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GIBBS FREE ENERGY OF FORMATION OF MAGNESIUM TUNGSTATE FROM EMF MEASUREMENTS

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ABSTRACT

The Gibbs free energies of formation of $MgWO_4$ from component oxides have been determined in the temperature range 938–1015 K from a solid state galvanic cell incorporating MgF_2 as the solid electrolyte. The values thus obtained are in reasonably good agreement with those obtained from the literature.

INTRODUCTION

Magnesium fluoride has been used as a solid electrolyte for the determination of the thermodynamic properties of solid solutions and compounds involving MgO by the high temperature galvanic cell technique [1–3]. In the present work, this technique was used for determining the Gibbs free energy of formation of $MgWO_4$. According to the phase diagram [4], $MgWO_4$ is the only compound existing in the system $MgO-WO_3$. Rezukhina and Levitskii [5] determined the thermodynamic properties of $MgWO_4$ in the temperature range 1220–1370 K from EMF measurements of solid oxide galvanic cells using the solid electrolyte $ThO_2-La_2O_3$. An Fe/FeO reference electrode was employed and $MgWO_4 +$ (MgO + W) was used as the working electrode in these cells. The Gibbs free energies of formation of $MgWO_4$ were obtained from the experimental cell EMFs and the Gibbs free energies of formation of "FeO". Barin et al. [6] estimated the Gibbs free energies of formation of $MgWO_4$ above 298.15 K from heat of formation and entropy data at 298.15 K and high temperature heat capacity and entropy data. The Gibbs free energies of formation of $MgWO_4$ from the component oxides can be obtained by combining the results of Rezukhina and Levitskii [5] with the Gibbs' free energy of formation of WO_3 obtained

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by Barin et al. [6]. The values thus obtained at 1220–1370 K are in good agreement with the estimated data of Barin et al. [6] and those calculated from the high temperature heat capacity data of Kubaschewski and Alcock [7]. The former values are more negative by 8–12 kJ at lower temperatures. In this work the Gibbs free energies of formation of $MgWO_4$ are determined directly by setting up a cell incorporating MgF_2 as the solid electrolyte.

EXPERIMENTAL

Materials

Magnesium fluoride (99.9%) from Cerac Inc. was used for making the solid electrolyte pellets and electrodes. The electrolyte was prepared by pressing the powder to a pressure of 235 MPa in a cylindrical die. The green pellet was then sintered in an atmosphere of CO_2-free dry argon gas (UHP, Canadian Liquid Air) at 1323 K for 4 h. $MgWO_4$ (99.9%) and WO_3 (99.9%) from Cerac Inc. were used to make the working electrodes.

Cell operation

The apparatus used in the present work was similar to the type B assembly described in earlier work [8]. The performance of the polycrystalline MgF_2 as a solid electrolyte was checked by operating the cell

$$\mathrm{Pt,O_2(g)\,|\,MgO,MgF_2\,|\,MgF_2\,|\,MgO\cdot 2TiO_2,TiO_2\,|\,Pt,O_2(g)}$$

in the temperature range 1173–1273 K. The objective of this experiment was to check to suitability of MgF_2 as a solid electrolyte with $t(F^-)$ close to unity in order to obtain reliable thermodynamic results on metal oxide systems. The Gibbs free energies of formation of the magnesium titanates have been measured by Shah et al. [9] using this technique. The EMFs obtained in the present work using the above cell are in good agreement with Shah et al.'s reported results. The Gibbs free energies of formation of $MgO\cdot 2TiO_2$ from the pure oxides calculated from the EMFs are also in good agreement with the results of Elliott et al. [10] when the reported error limits are taken into account (Table 1).

TABLE 1

Standard Gibbs free energy of formation ($kJ\ mol^{-1}$) of $MgO\cdot 2TiO_2$

T (K)	Present work	Shah et al. [9]	Elliott et al. [10]
1273	−36.92	−38.35	−36.37
	(±0.19)	(±0.19)	(±1.88)
1173	−34.00	−35.51	−34.83
	(±0.19)	(±0.39)	(±1.88)

The cell employed in this investigation was of the type

$Pt,O_2(g)\,|\,MgO,MgF_2\,|\,MgF_2\,|\,MgWO_4,WO_3,MgF_2\,|\,Pt,O_2(g)$

The tungstate working electrode was prepared by mixing $MgWO_4$ and WO_3 in roughly equimolar proportions. About 10–15 wt.% of MgF_2 was then added to the mixture.

