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GIBBS FREE ENERGY OF FORMATION OF MAGNESIUM STANNATE FROM EMF MEASUREMENT

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ABSTRACT

The Gibbs free energies of formation of Mg_2SnO_4 from component oxides have been determined in the temperature range 1173–1293 K from a solid-state galvanic cell incorporating MgF_2 as the solid electrolyte. The values so obtained are in good agreement with those reported in the literature, and the heat and entropy of formation derived can be considered to be in reasonable agreement within the limits of experimental error.

INTRODUCTION

The thermodynamic properties of Mg_2SnO_4 were obtained from the temperature dependence of its high pressure decomposition determined by Jackson et al. [1] in the temperature range 1073–1473 K. Navrotsky and Kasper [2] determined the heat of formation of Mg_2SnO_4 by calorimetry. Jacob and Valderrama-N [3] employed a ThO_2–Y_2O_3 solid-electrolyte cell in the temperature range 873–1273 K to determine the Gibbs free energy of formation of Mg_2SnO_4. While the values so determined are in good agreement with those obtained by Jackson et al. [1] the heat and entropy of formation are slightly smaller. The calorimetric heat of formation of Mg_2SnO_4 reported by Navrotsky and Kasper [2] is in excellent agreement with that derived by Jacob and Valderrama-N [3] from the high temperature dependence of the Gibbs free energy of formation. These authors report that the thermodynamic properties of Mg_2SnO_4 determined by them from EMF measurements are more reliable than those of Jackson et al. [1] in view of the good reversibility and reproducibility of the cell EMF results obtained. In the present work a solid-state galvanic cell with MgF_2 as the solid electrolyte was used to measure the Gibbs free energy of formation of Mg_2SnO_4 from its component oxides in the temperature range 1173–1293 K. The suitability and reliability of this technique for the determination of the thermodynamic properties of solid solutions and compounds involving MgO are well documented [4–7].

EXPERIMENTAL

Materials

Magnesium fluoride for making the solid-electrolyte pellets was made according to the method of Taylor and Schmalzried [4]. 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 oxygen gas at 1323 K for 4 h. The dimagnesium stannate (Mg_2SnO_4) was synthesized from fine powders of dried reagent grade SnO_2 and MgO. These starting materials were mixed in the correct ratio under acetone. The equilibrium phase of Mg_2SnO_4 was prepared by sintering the oxide mixture pellets at 1483 K in a platinum boat under air for 24 h. The formation of Mg_2SnO_4 was confirmed by the X-ray diffraction technique.

Cell operation

The assembly used in the present work was similar to that described earlier [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 polycrystalline MgF_2 solid electrolyte used was sandwiched between the MgO reference electrode and the titanate working electrode. The object of these measurements was to check the suitability of MgF_2 as a solid electrolyte with $t(F^-)$ close to unity for obtaining reliable thermodynamic results on metal oxide systems. Shah et al. [9] used the above cell to measure the Gibbs free energies of formation of various magnesium titanates. The EMFs obtained in the present work for the above cell agreed with those reported by Shah et al. [9]. The Gibbs free energies of formation of $MgO \cdot 2TiO_2$ from the pure oxides calculated from the EMFs are in good agreement with the results of Elliott et al. [10] when the reported error limits are taken into account.

The cell employed in this investigation is of the type

$$\mathrm{Pt,O_2(g)/MgO,MgF_2/MgF_2/Mg_2SnO_4,SnO_2,MgF_2/Pt,O_2(g)}$$

The stannate working electrode was prepared by mixing the Mg_2SnO_4 and SnO_2 in roughly equimolar proportions. Both the reference and the working electrode pellets containing about 10–15 wt.% of MgF_2 were sintered at 1323 K in dry CO_2-free oxygen gas before use.

The EMF is due to the reaction

$$\mathrm{2MgO(s) + SnO_2(s) = Mg_2SnO_4(s)} \qquad (1)$$

The reactions at the two electrodes can be represented as follows in accordance with Benz and Wagner [11] for a similar cell. At the reference electrode where pure MgO is in contact with MgF_2 electrolyte

$$2MgO(s) + 4F^- = 2MgF_2 + O_2(g) + 4e^- \qquad (2)$$

At the working electrode, where ($Mg_2SnO_4 + SnO_2$) is in contact with the MgF_2 electrolyte

$$2MgF_2 + O_2(g) + SnO_2(s) + 4e^- = Mg_2SnO_4(s) + 4F^- \qquad (3)$$

Therefore the measured EMF E is related to the Gibbs free energy change of reaction (1) by the expression

$$-4E\mathrm{F} = \Delta G \qquad (4)$$

where F is the Faraday constant. These cell reactions clearly indicate that oxygen is necessary for the operation of the cell. If the same oxygen pressure prevails at the two electrodes, the overall reaction is as given by reaction (1). An atmosphere of CO_2-free dry oxygen was provided throughout the working period of the cell. The mechanism outlined does not depend on the presence of oxygen ions in the electrolyte. It assumed that the conductivity is due solely to the fluoride ions.

