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Oxygen Equilibrium Pressure above V_2O_{5-x} and Thermodynamic Properties of This Oxide System

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Measurements of oxygen equilibrium pressure above the V_2O_{5-x} oxide system have been performed within the temperature range 575 to 615°C. The results have been used to determine the standard enthalpy and entropy in the reaction $V_6O_{13} + O_2 = 3\ V_2O_5$. The thermodynamic properties of the V_2O_{5-x} system (at $x < 1$) cited in the literature have been discussed for all the equilibria postulated.

Introduction

In an earlier paper (*1*) we found that in the oxide system V_2O_{5-x} at 600°C the reaction equilibrium is

$$V_6O_{13}(s) + O_2 = 3\ V_2O_5(s) \qquad (1)$$

The equilibrium oxygen pressure above the V_2O_{5-x} system is independent of the composition of the system in the range $0.02 < x < 0.43$. The introduction (or the removal) of a new portion of oxygen initially disturbs the equilibrium, but the system in which two solid oxide phases coexist soon gains it back. The system is univariant and, under isothermal conditions, zero-variant.

Such properties of the system suggest that equilibrium is established between two pure oxide phases or, as is more probable, between defected phases which do not change their degree of defecting in the course of varying the composition of the system (measured by the values of x). These variations occur as a result of changes in the contents of both phases in the system.

For $x < 0.02$ the V_6O_{13} phase vanishes, and consequently, the oxygen pressure greatly increases with the subsequent decrease of x. The observed variation in oxygen pressure is characteristic of the solid solution of oxygen vacancies in the V_2O_5 lattice. Hence, equilibrium can be obtained at an infinite number of values P for a given T.

This pressure was very often measured as the equilibrium oxygen pressure above V_2O_5 or vanadia catalysts as a measure of oxygen binding energy. This was done although the bivariant equilibrium caused instability of that parameter at constant temperature. For this reason one may observe a dependence of the measurement results in relation to the experimental conditions. This problem will be discussed in a separate paper (*2*).

This first aim of the present study is to determine the standard changes in thermodynamic functions for reaction (1) by measurements of equilibrium oxygen pressure at various temperatures. The second is to compare and discuss the data available in the literature on the thermodynamic properties of the V_2O_{5-x} oxide system.

The oxide system was obtained by thermal decomposition of NH_4VO_3 with gaseous products being continuously pumped out. The

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participation of redox reactions in the course of ammonium cation removal caused the formation of the V_2O_{5-x} oxide system—reduced in relation to V_2O_5. In this system the phase equilibrium $V_2O_5(s)$–$V_6O_{13}(s)$–$O_2(g)$ was spontaneously reached at high temperatures (*1*).

The generation of a new phase, different from the rutile V_2O_4, in the course of reduction of V_2O_5 was observed first by Hoeschek and Klemm (*3*) and next by Flood and Kleppa (*4*). Aebi (*5*) defined it as a new oxide with the formula V_6O_{13}. Brewer (*6*) and Stringer (*7*) assumed the thermodynamic functions determined by Flood and Kleppa as appropriate to the equilibrium of reaction (1), whereas Flood and Kleppa ascribed their own results to reaction (2):

$$2\,V_2O_4 + O_2 = 2\,V_2O_5, \qquad (2)$$

In addition, reaction (1) equilibrium has been the subject of two more recent studies: the EMF measurements of solid cells by Fotiev and Volkov (*8*) and the thermogravimetric study of various vanadium oxides by Endo *et al.* (*9*). Details will be given in the Discussion.

Experimental

The present paper is a continuation of a previous one (*1*). The preparation, pretreatment, measurements, and apparatus have been described there. Here only the most important points are repeated.

The oxide system V_2O_{5-x} was produced by the thermal decomposition of NH_4VO_3. Samples of V_2O_{5-x} were spread out in a layer about 0.5 mm thick. After pretreatment mass spectrometric analysis showed that only oxygen was removed from the sample.

Pressure measurements were performed with a McLeod-type manometer using a cathetometer for readings. Partial oxygen pressure was determined by mass spectrometry analysis of the gaseous phase in the reactor after the pressure reached a constant value.

Changes in x were caused by absorption of carefully measured amounts of oxygen. It was shown that partial oxygen pressure reached a constant value (for x = constant), under isothermal conditions regardless of the direction of oxygen transition. This transfer is more rapid when the value of x decreases.

