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Thermodynamic Study of Nonstoichiometric Tungsten trioxide WO_{3-x} by EMF Measurements at High Temperature.

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The values of $\Delta G(O_2)$, $\Delta H(O_2)$, and $\Delta S(O_2)$ have been determined from electrochemical cell measurements, within the whole homogeneity range of WO_{3-x}, between 700 and 900°C. The samples have been previously prepared by equilibration of WO_3 pellets with CO–CO_2 mixtures and their composition has been determined by thermogravimetry. A single phase has been found between WO_3 and $WO_{2.9760}$. The results may be understood by considering a structure involving point defects, singly ionized oxygen vacancies $V_O^{\cdot}$ between WO_3 and $WO_{2.9880}$. For larger departure from stoichiometry, the variations of $\Delta H(O_2)$ and $\Delta S(O_2)$ suggest the formation of more complex defects. The enthalpy of formation of $V_O^{\cdot}$ has been calculated: 78 kcal · mole^{-1}.

Introduction

In spite of the large number of studies concerning higher oxides of tungsten, which have followed the pioneer work of Hagg and Magneli (*1*), there are still gaps in the knowledge of the thermodynamics of these oxides. For instance, there are no data available for partial molar entropies and enthalpies. Even the problem of the homogeneity range of the oxide WO_{3-x} is not yet solved. Several mechanisms of formation of crystallographic shear planes, the existence of which has been shown by electron microscopy studies (*2–9*), have been proposed (*10*), and their energy of formation has been the object of many calculations by Iguchi and Tilley (*11–15*). But none of these studies has been concerned with a thermodynamic approach, and it is not clear whether these oxides are biphasic or monophasic systems.

On the other hand, except for small departure from stoichiometry, the transport properties of these oxides have not been heavily studied. Sienko and Berak (*16, 17*), investigating the electrical properties of WO_3, studied their samples by X-ray diffraction and proposed a single phase between WO_3 and $WO_{2.9873}$. Ackermann and Rauh (*18*), then Gebert and Ackermann (*19*), by the same method of analysis, found a homogeneity range from WO_3 to $WO_{2.980}$. Recently, Bonnet *et al.* (*20*) carried out electrical resistivity measurements at 750°C and suggested the possibility of several phases in the same range of composition.

On the other hand, Choain-Maurin and Marion (*21*) measured the electrical conductivity σ in terms of partial oxygen pressure p_{O_2} and found $\sigma \propto p_{O_2}^{-1/6}$, that may be interpreted by the presence of doubly ionized oxygen vacancies $V_O^{\cdot\cdot}$. Sienko and Berak also assumed oxygen vacancies, but

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concluded that the segregation of defects occurs even for $x < 0.0001$ at room temperature. They believed that the basic defect unit was the Anderson–Hyde disk of shear. More recently, Berglund and Sahle (*22*) pointed out the presence of $\{102\}$ *CS* in reduced tungsten trioxide between WO_3 and $WO_{2.977}$. For the composition $WO_{2.963}$ and more reduced oxides, they found the simultaneous presence of $\{102\}$ and $\{103\}$ *CS*. All their samples have been prepared by means of controlled atmospheres and studied by high-resolution transmission electron microscopy.

Finally, WO_3 has been also studied by spectroscopic methods. De Angelis *et al.* (*23, 24*), by XPS, pointed out the presence of tungsten with oxidation states lower than six; $WO_{2.96}$ contains about 10% of tungsten as W^{5+}. Using ESR, Alquié *et al.* (*25*) suggest a catalytic activity caused by oxygen vacancies between WO_3 and $WO_{2.9940}$.

The results that we summarized are incomplete; particularly, no measurements of $\Delta G(O_2)$ have been carried out. That has moved us to study the thermodynamic properties of WO_{3-x} by the method of equilibration between oxides and buffer gaseous mixtures, and by the method of solid-state electrochemical cells.

A. Experimental

(a) Preparation of WO_{3-x} Samples

(1) A preliminary study was carried out at 750°C by the method of equilibration between WO_{3-x} and CO–CO_2 mixtures. The experimental device used has been previously described (*25*). It consisted of:

—A Ugine Eyraud B 60 thermobalance which had a useful sensitivity of 0.015 mg corresponding to $\delta x = 10^{-4}$ for a sample weighing 2 g.

—A Chevenard furnace

—Wösthoff pumps which proportioned and moved the gas mixture. The gases are purified as was mentioned before (*27*). The oxide used was Merck WO_3. The impurities were Pb (0.001%), Fe (0.001%), and Ca (0.005%).