The in-situ temperature of the cell was measured with a Pt–PtRh(13% Rh) thermocouple welded to the Pt foil in contact with the reference electrode of the cell. The Pt wire of the couple also served as the lead wire for measuring the cell EMF. The temperature of the furnace was controlled by another thermocouple. The temperature measured was controlled to within ±3 K. The reversible EMF of the cell was measured as a function of temperature between 1173 and 1293 K. The EMFs were reproducible on temperature cycling. The times of equilibration varied from 1 to 4 h depending upon the temperature.

RESULTS

The experimental values of the EMFs of the cell on heating and cooling are plotted as a function of temperature in Fig. 1. Within experimental error, the EMFs varied linearly with temperature. The cell with pure MgO on both sides gave EMFs close to zero. Changes in gas flow rate also did not affect the cell EMF. Reproducible EMFs were obtained even after an initial polarization of the cell by passing an external current. The cell EMF could be read on the potentiometer correct to ±0.2 mV. It was found that the EMF was reproducible to within ±1 mV when taken through a thermal cycle. This uncertainty in the EMF is the main source of error and an error of this magnitude has been reported by previous workers.

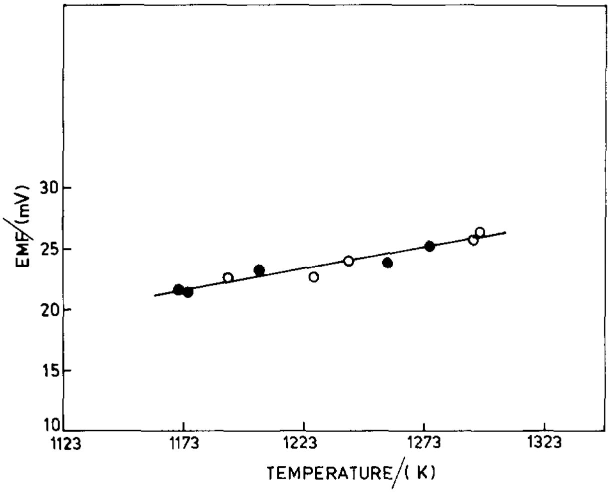

Fig. 1. Plot of EMF, E, against temperature, T, for the cell $Pt,O_2(g)/MgO,MgF_2/MgF_2/Mg_2SnO_4,SnO_2,MgF_2/Pt,O_2(g)$
○, heating; ●, cooling.

There is an error of ±3 K in the temperature measurements but this is not likely to introduce any serious error, since the variation of EMF with temperature was quite small.

DISCUSSION

The least-mean-square analysis of the EMFs in Fig. 1 suggests the following equation for the EMF of the cell

$$E = -18.75 + 0.0345T\ (\pm 1)\ \text{mV}\ (1173\text{–}1293\ \text{K}) \qquad (5)$$

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

$$\Delta G = -4EF = 7238 - 13.334T\ (\pm 386)\ \text{J mol}^{-1} \qquad (6)$$

Jacob and Valderrama-N [3] expressed the Gibbs free energy of formation of Mg_2SnO_4 from the component oxides as

$$\Delta G = 5941 - 12.385T\ (\pm 335)\ \text{J mol}^{-1} \qquad (7)$$

in the temperature range 873–1273 K using EMF data on a solid-oxide galvanic cell.

The heat and entropy of formation of Mg_2SnO_4 from its component oxides have been derived as 9372 (±3766) J mol^{-1} and 15.48 (±3.766) J deg^{-1} mol^{-1} respectively from the temperature dependence of the high pressure decomposition of Mg_2SnO_4 determined by Jackson et al. [1].

At a mean temperature of 1233 K, the Gibbs free energy of formation of Mg_2SnO_4 obtained in the present work is -9203 J mol^{-1}. This is compared with the values of -9330 J mol^{-1} obtained by Jacob and Valderrama-N [3] and -9716 J mol^{-1} calculated from the high-pressure studies of Jackson et al. [1]. The agreement between these results is good considering the different experimental techniques and the errors involved. The heat of formation of Mg_2SnO_4 from the component oxides from the present work 7238 ± 1206 J mol^{-1} is slightly higher than the values of 5941 ± 1046 J mol^{-1} and 4728 ± 2008 J mol^{-1} reported by Jacob and Valderrama-N [3] and Navrotsky and Kasper [2] respectively. The heat and entropy of formation of Mg_2SnO_4 from the component oxides obtained in the present work are slightly smaller than the corresponding values derived from the temperature variation of the decomposition pressure of Mg_2SnO_4 from Jackson et al. [1]. The negative free energy of formation and the positive heat of formation combined together confirms that Mg_2SnO_4 is an entropy stabilized compound.

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