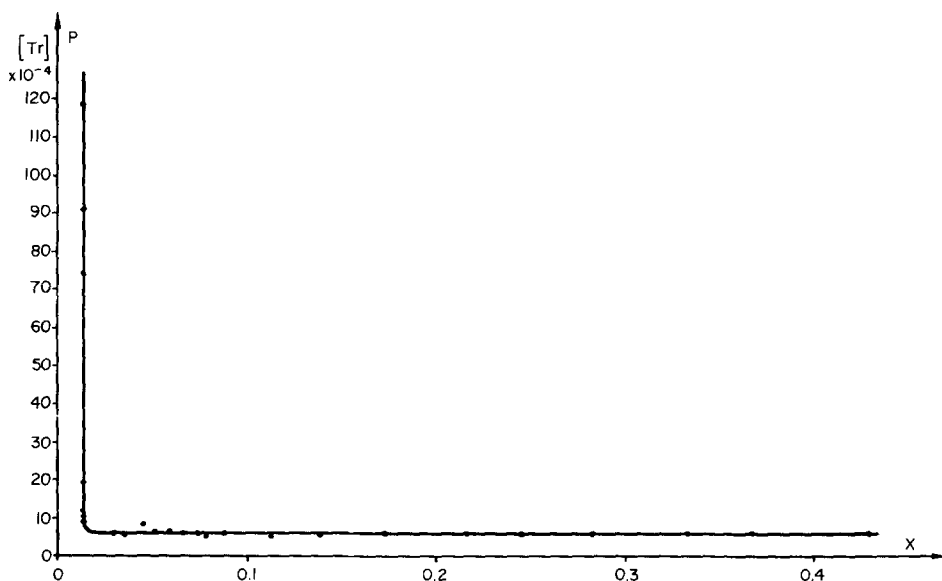


FIG. 2. Oxygen equilibrium pressure as a function of  $x$ .

sorbed by the solid phase the amount of higher oxide increases at the expense of the lower oxide. For  $x \leq 0.02$  the lower oxide disappears and the system becomes bivariant, and under isothermal conditions univariant. As a result the equilibrium pressure for  $x \leq 0.02$  depends strongly on the composition of the system, i.e., on the concentration of anionic vacancies in the oxide with the higher oxidation state.

The high average vanadium oxidation state

(4.98–5.00) suggests that the corresponding oxide phase is the  $V_2O_5$  phase. X-ray powder analysis confirms it. It can be seen in Fig. 3a that only  $V_2O_5$  lines are present, and that the degree of sample crystallization is high.

In the range of the lower average oxidation state of vanadium atoms between +4 and +5, Wadley (11) postulated the existence of a homologous series of compounds  $V_{2n}O_{5n-2}$  ( $n = 2, 3, 4, \dots$ ). However, the results of the studies obtained up to this point lead to the