Procedure. Two grams of WO_3 powder was heated at 750°C in a dry air flow in the thermobalance. We ascertained that the weight corresponding to WO_3 remained constant during 24 hr. The air was replaced by a CO–CO_2 mixture with a constant and known composition, and the oxide slowly reached equlibrium with the gaseous mixture.

We recorded the weight variations in the solid phase, and we assumed that the equilibrium was reached when the weight remained constant to 0.015 mg during 24 hr. During each experiment, we verified the constancy of the indication corresponding to WO_3 by periodical oxidations of the sample in dry air. In these conditions, we noticed that this indication became reproducible only after two or three oxidation–reduction cycles. At this temperature no vaporization was detected. The composition of an oxide was calculated by the difference of weight with WO_3 in air, corresponding to the composition $WO_{2.9999}$ according to Sienko and Berak (*16*).

The oxygen partial pressure p_{O_2} was calculated from the data of Elliott and Gleiser (*28*). We obtained:

$$\log_{10} p_{O_2} = -19.738 + 2 \log_{10} \frac{p_{CO_2}}{p_{CO}}.$$

We started with reduction. More and more reducing gaseous mixtures were blown on the oxide. For each value of p_{O_2}, we noticed a decrease of weight ending after 15 hr of reaction. With $p_{O_2} = 10^{-17.138}$ we observed a continuous decrease of weight pointing out the reduction of WO_3 into $WO_{2.90}$. The homogeneity range boundary corresponding to the lower value of p_{O_2} was $WO_{2.9760}$.

(2) For cell experiments, WO_3 powder was sintered in air at 1000°C in the shape of

pellets. The pellets were reduced at 750°C with $CO-CO_2$ mixtures. After equilibration, we substituted the buffer mixture with argon, and the sample was quenched. Then the sample was placed in the cell. The argon used was carefully purified by passing on TiZr at 800°C to avoid oxidation of the samples.

(*b*) *Measurement of Electromotive Force*

The solid cell employed was of the type:

$$Fe,\ Fe_{0.95}O/\text{Solid electrolyte}/WO_{3-x},$$

where the solid electrolyte was a solid solution of 0.91 ZrO_2 and 0.09 Y_2O_3. The Fe–FeO electrode was employed as the reference electrode. An assessment of available calorimetric and high-temperature equilibria data (*29*) produced the following free-energy equation for the reaction

$$1.9\ Fe + O_2 \rightarrow 2\ Fe_{0.95}O;$$

$$\Delta G(O_2) \quad (\text{calories mole}^{-1}) = RT \ln p_{O_2} = -126470 + 31.26\ T.$$

The three pellets of (Fe, FeO), solid electrolyte and WO_{3-x} were pressed between two Pt disks which were welded to Pt wires for electrical contacts.

After the pellets were placed in position, the system was evacuated to 10^{-5} Torr for 1 hr; purified argon was introduced at room temperature and the temperature increased to 750°C. The emf measurements were carried out with a flow rate of 10 l/hr. We noticed an emf constant value after 3 days. The observed values at 750°C were in good agreement with the calculated value from the $CO-CO_2$ mixtures, within 10 mV. The measurements were carried out which a Schlumberger high-impedance ($>10^{-10}$ohm) microvoltmeter.

Results and Discussion

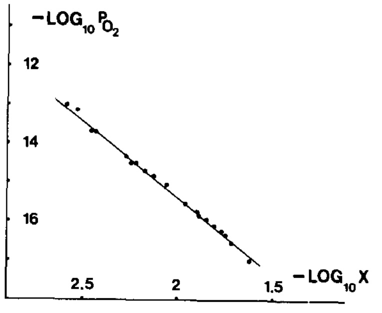


FIG. 1. $\log_{10} p_{O_2}$ vs $-\log x$

The isotherm curve $-\log x$ vs $-\log_{10} p_{O_2}$ at 750°C corresponding to the preliminary study is plotted in Fig. 1. It is a straight line, the slope of which is $-1/n$ with $n = 3.9$. This value is close to $n = 4$, which would correspond to a defect structure involving either singly ionized oxygen vacancies $V_O^{\cdot}$ or tungsten interstitials $W_i^{5\cdot}$. Applying Kröger's notation (*30*), the following defect reactions may be written:

$$O_O^x \rightleftarrows V_O^{\cdot} + e' + \tfrac{1}{2}O_2\ (\text{gas}) \qquad (1)$$

or

$$W_W^x + 3O_O^x \rightleftharpoons W_i^{5\cdot} + 5e' + \tfrac{3}{2}O_2\ (\text{gas}). \qquad (2)$$

Each term has the usual significance. Applying the law of mass action, we obtain:

$$K_{V_O^{\cdot}} = [V_O^{\cdot}][e']\,p_{O_2}^{-1/2}$$

$$\text{and} \qquad K_{W_i^{5\cdot}} = [W_i^{5\cdot}][e']^5 p_{O_2}^{-3/2}.$$

In both cases, we have $x \propto p_{O_2} - \frac{1}{4}$.

