

High Temperature Thermodynamics of the Vanadium-Oxygen System for $0 \leq O/V \leq 1.5$

I. Determination of $\Delta G(O_2)(O/V)$ by Electromotive Force Measurements

R. TETOT AND C. PICARD

Laboratoire des Composés non stoechiométriques, Bâtiment 415, Université de Paris-Sud, 91405 Orsay Cédex, France

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An electromotive force method has been applied in order to determine $\Delta G(O_2)$, the partial molar Gibbs free energy of mixing of oxygen in the oxides VO_x ($x = 0.2, 0.3, 0.35, 0.6, 0.8, 1.0, 1.2, 1.3$) between 1223 and 1373 K. The results of this study differ greatly from the published data which are discussed. © 1987 Academic Press, Inc.

I. Introduction

The equilibrium oxygen partial pressures, P_{O_2} , have been measured between 1223 and 1373 K for eight VO_x samples with $x = 0.2, 0.3, 0.35, 0.6, 0.8, 1.0, 1.2,$ and 1.3 by an electromotive force (emf) method involving the yttria-doped thoria (YDT) solid electrolyte and the two-phase mixture $Ta-Ta_2O_5$ as the reference electrode.

The phase diagram (1-2) concerning the investigated composition range is represented in Fig. 1. For increase x , we have, first, two solid solutions (α and β) of oxygen in vanadium (only the second one has been studied), an ordered γ phase, and a large monoxide phase δ which extends up to $x \approx 1.30$. Let it be noted that the lower phase boundary of the δ phase differs greatly from one study to another (between 0.6 to 0.8 at 1323 K).

Two of these phases are of particular interest.

(i) The solid solution β : This is the only

case among the IVA and VA transition metal-oxygen systems for which it is possible to measure $\Delta G(O_2) = RT \ln P_{O_2}$, the partial molar Gibbs free energy of mixing of oxygen. In a next paper, we will present the direct measurements of $\Delta H(O_2)$, the partial molar enthalpy of mixing of oxygen. Knowledge of these two thermodynamic quantities makes this phase a suitable system for future theoretical studies of concentrated solutions of oxygen in metals.

(ii) The monoxide VO (δ phase): This case is representative of a particular family of nonstoichiometric phases with a very large homogeneity range involving very high concentrations of vacancies on metal and nonmetal sublattices.

Many emf studies have already been performed on the V-O system (e.g., Steckel and Altstetter (3) on α and $\alpha + \beta$ fields; Fromm and Kirchheim (4) on $\alpha, \alpha + \beta,$ and β fields; Večer and Savitskii (5) on $\alpha + \beta$ two-phase region only; and Vasil'eva *et al.* (6-10) on α to δ fields).

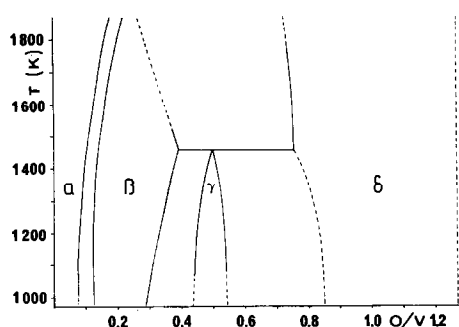
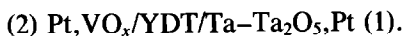


FIG. 1. Phase diagram of the V-O system after Alexander and Carlson (1) and Yakovkva and Krasilavo (2).

II. Experimental

II.1. General Features

We have measured the emf on the following cells:



The emf is given by the Wagner relationship (11):

$$E_{(v)} = \frac{RT}{4F} \int_{P_{O_2}^I}^{P_{O_2}^{II}} t_{\text{ion}} d \ln P_{O_2}$$

where $P_{O_2}^I$ and $P_{O_2}^{II}$ are, respectively, the oxygen partial pressure of the reference electrode and of the VO_x electrode; R , F , and T are, respectively, the ideal gas constant, the Faraday constant, and the absolute temperature; and t_{ion} is the ionic transference number of the electrolyte, which generally depends on T and P_{O_2} .