Results and Discussion

The curves of oxygen equilibrium pressure above V_2O_{5-x} as a function of x under isothermal conditions are shown in Fig. 1. At 600°C two different regions on the curve may be observed. According to the aim of the present work measurements at other temperatures were carried out only in the region in which oxygen pressure does not change with the composition of the oxide system. In this range of x the univariant equilibrium was reached; the oxygen equilibrium pressure is variable with temperature only.

$$V_6O_{13} + O_2 = 3\,V_2O_5, \qquad (1)$$

$$K = (P^{\mathrm{eq}}_{O_2})^{-1} = P^{-1}.$$

Standard changes in thermodynamic functions were calculated using the measured oxygen pressure values in the well-known equations:

$$\Delta G^\circ = -RT \ln K = 4.575\,T \log P,$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ,$$

$$\log P = \frac{\Delta H^\circ}{4.575}\frac{1}{T} - \frac{\Delta S^\circ}{4.575}.$$

Within the temperature range 575 to 615°C the approximation $\Delta C_p^\circ = 0$ is satisfactorily fulfilled, and consequently, ΔH° and ΔS° are constant. The following results have been obtained in calculations by the least-squares method:

$$\Delta G^\circ\ (575^\circ\mathrm{C}) = -25.50 \pm 0.47\ \text{kcal/mole of } O_2$$

$$\Delta G^\circ\ (585^\circ\mathrm{C}) = -25.03 \pm 0.47\ \text{kcal/mole of } O_2$$

$$\Delta G^\circ\ (600^\circ\mathrm{C}) = -24.34 \pm 0.48\ \mathrm{kcal/mole\ of\ O_2}$$

$$\Delta G^\circ\ (615^\circ\mathrm{C}) = -23.68 \pm 0.49\ \mathrm{kcal/mole\ of\ O_2}$$

and then

$$\Delta H^\circ = -63.50 \pm 0.46\ \mathrm{kcal/mole\ of\ O_2}$$

$$\Delta S^\circ = -44.84 \pm 0.55\ \mathrm{cal/mole} \times \mathrm{mole\ of\ O_2}$$

The results of the present paper as well as others (*4*, *8*, *9*) on equilibrium (1) are presented together in Table I.

Flood and Kleppa (*4*) studied the reduction of V_2O_5 by SO_2 and, using data for the reaction $2\,SO_2 + O_2 = 2\,SO_3$, these authors calculated ΔH° and ΔG° for reaction (2), i.e., $2\,V_2O_4 + O_2 = 2\,V_2O_5$. However, X-ray analysis showed that the product had a structure different from that of V_2O_4. Brewer (*6*) and Stringer (*7*) then described these data for reaction (1) and calculated the enthalpy of formation V_6O_{13}. It may be added that the results of (*4*) were in indirect measurements of equilibration in contrast to those of the present work.

Fotiev and Volkov (*8*) have measured the EMF of the solid cells composed of vanadium oxides. They have given equations of the following type:

$$\log P = A/T - B \log T + C$$

for reaction (1) and reactions (3), (4) and (5). In the case of equilibrium (1), however, they gave $B = 0$.

$$6\,V_2O_4 + O_2 = 2\,V_6O_{13}, \qquad (3)$$

$$2\,V_6O_{13} + O_2 = 4\,V_3O_7, \qquad (4)$$

$$4\,V_3O_7 + O_2 = 6\,V_2O_5. \qquad (5)$$

Starting from these equations, where log P versus T, we may calculate the analytical form