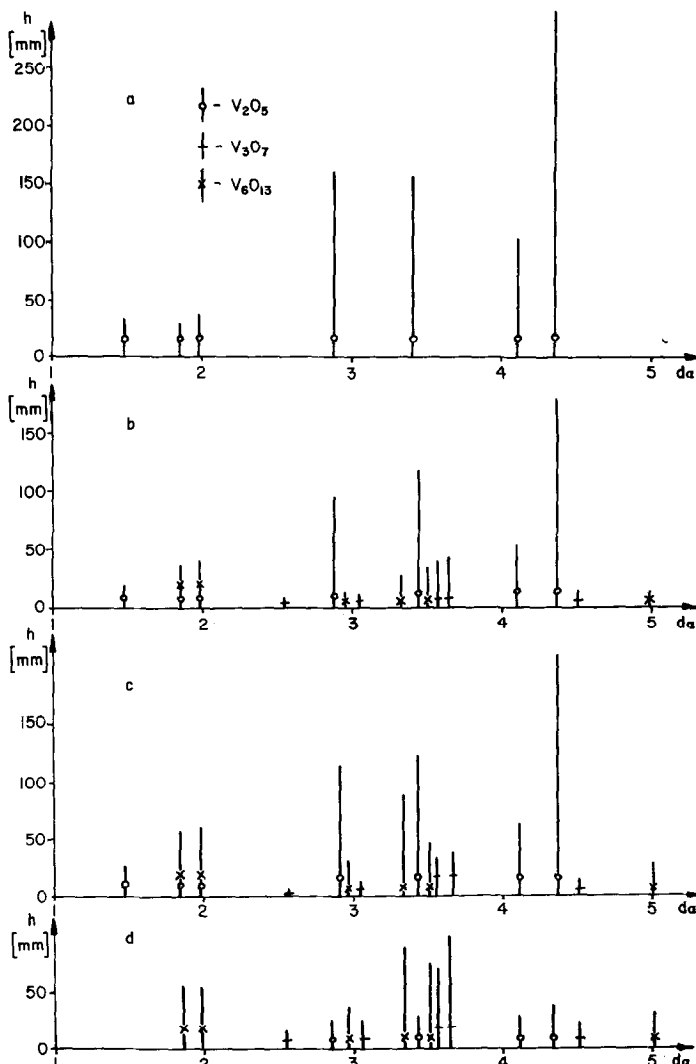


FIG. 3. X-ray pattern of samples after cooling from the equilibrium state to room temperature. (a)  $V_2O_{5-0.20}$ , (b)  $V_2O_{5-0.158}$ , (c)  $V_2O_{5-0.158}$ , (fast cooling) (d)  $V_2O_{5-0.426}$ .

conclusion that stable vanadium oxides exist only for some values of  $n$ .

$$\text{For } n = 2 \quad VO_2 = V_2O_4,$$

$$\text{for } n = 3 \quad V_6O_{13} = V_2O_{4.333} = V_2O_{5-0.667}, \quad (12, 13)$$

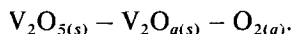
$$\text{for } n = 4 \quad V_4O_9 = V_2O_{4.500} = V_2O_{5-0.500}, \quad (14)$$

$$\text{for } n = 6 \quad V_3O_7 = V_2O_{4.667} = V_2O_{5-0.333}, \quad (13, 15)$$

$$\text{for } n = \infty \quad V_2O_5.$$

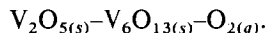
The oxide system studied by us consists, therefore, at the equilibrium state, of  $V_2O_5$  and one of the lower oxides.  $V_3O_7$  is excluded as an oxide corresponding to  $x = 0.3333$ , too low in comparison with the value of 0.43 observed in the two-phase oxide system.

In order to identify the phases present in the system, X-ray powder analysis of  $V_2O_{5-x}$  was carried out for samples with  $x > 0.02$ , i.e., in the range of three-phase equilibrium:



It can be seen in Figs. 3b-d that the powder diffraction patterns show lines characteristic of three solid phases  $V_2O_5$ ,  $V_6O_{13}$ , and  $V_3O_7$ . This result remains in contradiction with the results stated above.

However, the fact that the equilibrium pressure is constant in time, independent of the direction of oxygen transfer and of the changes of average chemical composition of the sample, indicates that the system for which the equilibrium pressure of oxygen is measured consists of three phases:



It could be suggested, therefore, that in the samples cooled to room temperature, in which X-ray analysis was carried out, a chemical reaction in which  $V_3O_7$  is formed takes place. Such a reaction would be possible, for example, if the system  $V_6O_{13(s)} - V_3O_{7(s)} - O_{2(g)}$  were stable at lower temperatures. In order to obtain unambiguous results the X-ray analysis should be carried out on the  $V_2O_{5-x}$  system at its equilibrium state at  $600^\circ\text{C}$ , but we are not in possession of an appropriate high-temperature and vacuum X-ray unit.

Other measurements were carried out instead, however. The samples of  $V_2O_{5-x}$  which were in equilibrium at  $600^\circ\text{C}$  were cooled at various rates and it was noticed that the faster the cooling, the lower the content of  $V_3O_7$  phase. The changes of oxygen pressure during cooling of the samples in the closed reactor are shown in Fig. 4. It turned out that when the rate of cooling was sufficiently low the stabi-

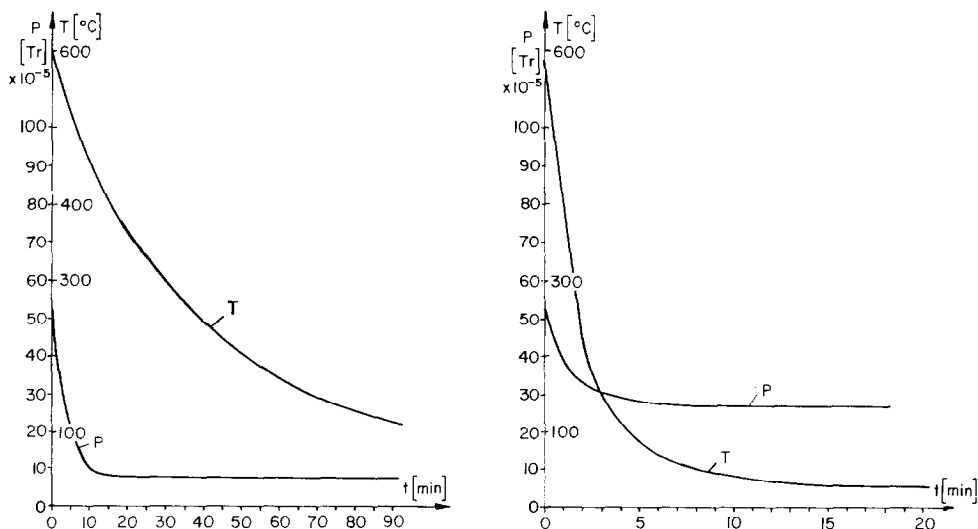
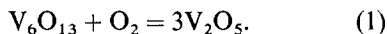