The apparatus and the experimental procedure have been largely detailed in a previous paper (12), where the measurements of very low P_{O_2} , in equilibrium with the monoxide TiO ($10^{-35} < P_{O_2} < 10^{-25}$ atm at 1323 K), have been described. P_{O_2} values in the V-O system are somewhat higher ($P_{O_2} > 10^{-26.5}$ atm) at the same temperature but nevertheless their measurement requires great experimental care. The principal feature of these preceding measurements was a great stability of the emf, essentially due to the good quality of our solid electrolyte

samples (SE) supplied by the CEN of Grenoble (France). In the same study, the P_{O_2} variations of the ionic transference number of these electrolytes have been determined down to 10^{-35} atm by using a U- UO_2 reference electrode, which had shown that $t_{\text{ion}} > 0.99$ for $P_{O_2} > 10^{-27}$ atm at 1323 K.

For this present study, the reference electrode was the two-phase system Ta- Ta_2O_5 owing to its low P_{O_2} and its good reversibility. Details on the preparation and the determination of $\Delta G(\text{O}_2)(T)$ of this electrode may be found elsewhere, and particular conditions of its use have already been discussed (12). In this study we have used the relation $\Delta G(\text{O}_2)(\text{Ta-Ta}_2\text{O}_5) = -192,400 + 39.4T$ cal mole $^{-1}$ in the whole temperature range.

The SE that we have used are 10 mm thick in order to eliminate an electronic conduction contribution caused by the pollution of the electrolyte by tantalum ions which occurs in long-lasting experiments (12).

For each experiment the reversibility of the cell has been checked by passing a small current through the cell in either direction and noting that the voltage returned to its original value after shutting off the current. This test verifies that the VO_x electrodes are homogeneous, therefore, that the samples do not present any overoxidized surface layers. Moreover, X-ray diffraction analysis of the surface has been carried out for $\text{VO}_{0.2}$ and $\text{VO}_{1.2}$ samples (see Section II.2).

II.2. VO_x Electrode Preparation

VO_x electrodes have been prepared from a mechanical mixture of V powder from Ventron (99.7% purity: C < 0.015, Fe < 0.05, Si < 0.015%) and V_2O_3 powder obtained by reduction of V_2O_5 from Johnson Matthey in dry hydrogen at 900 K for 5 hr and then at 1300 K for a day. Cold pressed specimens 8 mm in diameter and about 400 mg in weight were sintered, first up to 1400

K under vacuum and then at 1800 K under 200 Torr of argon for 2 days. The obtained samples were pounded, pressed, and sintered again in the same conditions.

All the sample surfaces, including the electrolytes, were mechanically polished in order to ensure intimate interfacial contacts. Before an experiment, the samples were annealed at 1400 K under vacuum for 2 days, protected from oxidation by zirconium getters. Such a procedure is necessary in order to avoid the erroneous emf created by nonhomogeneous electrodes (12).

The composition of the VO_x electrodes has been controlled by oxidizing in a CO-CO_2 gas mixture with 10% CO at 1300 K, corresponding to the composition $\text{O/V} = 1.5000 \pm 5 \cdot 10^{-4}$ (13), in an Ugine-Eyraud B 60 thermobalance with a useful sensitivity of 0.015 mg which corresponds to $\delta x \approx 0.001$ for our samples. The composition was found to be higher by about 0.02 than the desired composition of the initial mixture, which must be due to the residual oxygen present in the vanadium powder and to minor oxidation occurring during the various annealings.

Phase analysis of the surface of two samples at the boundaries of our investigated composition range, $\text{VO}_{0.2}$ and $\text{VO}_{1.2}$, has been carried out by X-ray diffraction in a CGR diffractometer. Monochromatized $\text{CuK}\alpha_1$ radiation has been used. $\text{Sin}^2\theta$ val-

TABLE IB
VALUES OF $\text{Sin}^2\theta$ AND I/I_0 FOR VO_x SAMPLES IN THE δ FIELD

<i>h k l</i>	Klemm and Grimm (14): $\text{VO}_{0.9}$		Present results: $\text{VO}_{1.20}$	
	I/I_0	$\text{Sin}^2\theta$	I/I_0	$\text{Sin}^2\theta$
1 1 1	30	0.10474	43	0.1049
2 0 0	80	0.1398	65	0.1393
2 2 0	100	0.2822	100	0.2792
3 1 1	60	0.3858	10	0.3841
2 2 2	60	0.41895	30	0.4200

ues are listed and compared with published data in Tables IA and IB. Only one phase has been detected in the two cases. For $\text{VO}_{1.2}$, the calculated lattice parameter, $a = 4.120 \pm 0.005 \text{ \AA}$, is in very good agreement with the values reported in the review on the V-O system by Stringer (16).