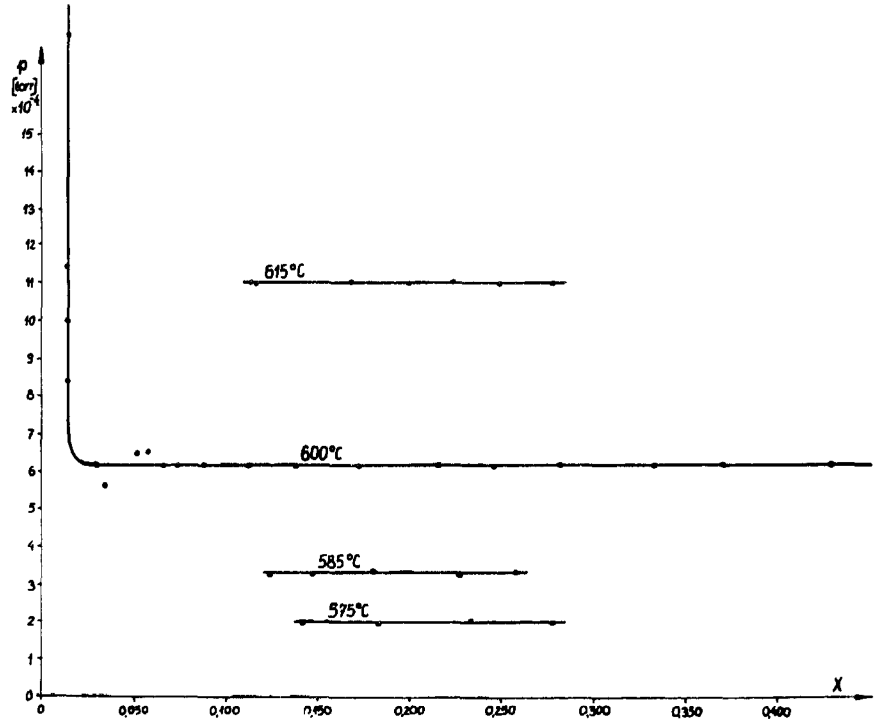

FIG. 1. Oxygen equilibrium pressure as a function of x at various temperatures.

TABLE I

THERMODYNAMIC DATA FOR EQUILIBRIA IN THE SYSTEM V_2O_{5-x} at $x < 1$

Equilibrium	References	Temperature range (°K)	$-\Delta H^\circ$ (kcal/mole of O_2)	$-\Delta S^\circ$ (cal/degree × mole of O_2)
$V_6O_{13} + O_2 = 3\,V_2O_5$, reaction (1)	Present paper	848–888	63.5	44.8
	4	838–888	58.1	41.9
	8	918–943	80.8	66.3
	"*8*"	853–918	77.0–0.0011 T	67.9–1.1 ln T
	10 (?)	573	69	—
$2\,V_2O_4 + O_2 = 2\,V_2O_5$, reaction (2)	"*8*"	873–923	84.46–0.0012 T	71.8–1.2 ln T
	11	293–943	64.48	45.6
	11	943–2073	84.3	40.3
	7, 12	298	61.2	—
	13	298	56.4	—
Calculated from the formation data	*7, 15, 16, 17*	298	58.8	38.0
	18, 19–20	298	58.0	37.6
$6\,V_2O_4 + O_2 = 2\,V_6O_{13}$, reaction (3)	*8*	873–923	87.4–0.0016 T	79.68–1.6 ln T
$2\,V_6O_{13} + O_2 = 4\,V_3O_7$, reaction (4)	*8*	873–923	99.3–0.0017 T	95.8–1.7 ln T
$4\,V_3O_7 + O_2 = 2\,V_6O_{13}$	*8*	873–923	54.77–0.00042 T	40.0–0.42 ln T
	9	853–918	54.8	40.8

of $\Delta G_f^\circ\ (T)$ for reaction (1) by using the relations

$$\Delta G^\circ(T) = -RT \ln K = RT \ln P.$$

Then, the values of ΔS°, ΔH°, and ΔC_p° may be calculated:

$$\Delta S^\circ\ (T) = -\frac{d\Delta G^\circ}{dT},$$

$$\Delta H^\circ(T) = \Delta G^\circ + T\Delta S^\circ,$$

$$\Delta C_p^\circ\ (T) = \frac{d\Delta H^\circ}{dT}.$$

The results of (*8*) may also be used to calculate the standard changes of thermodynamic functions for reactions (1) and (2) in another way, e.g.,

$$\Delta H_1^\circ = \tfrac{1}{2}(\Delta H_4^\circ + \Delta H_5^\circ),$$

$$\Delta H_2^\circ = \tfrac{1}{3}(\Delta H_3^\circ + \Delta H_4^\circ + \Delta H_5^\circ).$$

If such calculations were performed and the results were obtained from partial reactions, the references are given in Table I (and in Fig. 2) in quotation marks. The usefulness of the equations (where log P vs T) given by Fotiev and Volkov is attenuated though the results obtained through each method of calculation are different.

Endo *et al.* (*9*) have carried out thermogravimetric studies of one-phase samples of V_2O_5, V_6O_{13}, and V_3O_7 in a gaseous stream containing a very small concentration of oxygen. The equilibrium pressures for various equilibria between these phases have been approximated from the extreme values obtained for any phase. For reactions (1), (3), and (4) the measurements were carried out only at 651°C. The values of ΔH° and ΔS° were determined only for reaction (5).