The results are in disagreement with the electrical conductivity σ measurements carried out by Choain-Maurin and Marion who found $\sigma \propto p_{O_2} - \frac{1}{6}$, but these authors have not considered the strong composition dependence of the mobility of the charge carriers indicated by Berak and Sienko (*16*).

The isocomposition curves E vs $1/T$ are plotted in Fig. 2. These curves are parallel straight lines when $x < 0.012$ (domain I). If $x > 0.012$ (domain II), the slope decreases when x increases. The results of Rizzo *et al.* (*31*) for the two-phase $WO_3-WO_{2.90}$ system are plotted also. It is seen from the figure that no hysteresis loops are observed in cooling and heating processes.

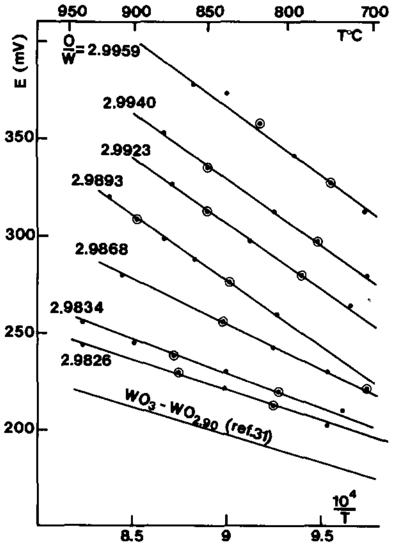


FIG. 2. EMF (E) vs ($1/T$) for different compositions. The two phases values correspond to the measurements of Rizzo *et al.* (*31*). ●, heating; ◉, cooling.

Thermodynamic Values

The relative partial molal quantities of oxygen may be calculated from the emf measurements. They can be defined as the changes in the thermodynamic quantities accompanying the reaction:

$$1 \text{ mole } O_2 \text{ (perfect gas, 1 atm)} + \infty\, WO_{3-x} \rightarrow \infty\, WO_{3-x}.$$

The relative partial molal free energy of oxygen $\Delta G(O_2)$ for the sample is calculated by the relation

$$\Delta G(O_2)\,(WO_{3-x}) = 4EF + \Delta G(O_2)\,(\text{Fe/FeO}),$$

where E is the emf and F is the Faraday constant. $\Delta G(O_2)$ is related to the relative partial molal enthalpy $\Delta H(O_2)$ and entropy $\Delta S(O_2)$ by the well-known relation

$$\Delta G(O_2) = \Delta H(O_2) - T\Delta S(O_2).$$

The $\Delta H(O_2)$ values can be calculated by the relation

$$\Delta H(O_2) = \left[\frac{\partial[\Delta G(O_2)/T]}{\partial(1/T)}\right]_x.$$

The linear variation of $\Delta G(O_2)$ as a function of temperature indicates that $\Delta H(O_2)$ and $\Delta S(O_2)$ are temperature independent in this range.

These quantities can be related to the enthalpy ΔH and entropy ΔS of formation of the defects. For example, for the defect represented by Eq. (1), where the oxygen gas is taken to be at 1 atm,

$$\Delta S(O_2) = -2\Delta S(V_O^{\cdot}),$$

where

$$\Delta S(V_O^{\cdot}) = \bar{s}_{V_O^{\cdot}} + \bar{s}_{e'} + \tfrac{1}{2} s^{\circ}_{O_2}(1 \text{ atm}) - \bar{s}_{O_O^x}.$$

The partial molal entropies $\bar{s}_i$ can be divided into vibrational $\bar{s}_i^v$ and configuration $\bar{s}_i^c$ terms. If the defects are randomly distributed, $\bar{s}_i^c = r \ln [i]$. Then,

$$\Delta S(V_O^{\cdot}) = \tfrac{1}{2} s^{\circ}_{O_2} + \bar{s}^{v}_{V_O^{\cdot}} + \bar{s}_{e'} - \bar{s}^{v}_{O_O^x} - R \ln [V_O^{\cdot}] + R \ln [O_O^x].$$