The overall cell reaction is

$$MgO(s) + WO_3(s) \rightleftharpoons MgWO_4(s) \qquad (1)$$

and the two half-cell reactions can be represented as follows in accordance with Benz and Wagner [11] for similar cells. At the reference electrode (anode) where pure MgO is in contact with MgF_2 electrolyte,

$$MgO(s) + 2F \rightleftharpoons MgF_2^-(s) + \tfrac{1}{2}O_2(g) + 2e^- \qquad (2)$$

At the working electrode (cathode) where $MgWO_4 + WO_3$ is in contact with the MgF_2 electrolyte

$$MgF_2(s) + \tfrac{1}{2}O_2(g) + WO_3(s) + 2e^- \rightleftharpoons MgWO_4(s) + 2F^- \qquad (3)$$

The measured EMF (mV) is related to the Gibbs free energy change of reaction (1) by the expression:

$$-2E^\circ F = \Delta G^\circ \qquad (4)$$

where F is the Faraday constant. These cell reactions clearly indicate that oxygen is necessary for their operation. An atmosphere of UHP oxygen from Canadian Liquid Air was provided throughout the working period of the cell. The half-cell reactions given assume that the electrolyte is reversible only to fluoride ions.

The in situ temperature of the cell was measured with a Pt–(Pt–13%Rh) thermocouple welded to the platinum foil in contact with the reference electrode of the cells. The platinum wire of the couple also served as the lead wire for measuring the cell EMF. The temperature of the furnace was controlled by a proportional controller to ±1 K. The cell EMFs were measured by a Keithley 616 digital electrometer with an input impedance of $10^{14}\ \Omega$. The reversibility of the galvanic cells under investigation was tested by passing a small current through the cells in each direction and noting that the observed EMFs returned to the original values. The temperature range in which the cell operations gave stable, reproducible EMFs was limited by the volatilisation of WO_3 from the working electrode at high temperatures and the sluggish cell response at low temperatures. The EMFs were reproducible on temperature cycling and the time of equilibration varied from 2 to 3 h.

RESULTS

The EMF vs. temperature plot of the cell on heating and cooling is shown in Fig. 1. A cell with pure MgO on both sides gave EMFs close to zero

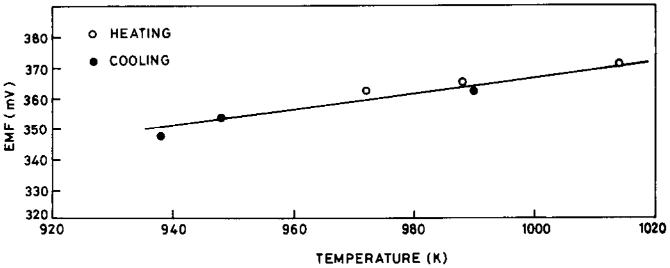

Fig. 1. Plot of EMF E against temperature T for the cell $\mathrm{Pt,O_2(g)\,|\,MgO,MgF_2\,|\,MgF_2\,|\,MgWO_4,WO_3,MgF_2\,|\,Pt,O_2(g)}$.

($\pm$0.5 mV). Changes in gas flow rate also did not affect the cell EMF. Reproducible EMFs were obtained even after an initial polarisation of the cell on passing an external current.

DISCUSSION

Least-mean-square analysis of the EMFs in Fig. 1 gives the following equation for the EMF of the cell:

$$E = 102.37 + 0.2646T\ (\pm 1.7)\ \mathrm{mV} \quad (938\text{–}1015\ \mathrm{K}) \tag{5}$$

This EMF is directly related to the standard free energy change of reaction (1):

$$\Delta G^\circ = -2E^\circ F = -19.759 - 0.0511T\ (\pm 1.0)\ \mathrm{kJ\ mol^{-1}} \tag{6}$$

Using this equation for the Gibbs free energy change of cell reaction (1), the standard Gibbs free energy of formation of $MgWO_4$ from the pure oxides was calculated at 938 and 1015 K, the temperature limits of cell operation. Corresponding values at these two temperatures were also calculated by combining the extrapolated results of Rezukhina and Levitskii [5] with the Gibbs free energy of formation of WO_3 from Barin et al. [6]. These two sets of experimental results are compared in Table 2 with the estimated high temperature free energy data of Barin et al. [6] and those calculated by the

TABLE 2

Standard Gibbs free energy of formation (kJ mol^{-1}) of $MgWO_4$

T (K)	Present work	Barin et al. [6]	Calculated from Rezukhina and Levitskii [5]	Calculated from Kubaschewski and Alcock [7]
938	−67.69 (±1.00)	−68.70 (±2.00)	−80.21 (±2.93)	−69.75
1015	−71.63 (±1.00)	−68.32 (±2.00)	−77.76 (±2.93)	−69.33

present authors from the high temperature heat capacity data for MgO(s) and WO_3(s) from Kubaschewski and Alcock [7] and those for $MgWO_4$(s) from Rezukhina and Levitskii [5]. While the present results are in good agreement with those of Barin et al. [6] and Kubaschewski and Alcock [7], they are more positive by about 6–12 kJ than those derived from the experimental results of Rezukhina and Levitskii [5] using the Gibbs free energy of formation of WO_3 from Barin et al. [6]. However, considering the different experimental techniques and the uncertainties involved, the agreement can be considered to be reasonably good. The present results may be considered to be more reliable since the Gibbs free energy of formation of $MgWO_4$ from the component oxides has been determined directly from the cell employed.

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