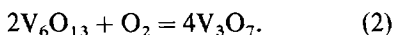
FIG. 4. The changes of oxygen pressure in the reactor in the process of cooling. (a) Standard rate of cooling, (b) fast cooling.

zation of pressure took place at about 440°C. This is the temperature at which the evolution of lattice oxygen from  $V_2O_5$  begins under vacuum (3) and, thus, the diffusion of oxygen atoms in the oxide lattice.

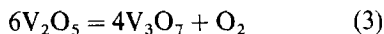
The small decrease of pressure during the cooling of the samples can be attributed only to the changes in the equilibrium at 600°C for the reaction



It cannot be assigned to the reaction

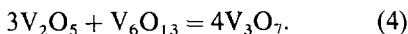


because the extent of reaction (2) calculated from the pressure change corresponds only to  $2 \times 10^{-3}$  mole % of  $V_3O_7$  in the sample, whereas the results of X-ray analysis show that the contents of the  $V_3O_7$  phase is at least 1000 times higher. The presence of  $V_3O_7$  cannot be ascribed to the reaction



either, since it requires the evolution of oxygen.

It is most likely that the formation of  $V_3O_7$  is due to the reaction



The degree of conversion of reaction (4) can be high enough to result in an amount of  $V_3O_7$  detectable by X-ray analysis. In addition, the average oxidation state of vanadium in the  $V_2O_{5-x}$  sample does not change in reaction (4). Therefore, the changes of  $x$  calculated from the amount of oxygen absorbed or released by the sample at 600°C agree with those calculated on the basis of the manganometric titration carried out on the sample cooled down to room temperature.

Our suggestions are supported by the results of the magnetochemical studies of Tridot and

Tudo (13). These authors observed that for samples obtained at 600°C three phases,  $V_2O_5$ ,  $V_6O_{13}$ , and  $V_3O_7$ , were present. But for samples obtained at 660°C the  $V_3O_7$  phase vanished and, depending on the average composition, only  $V_2O_5$  and  $V_6O_{13}$  could be detected.

## References

1. G. K. BORESKOV, V. V. POPOVSKII, AND V. A. SAZONOV, in "Proceedings of the 4th International Congress on Catalysis (Moscow, 1968)," Vol. 1, p. 439, Akad. Kiado, Budapest (1971).
2. W. SACHTLER AND Y. FARENFORT, in "Proceedings of the 4th International Congress on Catalysis (Moscow, 1968)," Vol. 1, p. 454, Akad. Kiado, Budapest (1971).
3. R. DZIEMBAJ, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.* **24**, 965 (1976).
4. G. K. BORESKOV, V. A. SAZONOV, AND V. V. POPOVSKII, *Dokl. Akad. Nauk. SSSR* **176**, 1331 (1967).
5. V. A. SAZONOV, V. V. POPOVSKII, AND G. K. BORESKOV, *Kinet. Katal.* **9**, 307, 319 (1968).
6. G. K. BORESKOV, *Kinet. Katal.* **8**, 1020 (1967).
7. YU. A. MISCHTCHENKO, N. D. GOLBSTEIN, AND A. I. GELBSTEIN, *Zh. Fiz. Khim.* **47**, 511 (1973).
8. F. FIGUERAS, M. FORISSIER, L. DE MOURGUES, M. PORTEFAIX, AND M. M. ROSSA-BRUSSIN, *Kinet. Katal.* **14**, 25 (1973).
9. J. P. JOLY, *J. Chim. Phys.* **72**, 1019 (1975).
10. A. BIELAŃSKI, K. DYREK, J. POŻNICZEK, AND E. WENDA, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.* **19**, 507 (1971).
11. A. D. WADSDLEY, *Acta Crystallogr.* **10**, 261 (1957).
12. W. PEARSON, *J. Iron Steel Inst. (Brit)* **164**, 149 (1950).
13. G. TRIDOT AND J. TUDO, *C.R. Acad. Sci. Paris, Ser. C.* **263**, 421 (1966).
14. M. TANIGUCHI AND A. MIYAZAKI, *Shokubai (Catal. Soc. Japan)* **10**, 103 (1968).
15. H. ENDO, M. WAKIHARA, AND M. TANIGUCHI, *Chem. Lett.* 905 (1974).