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Abstract

Full Text

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR Ya. I. Gerasimov, I. A. Vasil' eva, T. P. Chusova, V. A. Geiderikh, and M. A. Timofeeva

STUDY OF THE THERMODYNAMICS OF LOWER TUNGSTEN OXIDES BY THE E.M.F. METHOD AT HIGH TEMPERATURES

The equilibrium of the reduction of tungsten oxides by hydrogen, studied earlier ([1,2]), made it possible to calculate the thermodynamic functions of formation of tungsten trioxide from the elements.

The insufficient accuracy of measurement of high equilibrium constants and the dependence of the accuracy of the calculated data on the values for water vapor make it desirable to determine the thermodynamic functions of formation of tungsten oxides from the elements by another, independent route. For this purpose we chose the electromotive-force method, which, as applied to oxide electrodes, is described in ([3–6]). The procedure of these works was somewhat modified. Our experiments were carried out in vacuum in a specially constructed metal cell insulated with fused quartz. The furnace temperature was measured with a platinum–platinum-rhodium thermocouple and a potentiometer. As the electrolyte, a solid solution $0.85\,ZrO_2 + 0.15\,CaO$, possessing anionic conductivity, was used.

In the temperature interval 900–1230°K, the e.m.f. of cells of the type $WO_x \mid ZrO_2CaO \mid Fe_{0.95}O, Fe$ were measured, where $x = 2.719$ (1); 2.66 (2); 2.39 (3); 1.90 (4); 1.69 (5) and 1.45 (6). Oxides of the indicated composition were obtained by reduction with hydrogen of the low-temperature modification WO_3-α ([2]). The first three compositions correspond to a mixture of the phases $WO_{2.72}$ and WO_2, the last to mixtures of WO_2 and W. The mixture $Fe_{0.95}O$+Fe served as the reference electrode.

The experimental e.m.f. values of cells 1–3 and 4–6 are described by equations (1) and (2), respectively:

$$E_1 = 76.8 - 0.06T \text{ (mV)} \tag{1}$$

with an accuracy of representation of the mean experimental values by the equation of ±1.5 mV;

$$E_2 = -6.68 + 0.045T \text{ (mV)} \tag{2}$$

with an accuracy of representation of the mean experimental values by the equation of ±0.5 mV.

Combining ΔG of cells (1, 2), calculated from the known equation $\Delta G_{\text{cell}} = -zFE_{\text{cell}}$, and ΔG of formation of $Fe_{0.95}O$ from the elements (Lange' s data ([7])), gives, for the reaction

$$^1/_2\text{W} + {}^1/_2\text{O}_2 = {}^1/_2\text{WO}_2 \qquad \text{(I)}$$

the equation

$$\Delta G_1 = -68542 - 7.21T\lg T + 1.26 \cdot 10^{-3}T^2 - 0.47 \cdot 10^5 T^{-1} + 40.62T$$

(943–1230°K).

The values of ΔG_1 calculated from this equation in the temperature interval 973–1273°K, and the values of $\Delta G_1'$ for reaction (I) at these temperatures, obtained by us earlier ([2]) from equilibrium data, are presented in Table 1.

For the reaction

$$^{100}/_{72}\,\text{WO}_2 + {}^1/_2\text{O}_2 = {}^{100}/_{72}\,\text{WO}_{2.72} \qquad \text{(II)}$$

the equation is

$$\Delta G_2 = -65308 - 7.21\,T\lg T + 1.26 \cdot 10^{-3}T^2 - 0.47 \cdot 10^5 T^{-1} + 39.93\,T$$

(900–1173°K).

The values of ΔG_2 calculated from this equation in the interval 923–1173°K and the values of $\Delta G_2'$ for reaction (II) at these temperatures, obtained by us earlier ([2]) from equilibrium data, are presented in Table 2.

Table 1

T, °K	$-\Delta G_1$, kcal	$-\Delta G_1'$, kcal
973	48.8±1.5	49.5
1073	47.0±1.5	47.5
1173	45.2±1.5	45.4
1273	43.3±1.5	43.3

Table 2

T, °K	$-\Delta G_2$, kcal	$-\Delta G_2'$, kcal
923	47.1±0.5	47.2
1023	45.4±0.5	45.4
1123	43.7±0.5	43.6
1173	42.8±0.5	42.7

Combining reactions (I) and (II), respectively, gives for the reaction

$$W + 1.36\,O_2 = WO_{2.72} \qquad \text{(III)}$$

the equation

$$\Delta G_3 = -184106 + 9.23\,T\lg T + 3.43\cdot 10^{-3}T^2 - 1.28\cdot 10^5 T^{-1} + 109.9\,T.$$

For calculating the standard thermodynamic quantities we used the heat capacities of O_2 and W, data in ([8]), and for WO_2 the equation

$$c_p = 17.83 + 1.89\cdot 10^{-3}T - 3.342\cdot 10^5 T^{-2}$$

(accuracy ±3%), derived by us on the basis of the value $c_{p,298}$ for WO_2 ([9]), values of c_p for

Table 3

$-\Delta H^\circ_{298}$, kcal	$-\Delta G^\circ_{298}$, kcal	$-\Delta S^\circ_{298}$, e.u.	S°_{298}, e.u.	Source
134±1	122.0	41		([15])
134.5±5			15±2.5	([11])
137±1			19.7±1	([16])
140.94±0.2				([17])
136.6±2	124.0±2	41.7±1.5	15±1.5	Our data, obtained by the e.m.f. method

solids at the transformation temperature and averaged equations for the oxides UO_2 ([10]), VO_2 ([11]), and ThO_2 ([11]), with values of $c_{p,298}$ close to those of WO_2.

Using these values, we obtain for the reaction

$$W + O_2 = WO_2 \qquad \text{(IV)}$$

the equation

$$\Delta G_T = -136.6 - T(4.66M_0 + 0.21M_1 - 2.44M_{-2}) + 41.7T$$

(M_0, M_1, M_{-2} are the coefficients of the Temkin-Schwarzman equation [12]), whence

$$\Delta H^0_{298} = -136.6 \pm 2 \text{ kcal};$$

$$\Delta S^0_{298} = -41.7 \pm 1.5 \text{ e.u.};$$

$$\Delta G^0_{298} = -124 \pm 2 \text{ kcal}.$$

Using the values of S^0_{298} for W [13] and O_2 [14], we obtain for WO_2

$$S^0_{298} = 15.0 \pm 1.5 \text{ e.u.}$$

For comparison, Table 3 gives some literature data for the thermodynamic functions of formation of WO_2 from the elements under standard conditions.

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