II.3. Results and Discussion

The complete results obtained with eight VO_x samples ($x = 0.2, 0.3, 0.35, 0.6, 0.8, 1.0, 1.2$),

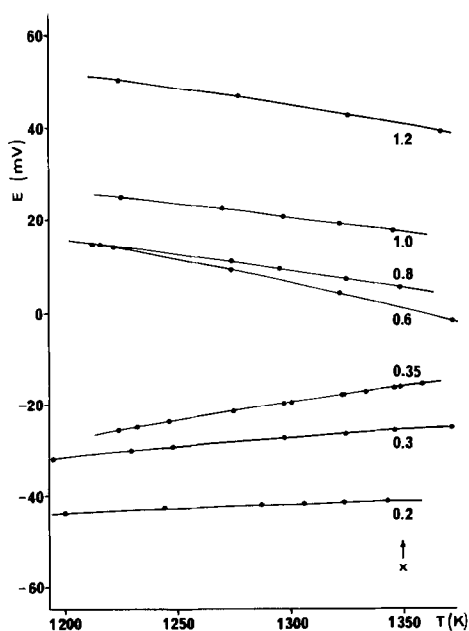


FIG. 2. Electromotive force versus T for the cells (2) Pt, $\text{VO}_x/\text{YDT}/\text{Ta-Ta}_2\text{O}_5$, Pt (1).

TABLE IA
VALUES OF $\text{Sin}^2\theta$ AND I/I_0 FOR VO_x SAMPLES IN THE β FIELD

<i>h k l</i>	Klemm and Grimm (14): $\text{VO}_{0.2}$		Henry <i>et al.</i> (15): $\text{VO}_{0.119}$		Present results: $\text{VO}_{0.2}$	
	I/I_0	$\text{Sin}^2\theta$	I/I_0	$\text{Sin}^2\theta$	I/I_0	$\text{Sin}^2\theta$
0 1 1	100	0.1170	100	0.1226	100	0.1284
1 1 0	80	0.1367	84	0.1320	76	0.1373
0 2 0	50	0.2707	27	0.2640	12	0.2691
1 1 2	60	0.3257				0.3057
1 2 1	100	0.3858	27	0.3864	28	0.3790

TABLE II
RESULTS OF emf MEASUREMENTS

x	$T(K)$	$E(mV)$	$\log P_{O_2}$	$\Delta H(O_2)$ (kcal mole ⁻¹)
0.2	1223	-43.2	-26.48	
	1273	-42.3	-25.09	
	1323	-41.6	-23.80	-197.6
	1373	-41.3	-22.62	
0.3	1223	-30.2	-26.27	
	1273	-28.0	-24.86	
	1323	-26.4	-23.57	-198.1
	1373	-25.2	-22.38	
0.35	1223	-25.7	-26.19	
	1273	-21.6	-24.76	
	1323	-17.9	-23.44	-203.3
	1373	-14.5	-22.22	
0.6	1223	14	-25.54	
	1273	9.7	-24.27	
	1323	4.2	-23.11	-177.8
	1373	-2.0	-22.04	
0.8	1223	14.5	-25.53	
	1273	11.3	-24.24	
	1323	7.6	-23.05	-182.3
	1373	3.2	-21.96	
1.0	1223	25.45	-25.35	
	1273	22.6	-24.06	
	1323	19.3	-22.88	-182.8
	1373	15.9	-21.78	
1.2	1223	50.6	-24.94	
	1273	47.3	-23.67	
	1323	43.2	-22.51	-177.8
	1373	38.7	-21.44	
1.3	1323	73	-22.06	

1.0, 1.2, and 1.3) between 1223 and 1373 K are reported in Table II and in Figs. 2 and 3, where the phase boundaries of Alexander and Carlson (1) have been used.

In Fig. 4, our results are compared with all available published data at 1273 K.

