Chemistry

R. F. KSENOFONTOVA, I. A. VASIL’EVA

1962

SovietRxiv

Abstract

Full Text

Chemistry

R. F. KSENOFONTOVA, I. A. VASIL’ EVA
and Corresponding Member of the Academy of Sciences of the USSR Ya. I. GERASIMOV

THERMODYNAMICS OF TUNGSTEN OXIDES OF VARIABLE COMPOSITION

Elements of the additional subgroups of the periodic system form oxides of variable composition. However, while in most cases we possess a fairly detailed thermodynamic description of oxides of stoichiometric composition, for oxides of variable composition this information is limited. The accumulation of a large amount of experimental material on the structures and thermodynamics of oxides of variable composition is necessary not only for a complete description of metal—oxygen systems, but also for solving the question of the regularities in the change of the extent and limits of the homogeneity regions of oxides on passing from one element of the periodic system to another.

To determine the thermodynamic functions of formation of tungsten oxides of variable composition, we used the electromotive-force method described in work (1).

In the temperature range 900-1100° K, the e.m.f. was measured for cells of the type
Mo, WO_x | electrolyte with anionic conductivity | Fe, $Fe_{0.947}O$; Mo,
where Mo denotes molybdenum (or platinum) current leads; WO_x is the oxide under investigation, where $x = 2.702—2.976$; Fe, $Fe_{0.947}O$ is the reference electrode.

The potential-forming process in the cell is the reaction:

$$1.9\,\mathrm{Fe} + \frac{2}{\delta}\,\mathrm{WO}_{x+\delta} = 2\mathrm{Fe}_{0.947}\mathrm{O} + 2\mathrm{WO}_x, \tag{I}$$

the change in thermodynamic potential of which is equal to ΔG_I. The change in thermodynamic potential of the reaction studied,

$$\frac{2}{\delta}\,\mathrm{WO}_{x+\delta} = \frac{2}{\delta}\,\mathrm{WO}_x + \mathrm{O}_2. \tag{II}$$

$\Delta G_\mathrm{II} = \Delta\overline{G}_{\mathrm{O2}}$ is determined from the relation

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

$$\Delta G_{\mathrm{I}} = -zFE = \Delta G_{\mathrm{II}} + 2\Delta G_{\mathrm{III}}, \tag{1}$$

where z is the valence of the transported ion; F is Faraday' s number (cal/V); E is the e.m.f. (V); ΔG_{III} is the change in thermodynamic potential of the reaction:

$$0.947\,\mathrm{Fe} + \frac{1}{2}\mathrm{O}_2 = \mathrm{Fe}_{0.947}\mathrm{O}. \tag{III}$$

Combining the equations for the dependence of ΔG_{I} on temperature with the equation

$$\Delta G_{\mathrm{III}} = -63570 + 16.06\,T, \tag{2}$$

given in work (2), one can obtain the equation for the dependence of ΔG_{II} on temperature for reaction (II) for different values of x. As the reference electrode, an equilibrium mixture of iron with wüstite was chosen. The equilibrium mixture obtained by reduction of chemically pure sesquioxide of iron was annealed for 10-12 hours at 800°C. The pressed pellets,

0.5 cm in diameter and 2-3 mm thick, were again annealed in vacuum at 900°C for 40-50 h.

The tungsten oxides studied were obtained by reducing the high-temperature modification of tungsten trioxide with hydrogen at a temperature of 750°. The gross composition of the oxides was determined by a gravimetric method after reduction from the loss in weight of a boat with the substance. Since tungsten oxides are volatile in vacuum at 750-800°, only an approximate composition was determined in this way. The composition was determined more accurately after the experiment by back-oxidation to WO_3 at temperatures of 650-700° in a stream of moist oxygen, with an accuracy of $±$0.005 g-atom of oxygen. The prepared tungsten oxides

Fig. 1. Dependence of the emf of the cell (reaction (1)) on temperature for different values of x in WO_x:
1 –2.950; 2 –2.945; 3 –2.920; 4 –2.915; 5 –2.905; 6 –2.877; 7 –2.750; 8 –2.719; 9 –2.702

Fig. 2. Dependence of the isotherms $\lg P_{O2}$ on the composition of tungsten oxides:
a –at 850°K; b –900°K; c –950°K; d –1000°K

were pressed into pellets 5 mm in diameter and 2-3 mm thick. The pellets were annealed in vacuum at a temperature of 800° for 3 days. As the electrolyte, a solid solution $0.85\,ZrO_2 \cdot 0.15\,CaO$ (mole fractions) was used. According to Refs. (2-5), this electrolyte possesses purely anionic conductivity in the temperature interval 600-1100°, which is a necessary condition for correspondence between the change in the thermodynamic potential of reaction (1) and the emf of the cell. The electrolyte was prepared by the procedure indicated in Ref. (1). The prepared pellets of the substances and the platinum or molybdenum current leads were clamped by means of screws between metal plates, insulated with fused quartz, of size $1.2 \times 1.5 \times 1$ cm^3. The experiments were carried out in a vacuum of 10^{-4}-10^{-5} mm Hg. To reduce the open surface, the tungsten oxide pellets were placed in platinum cups. The temperature of the cell was measured with a platinum-platinum-rhodium thermocouple, a mirror galvanometer, and a PPTN-type potentiometer. The temperature was maintained to within $±$0.5° by means of a special thermoregulator. The emf values obtained in the experiment were considered equilibrium values if, upon decreasing and increasing the temperature, they were reproduced with an accuracy of $±$0.5-1 mV.

