

Letter

Thermodynamics of the formation of high calcium tantalates from e.m.f. measurements

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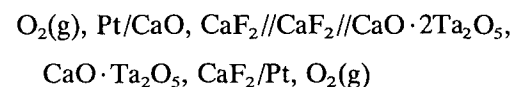
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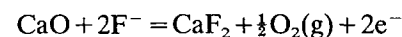
1. Introduction

The phase diagram [1] of the system CaO–Ta₂O₅ shows the existence of four compounds below 1733 K: CaO·2Ta₂O₅, CaO·Ta₂O₅, 2CaO·Ta₂O₅ and 4CaO·Ta₂O₅. The Gibbs energy of formation of calcium ditantalate has been determined [2] in the temperature range 1250–1300 K using a CaF₂ solid electrolyte galvanic cell. From the data so obtained and from e.m.f. measurements using similar galvanic cells in the present work, the Gibbs energies of formation of CaO·Ta₂O₅, 2CaO·Ta₂O₅ and 4CaO·Ta₂O₅ from the component oxides were determined in the temperature range 1227–1273 K. The high temperature galvanic cell technique with calcium fluoride as the solid electrolyte has been employed for the determination of Gibbs energies of formation of compounds of calcium oxide [3–5]. The Gibbs energies of formation of CaO·Ta₂O₅, 2CaO·Ta₂O₅ and 4CaO·Ta₂O₅ can be determined by setting up the following cells incorporating CaF₂ as the solid electrolyte.

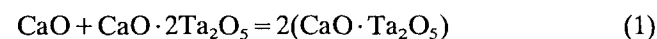
1.1. Cell A



The reaction at the CaO–CaF₂ interface is



The reaction at the CaF₂–CaO·2Ta₂O₅, CaO·Ta₂O₅, CaF₂ interface is $\text{CaF}_2 + \frac{1}{2}\text{O}_2(\text{g}) + \text{CaO} \cdot 2\text{Ta}_2\text{O}_5 + 2\text{e}^- = 2(\text{CaO} \cdot \text{Ta}_2\text{O}_5) + 2\text{F}^-$. Therefore the net cell reaction is

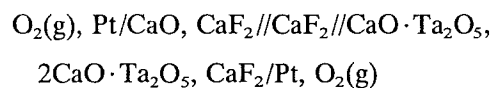


The Gibbs energy change of reaction (1) is given by

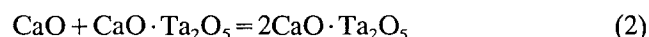
$$\Delta G^0 = -2FE$$

where E is the e.m.f. of the cell and F the Faraday constant (in SI units).

1.2. Cell B



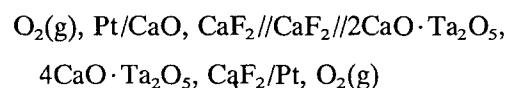
The cell reaction is



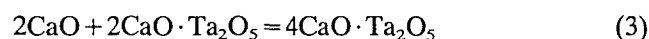
The Gibbs energy change of reaction (2) is given by

$$\Delta G^0 = -2FE$$

1.3. Cell C



The cell reaction is



The Gibbs energy change of reaction (3) is given by

$$\Delta G^0 = -4FE$$

Using the Gibbs energy of formation of CaO·2Ta₂O₅ determined in previous work [2], the Gibbs energies of formation of CaO·Ta₂O₅, 2CaO·Ta₂O₅ and 4CaO·Ta₂O₅ from the component oxides can be calculated from the Gibbs energy changes involved in reactions (1), (2) and (3) respectively.

2. Materials

The calcium tantalates were prepared from fine powders of dried reagent grade Ta₂O₅ and CaCO₃. These starting materials were mixed in the correct ratio under acetone. The equilibrium phases of mono-, di- and tetra-calcium tantalates were prepared by sintering the oxide mixture pellets at 1623 K for 72 h with intermittent grinding. Formation of the tantalates was confirmed by X-ray diffraction. The electrode pellets were prepared by mixing the appropriate compounds in roughly equimolar proportions. About 15 wt.% of CaF₂ was then added to the mixture, the mixed powder was pressed into cylindrical pellets and sintered at 1273 K in dry, CO₂-free oxygen gas before use. Polycrystalline calcium fluoride solid electrolyte pellets were used.

3. Experimental details

The assembly used was similar to that described by Vecher and Vecher [6]. A Pt/Pt-13% Rh thermocouple welded to the platinum foil in contact with the reference electrode served to measure the temperature of the cell. The platinum wire of the couple also functioned as the lead wire for measuring the cell e.m.f. The temperature of the furnace was controlled by another thermocouple to within ± 3 K. A Keithley 617 digital electrometer with an input impedance of $10^{14} \Omega$ was used to measure the cell e.m.f. and the thermal e.m.f. The reversible e.m.f.s of the cells were measured in the temperature range 1227–1273 K. The reproducibility of the e.m.f. was checked by thermal cycling and coulometry.

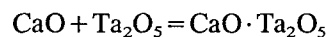
4. Results and discussion

The mean values of the experimental e.m.f. of cells A, B and C were found to be 295.3 ± 2 mV, 195.2 ± 2 mV and 161.2 ± 2 mV respectively in the temperature range 1227–1273 K.

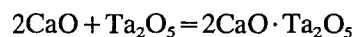
The e.m.f. of 295.3 ± 2 mV at a mean temperature of 1250 K for cell A is directly related to the standard Gibbs energy change of $-57.00(\pm 0.4)$ kJ mol⁻¹ for reaction (1) at 1250 K. This value is combined with the standard Gibbs energy of formation of CaO·2Ta₂O₅ from the component oxides determined from previous work [2] to be

$$\Delta G^{\circ} = -0.029(T - 1250) - 73.232(\pm 1.0) \text{ kJ mol}^{-1}$$

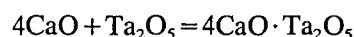
in the temperature range 1250–1300 K. The Gibbs energy of formation so obtained is $-65.14(\pm 0.6)$ kJ mol⁻¹ at 1250 K for the reaction



This value is combined with the standard Gibbs energy change of $-37.10(\pm 0.4)$ kJ for reaction (2) at 1250 K obtained from the e.m.f. of 195.2 ± 2 mV for cell B at a mean temperature of 1250 K. The Gibbs energy of formation so obtained is $-102.82(\pm 0.7)$ kJ at 1250 K for the reaction



This value is combined with the standard Gibbs energy change of $-62.23(\pm 0.8)$ kJ for reaction (3) at 1250 K obtained from the e.m.f. of 161.2 ± 2 mV for cell C at a mean temperature of 1250 K. The Gibbs energy of formation so obtained is $-165.05(\pm 1.0)$ kJ at 1250 K for the reaction



References

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