In the composition range $0.3 \leq O/V \leq 0.8$, corresponding to $\beta + \gamma$, and $\gamma + \delta$, all results are comparable. The results of Fromm and Kirchheim (4) are all shifted by one unit of $\log P_{O_2}$ with regard to ours. This may be explained by the fact that these authors have carried out their measurements

with the two-phase reference electrode, $\alpha + \beta$, for which the P_{O_2} has been determined with the single-phase reference electrode $TaO_{0.002}$. It is obvious that, under these conditions, their results largely depend on the accuracy of the composition of this last electrode, which can be modified by oxidation caused by, e.g., degassing of refractory tubes and a short-circuit in the cell due to the constant small electronic conduction in the SE. Thus, a small correction of the P_{O_2} of the $\alpha + \beta$ electrode would lead to a satisfactory agreement between our results and those of Fromm and Kirchheim.

The same arguments may be advanced concerning the results of Steckel and Altstetter (3) in the $\alpha + \beta$ field, obtained with the single-phase electrode $NbO_{0.0045}$.

In contrast, the results of Vecher and Savitskii (5) in the $\alpha + \beta$ field, obtained with the reversible two-phase electrode Nb-NbO, fall on an extrapolation of our results into the β field.

The results of Fromm and Kirchheim (4) and Steckel and Altstetter (3) have been criticized by Vasil'eva and Seregin (9, 10), whose results are in contradiction with all the others, including ours. The values proposed by these last authors for the β field, $0.244 < O/V < 0.299$ (9), have been obtained in a classical way with the two-phase $\beta + \gamma$ reference electrode and a 0.99 ThO_2 , 0.01 CaO SE. A thorough discussion of

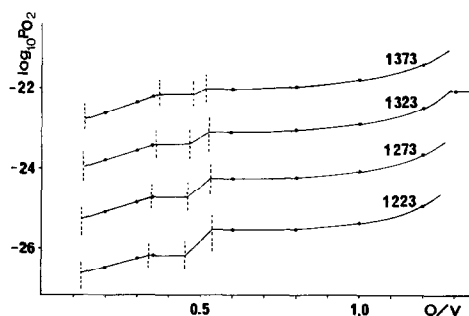


FIG. 3. $\log P_{O_2}(O/V)$ at 1223, 1273, 1323, and 1373 K. The phase boundaries are from Alexander and Carlson (1) and Yakovkva and Krasilavo (2).

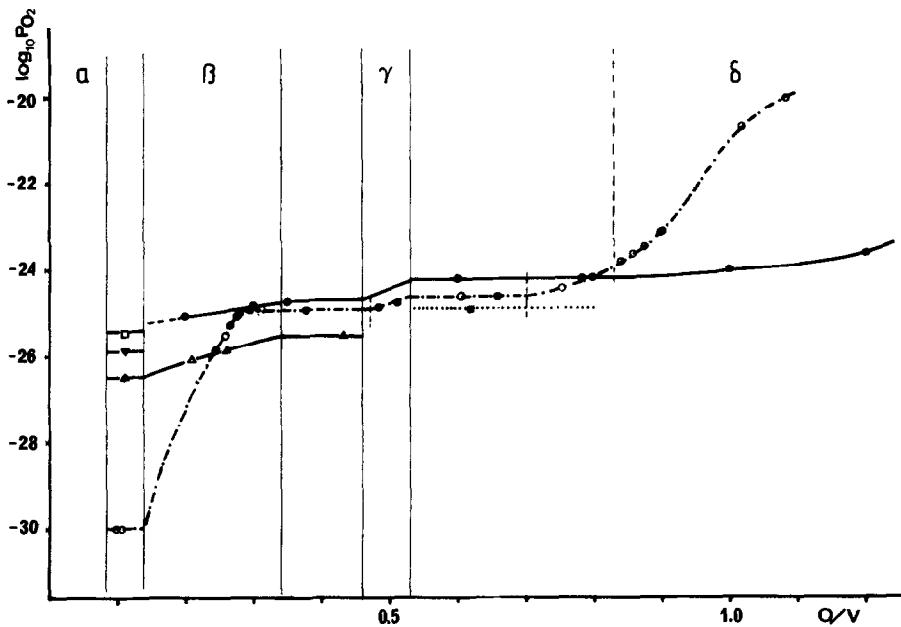


FIG. 4. $\log P_{O_2}(O/V)$ at 1273 K. (—●—) present study, (—▼—) (3), (—△—) (4), (—□—) (5), (⊕ · ⊕ · ⊕ · —) (6-10), (· · ■ · ·) Alcock from (4). The phase boundaries are from Alexander and Carlson (1) and Yakovkva and Krasilavo (2).