It should be remembered that our samples were produced by thermal decomposition of ammonium metavanadate (*1*). During the course of decomposition redox reactions took place and the product is described by the formula V_2O_{5-x}. It is necessary to emphasize

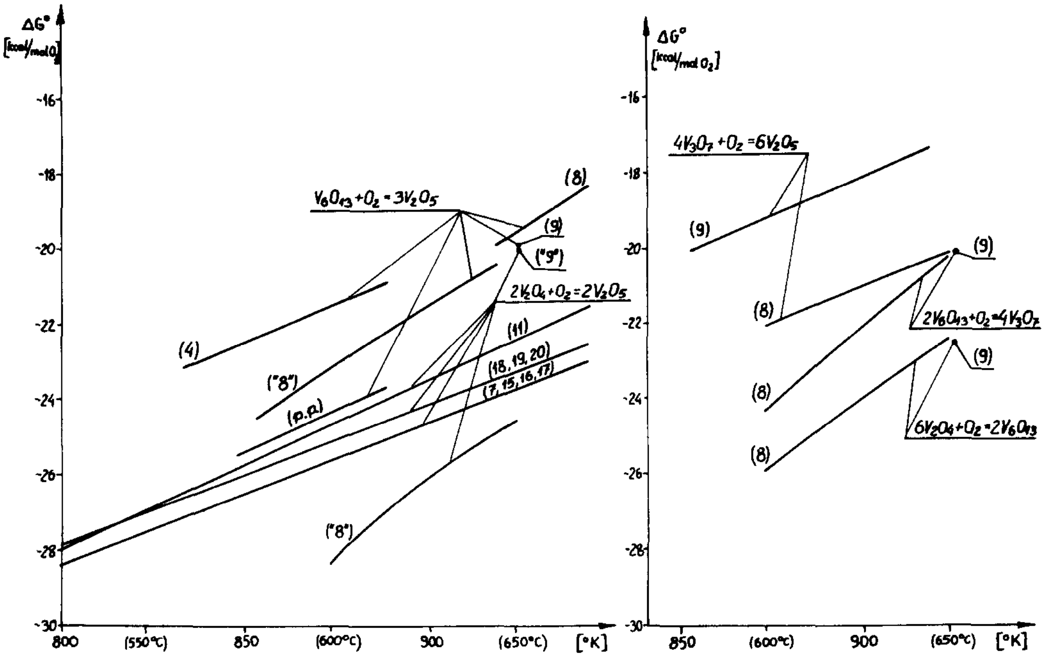

FIG. 2. ΔG° as a function of T for various equilibria obtained from the available sources. When it was taken from data on partial reactions, the reference numbers are in quotation marks. The present paper is referred to as p.p.

the spontaneous formation of the V_2O_5 and V_6O_{13} phases. At high temperatures equilibrium between them was reached.

Hence, the initial heats of reoxidation of vanadia molybdena catalysts measured calorimetrically by Pankratyev and Tichy (*10*) are included in Table I. These catalysts were produced by thermal decomposition of ammonium metavanadate and paramolybdate. On such catalysts the oxidation of acrolein was carried out to a steady state of reaction. The degree of reduction of the catalysts is comparable to the values of x in the present paper. There is some probability that the catalysts' reoxidation heats are in fact the heats of reaction (1).

Among other things the importance of vanadia catalysts and the participation of lattice oxygen in their action (*2*) spurred an interest in the thermodynamic properties of higher vanadium oxides, especially in the partial decomposition enthalpy of V_2O_5. Formerly, it had been assumed that this decomposition led to a reverse reaction (2).

The data for reaction (2) are the eldest. They were given explicitly by Rostocker in his monograph on vanadium (*11*). The calorimetric measurements of the heat of reaction (2) carried out by Siemonsen and Ulich (*12*) have been generally recognized. Similarly, the calorimetric measurements (at low temperature) of the heat capacity and entropy of V_2O_4 and V_2O_5 were done by Anderson (*14*).