The experimental emf values for oxides of different compositions are presented in Fig. 1. By the method of least squares, from the mean values of the emf measured by us for each composition WO_x, equations were derived for the dependence of the emf on temperature in the interval 900-1100°K, presented

–

shown in Table 1. The same table gives the values of the change in the thermodynamic potential $\Delta \bar{G}_{O_2}$ of reaction (II).

Table 1

x	$E = a + bT \pm 0.5$-1, mV	$\Delta \bar{G}_{O_2} = a + bT$, cal/mol
2.702	$-11.88 + 0.0577\,T$	$128\,236 - 37.44\,T$
2.719*	$6.68 + 0.045\,T$	$126\,520 - 36.27\,T$
2.750	$+33.20 + 0.0286\,T$	$124\,080 - 34.76\,T$
2.877	$-102.80 + 0.2025\,T$	$136\,630 - 50.80\,T$
2.905	$-0.66 + 0.1100\,T$	$127\,200 - 42.27\,T$
2.915	$-25.63 + 0.1550\,T$	$129\,510 - 46.42\,T$
2.920	$+86.76 + 0.935\,T$	$119\,140 - 40.75\,T$
2.945	$+58.12 + 0.1579\,T$	$121\,780 - 46.69\,T$
2.950	$+15.01 + 0.1698\,T$	$125\,760 - 47.79\,T$
2.976	$-332.18 + 0.6389\,T$	$157\,790 - 91.07\,T$

* Data obtained in work (1).

From Table 1 it is evident that the emf of the cell and $\Delta \bar{G}_{O_2}$ of reaction (II) vary linearly with temperature, and that with increasing oxygen content in the oxides the emf values increase, as is also seen from Fig. 1.

Using the relation $\Delta\bar{G}_{O_2} = -RT\ln P_{O_2}$, one can calculate the value of the oxygen pressure.

The dependence of the isotherms $\lg P_{O_2}$ on composition is shown in Fig. 2. The figure shows that at temperatures of 850–900°K, in the composition interval $x =$ 2.89–2.72, there is a two-phase region for which the values of the thermodynamic potential of formation of $WO_{2.90}$ from $WO_{2.72}$ and O_2 agree (within 1.5–2 kcal) with the data on the equilibrium of tungsten oxides with hydrogen obtained earlier (6). With increasing temperature the extent of the two-phase region decreases, and above 1000°K it is transformed into a single-phase region. In the composition intervals $x = 2.97$–2.89 and $x = 2.75$–2.70 there are homogeneous nonstoichiometric phases. The following possible mechanisms may be proposed for the incorporation of oxygen from the gas phase into the crystal lattice of tungsten oxides. Oxygen from the gas phase, entering the crystal lattice of the lower tungsten oxide, completes its oxygen lattice. This is accompanied by the formation of compensating vacant sites in the cation lattice of the oxide. Below the critical temperature ($\sim$ 1000°K), when the concentration of vacant cation sites exceeds the "saturation" limit, the crystal lattice forms two phases.

Another mechanism may also be assumed: oxygen from the gas phase oxidizes W^{4+} to W^{6+}, with intermediate oxygen ions being formed. One can confirm one or another mechanism of formation of solid solutions by means of a high-temperature X-ray study of the structure of tungsten oxides and comparison of the X-ray density calculated from these data with the density determined experimentally, which is the task of a special investigation.

Moscow State University
named after M. V. Lomonosov

Received
9 XII 1961

REFERENCES

1. Ya. I. Gerasimov, I. A. Vasil' eva et al., ZhFKh, **36**, No. 4 (1962).
2. H. Peters, H. H. Möbius, Zs. phys. Chem., **209**, No. 6, 298 (1958).
3. F. Hund, Zs. phys. Chem., **199**, 142 (1952).
4. C. Wagner, K. Kiukkola, J. Electrochem. Soc., **104**, No. 6, 379 (1957).
5. H. Peters, G. Mann, Zs. Electrochem., **63**, No. 2, 244 (1959).
6. I. A. Vasil' eva, Ya. I. Gerasimov, Yu. P. Simanov, ZhFKh, **31**, No. 3, 682 (1957).

Note: Figure translations are in progress. See original paper for figures.