these results cannot be made because of the lack of experimental details given in the paper, concerning, for example, the heat treatment of the samples, the magnitude of the emf drifts, or the time necessary to obtain a stable emf. However, let us insist on the importance of the annealing of every sample (ES and electrodes) that we have made just before experiments in order to eliminate an overoxidized layer arising from polishing or even from the oxidation at the air contact. It is obvious that this annealing is all the more necessary since the diffusion kinetics in the sample are slow, which is the case for the V-O system. This is the reason why we have always used the Ta-Ta₂O₅ reference electrode, which is well known for its reversible behavior, while it is not certain that the system β + γ used by Vasil'eva *et al.* is a good reversible reference electrode. Any overoxidized layer on this electrode can be responsible for the low values that they have obtained in the β

field. An extrapolation drawn from these points leads to the results that they have obtained in the α + β field (10). These last results have been obtained by the so-called nonstationary emf measurements described by Barby (17-19). This method involves passing different currents (100-800 μA) through the cell during various times (20-90 min) in order to reduce the surface of the α + β electrode at the interface α + β/SE. After cutting the current, a plot of emf versus time allowed to measure the homogenization of the electrode. After about 20 min, Vasil'eva *et al.* observed a constant emf which they think is characteristic of the α + β field. However, the emf is stable only during about 40 min and then falls by about 100 mV/hr. Such a drift cannot be due only to the short circuit in the cell and must, rather, correspond to ongoing electrode homogenization.

Therefore, we suppose that this constant value must be attributed to a transitional

metastable state of the cell and that the real emf equilibrium value, which must be stable over a longer time, should be observed later. Moreover, this argument is in agreement with our own observations. As a matter of fact, all our results correspond to a true equilibrium state; no emf drift was observed during several days and the reversibility of the cell for each experiment was checked in the way described above. However, though the sample is as homogeneous as it can possibly be (annealing just before the experiment), this equilibrium state requires a long time to be reached in the case of the V-O system, the necessary time extending, at 1323 K, from a few hours for $O/V < 0.35$ to several days for $x > 0.6$ (see Fig. 5). This means that the kinetic homogenization is slow, which is not favorable when using of the nonstationary emf method.

In the composition range $0.8 < O/V < 1.083$, the only available data are those of Vasil'eva and Granovskaya (6), obtained with a Fe-FeO reference electrode. These results, $10^{-19} \text{ atm} < P_{O_2} < 10^{-24} \text{ atm}$, are in disagreement with ours and, in another connection, in contradiction with the experimental evidence that no oxide in the monoxide phase VO_x can be obtained by

reduction in nearly pure hydrogen for which $P_{O_2} \approx 10^{-24} \text{ atm}$ at 1273 K. We think that these discrepancies are probably due to the difficulty, already raised, of obtaining the real equilibrium emf which requires long-lasting experiments.

Several experiments, completed by oxygen analysis by thermogravimetry, surface analysis before and after experiments by X-ray diffraction, and reversibility tests (Fig. 5), have been performed in β and δ fields where deep discrepancies exist and have given reproducible results.

II.4. Accuracy of Our Results

(i) Our measurements have been made with a Schlumberger millivoltmeter with an input impedance of $10^{14} \Omega$. The uncertainty, δE , in the emf is 0.1 mV when $x < 0.6$ and 0.2 mV when $x > 0.6$, which represents the maximum emf fluctuations for 1 day. A slight drift for $VO_{1.30}$ increases δE up to 1 mV.

(ii) The temperature of each electrode is known within $\pm 2 \text{ K}$, producing $\delta P_{O_2}(VO_x)$ of less than 3.0×10^{-3} . The temperature gradient within the cell involves an uncertainty of 1.2 mV.

(iii) In a previous study (12), it has been shown that for our SE,

$$t_{\text{ion}} = \left[1 + \left(\frac{P_{O_2}}{P_{O_2}^{\ominus}} \right)^{-1/4} \right]^{-1}$$

with $P_{O_2}^{\ominus} = 6.10 \cdot 10^{-35} \text{ atm}$ at 1323 K.

Then, for the lowest measured P_{O_2} , 10^{-24} atm , $t_{\text{ion}} = 0.9972$ which involves $\delta E = 0.12 \text{ mV}$. This uncertainty tends to zero when P_{O_2} increases and is negligible when $P_{O_2} > 10^{-23} \text{ atm}$.