Based on these data the enthalpy of formation and entropy of V_2O_5 and V_2O_4 have been calculated and are collected in the various thermodynamic tables of vanadium oxides (*15–19*):

$\Delta H^\circ_{f,\,V_2O_5} = -$ 370.6 kcal/mole (7, *15–17*)
$= -$ 372.7 kcal/mole (7, *18–20*)
$\Delta H^\circ_{f,\,V_2O_4} = -$ 341.2 kcal/mole (7, *15–17*)
$= -$ 344 (7, *18–20*)
$S^\circ_{V_2O_5} =$ 31.3 cal/degree × mole (7, *11*, *14*, *15*, *18*)
$S^\circ_{V_2O_4} =$ 24.5 cal/degree × mole (*14*, *15*)
$=$ 24.3
$S^\circ_{O_2} =$ 49.00 cal/degree × mole (*18*, *19*).

Hence, it is possible to calculate the standard changes of thermodynamic functions for reaction (2):

$$\Delta H^\circ_2 = 2\Delta H_{f,\,V_2O_5} - 2\Delta H^\circ_{f,\,V_2O_4},$$

$$\Delta S^\circ_2 = 2S^\circ_{V_2O_5} - 2S^\circ_{V_2O_4} - S^\circ_{O_2}.$$

The results referring to 25°C are presented in the table. For lack of certain data on the temperature dependence of $C_{p_{V_2O_5}}$ and $C_{p_{V_2O_4}}$ within the whole range of temperatures, calculation of ΔH° and ΔS° values for a temperature of nearly 600°C is not possible. The values of ΔH° and ΔS° resulting from the EMF measurements (*8*) depart seriously from the other data for reactions (1) and (2). But these differences compensate for each other; hence, the ΔG° (T) curves diverge less (see Fig. 2).

One's attention is immediately drawn to the similarity of the results of both reactions (1) and (2). This may be a consequence of the similar standard change in enthalpy and entropy evaluated for 1 mole of gaseous oxygen in both equilibria.

A different interpretation cannot be excluded. The experimental details given in papers on calorimetric measurements of the oxidation heat (*12*, *16–20*) show that the compositions of the samples were not V_2O_5 or V_2O_5, but intermediate V_2O_{5-x}. In determining the analysis the extent of oxidation of the V_6O_{13} oxide phase was not taken into account. Reaction (1) might then have occurred and would have influenced the calorimetric results.

The thermodynamic properties of the V_2O_{5-x} system are rather complicated. Within the range $(0 < x < 1)$ five phases are observed: V_2O_5, V_3O_7, V_4O_9, V_6O_{13}, and V_2O_4. In relation to temperature, oxygen pressure, and composition of the system the various oxide phases may coexist. At $x < 0.43$ and in the vicinity of 600°C they are V_2O_5 and V_6O_{13}, and cooling the system results in the formation of V_3O_7 (*1*). The phase diagrams of the V–O system which have been published up to now show too little or nothing at all about the range of composition discussed (*7*, *11*, *21*).

In further studies direct measurements of equilibria should be carried out to a greater extent, in spite of the troublesome and time-consuming nature of such measurements. X-ray studies give no information as to whether equilibrium is reached. Callorimetric measurements in a case as complicated as the V_2O_{5-x} system leave in question the participation of an individual reaction in the total heat.

It might be of use to add something about the equilibria which are reached above the melting point of the V_2O_{5-x} system. This may be described by the reaction:

$$\frac{2}{x_1 - x_2} V_2O_{5-x_1}\,(l) + O_2\,(g) = \frac{2}{x_1 - x_2} V_2O_{5-x_2}\,(l) \qquad (6)$$

The classical study by Milan (*22*) is frequently cited as an example where equilibrium oxygen pressure above V_2O_{5-x} changes with x.

Milan's results do not, however, contradict those of the present work. In the molten oxide system the formation of a solution of anionic vacancies in the broad range of x may be expected. Then the system consists of two phases: the liquid and the gaseous. On the basis of Gibbs' rule equilibrium (*6*) would be bivariant, as was observed.

Recently, Desagher *et al.* (*23*) studied the departure from stoichiometry of V_2O_5 above the melting point (700–900°C). The authors assumed that there is an ideal solution of anion vacancies and electron defects in molten V_2O_5. They determined the mutual dependence among composition, oxygen pressure, and temperature. Next, they calculated the enthalpy of reaction (6) as −43 kcal/mole of O_2.

Below the melting point the bivariant equilibrium is reached at small values of x, less than 0.02. The discussion of both equilibria (univariant and bivariant) in the system V_2O_{5-x}(s)–O_2 in relation to the concept of oxygen binding energy used in heterogeneous catalysis is the subject of another paper (*2*).

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