The quantity $s^{\circ}_{O_2}$ is about 60 e.u. in the temperature range of this investigation. For small departure from stoichiometry, the term $R \ln [O_O^x]$ is negligible, and $\bar{s}_e$, can be calculated from the thermodynamic potential $\mu_{e'}$ of electrons. We carried out Seebeck coefficient measurements which indicated that above 650°C WO_{3-x} may be considered as a wide-band semiconductor. In the band model $\mu_{e'}$ is given by $\mu^0_{e'} + RT \ln [e']$, where $\mu^0_{e'}$ does not depend on the concentration $[e']$, assuming low concentrations of electrons so that Boltzmann statistics hold. Then,

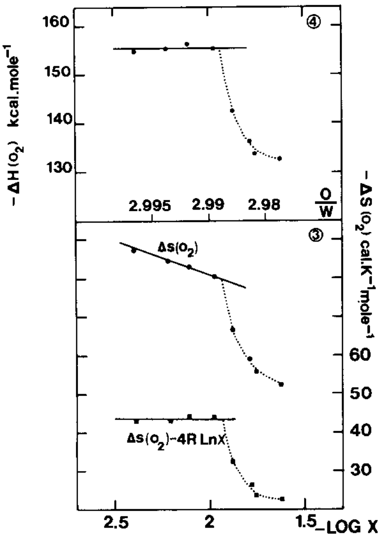
$$\bar{s}_{e'} = -\frac{\partial \mu_{e'}}{\partial T_P} = -\frac{\partial \mu^0_{e'}}{\partial T} - R \ln [e'].$$

If the vibrational terms s_i^v are independent of composition and if we take into account $[V_O^{\cdot}] = [e'] = x$ we obtain

$$\left(\frac{\partial\, \Delta S(O_2)}{\partial \ln x}\right)_T = -2\left(\frac{\partial\, \Delta S(V_O^{\cdot})}{\partial \ln x}\right)_T = 4R.$$

We must notice that the same result may be obtained in the case of $W_i^{5\cdot}$. In fact, the difficulty of imagining isolated interstitial tungsten, randomly distributed without formation of an array of such defects compel us to assume that oxygen vacancies are the only possible point defects.

The curve $\Delta S(O_2)$ vs ln x is plotted in Fig. 3. This curve is a straight line between $x = 0$ and $x = 0.012$ (domain I), the slope of which is $4R$ that is in good agreement with the assumption of point defects. On the other, for $x > 0.012$ (domain II), ΔS (O_2) decreases highly. The curve $\Delta H(O_2)$, plotted in Fig. 4 has the same behavior. In the domain I, $\Delta H(O_2)$ is a constant equal to -155 kcal · mole^{-1} and decreases in the domain II. The results seems in disagreement with the fact that the domain I and II cannot be observed in the line log x vs log p_{O_2}, the linearity of which, within the whole homogeneity range, being attributed to a single type of defect in dilute solution. This phenomenon has been already observed in CeO_{2-x} by Panlener *et al.* (*32*). In this oxide, for small departure from stoichiometry, log x vs log p_{O_2} is a straight line, that is interpreted by a single type of defect, but $\Delta H(O_2)$ depends on the composition that is confirmed by direct measurements, using calorimetry, by Campserveux and Gerdanian (*33*).



FIGS. 3 and 4. $-\Delta H(O_2)$ and $-\Delta S(O_2)$ vs $-\ln x$ and the composition O/W.

The variation of $\Delta H(O_2)$ is explained (*32*) assuming a regular solution model where the enthalpy of mixing is nonzero while the excess entropy is zero.

In the case of WO_{3-x}, a statistical treatment carried out by Boureau and Marucco (*34*) has shown that these results may be explained by the following assumptions.

(a) for $x < 0.012$ (domain I), the only defects are oxygen vacancies, randomly distributed. There are no interactions between these vacancies. In this domain the nonconfigurational entropy ΔS_{n-c} expressed by the relation $\Delta S(O_2) - 4R \ln x$ is constant.

(b) for $x > 0.012$ (domain II), the vacancies may agregate to form collapsing planes (*CS*). There is a strong attraction between *CS* as it was predicted by Iguchi and Tilley (*11–15*) and also a short-range interaction between *CS* and vacancies. ΔS_{n-c} decreases strongly that may indicate a change in the vibrational entropy if ordered interstitials take the place of vacancies.

In these conditions, we may assume that the observed crystallographic shear planes, in the domain I, are not stable defects at high temperature. In this domain, it is possible to calculate the standard enthalpy of formation of $V_O^{\cdot}$. We have $2\Delta H_f^\circ(V_O^{\cdot}) = -\Delta H(O_2)$ and we obtain $\Delta H_f^\circ(V_O^{\cdot}) = 77.7$ kcal · mole^{-1}, value near to 69 kcal · mole^{-1} proposed by Kofstad (*35*).

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