Then the uncertainties on $\log P_{O_2}$ vary from 9×10^{-2} to 10^{-1} when x varies from 0.2 to 1.3.

II.5. Derived $\Delta H(O_2)$

From our emf measurements, we have derived at 1323 K

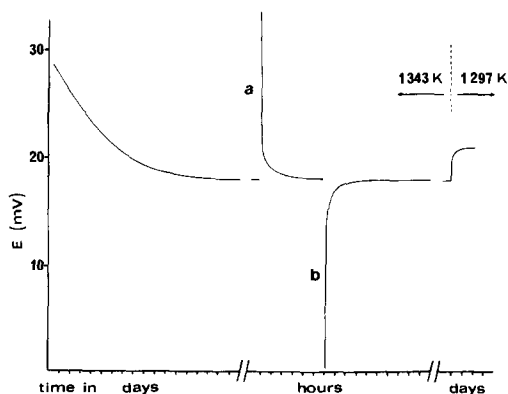


FIG. 5. Electromotive force values vs time of the cell $VO_{1.0}/YDT/Ta-Ta_2O_5$; (a, b) relaxation of the emf after a $100\text{-}\mu\text{A}$ electrical current flow.

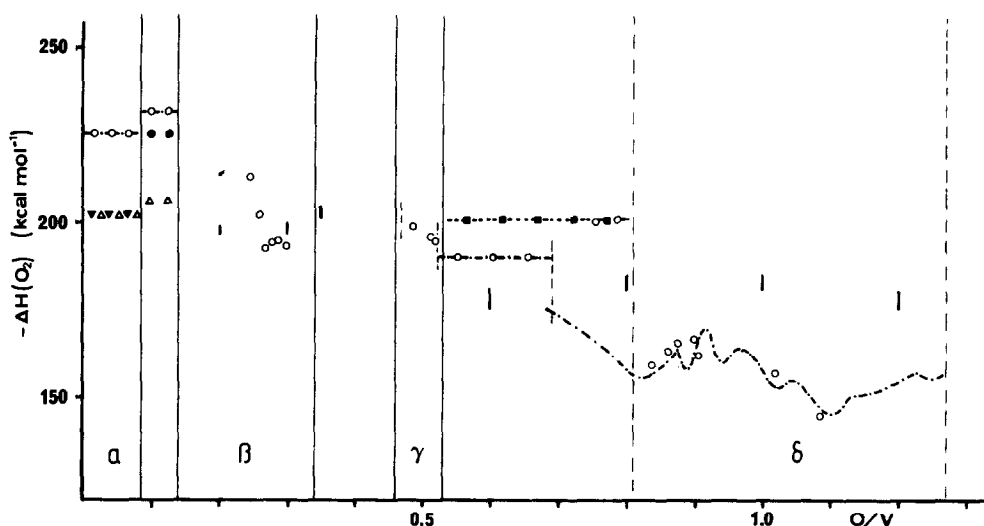


FIG. 6. $\Delta H(\text{O}_2)(\text{O}/\text{V})$ at 1323 K derived from emf measurements. (○) present study, (—▼—) (3), (—△—) (4), (—●—) (5), (---) and (○) (6-10), (---■---) Alcock from (4). The phase boundaries are from Alexander and Carlson (1) and Yakovkva and Krasilavo (2).

$$\Delta H(\text{O}_2) = \left[\partial \frac{\Delta G(\text{O}_2)}{T} / \partial \frac{1}{T} \right]_x.$$

For these calculations, we have used, at 1323 K, $\Delta H(\text{O}_2)(\text{Ta}-\text{Ta}_2\text{O}_5) = -192.6 \pm 0.5 \text{ kcal mole}^{-1}$ (20).

The results are reported in Table II and plotted in Fig. 6 and compared with earlier studies, all obtained in the same way. It can be observed that, in spite of the large discrepancies observed between the emf results, the various derived values of $\Delta H(\text{O}_2)$ are not very different. It is particularly striking in view of the results of Fromm and Kirchheim (4) and Steckel and Altstetter (3) in the α phase. This is due to the fact that only the temperature variations of emf are needed to obtain $\Delta H(\text{O}_2)$.

In a future paper, we will publish $\Delta H(\text{O}_2)$ values obtained by direct measurements performed with a high-temperature microcalorimeter. This technique has always given the most reliable results when it is applied.

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