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Determination of standard Gibbs free energy of formation for $CaKPO_4$, $CaK_4(PO_4)_2$, $CaK_2P_2O_7$, and $Ca_{10}K(PO_4)_7$ from solid-state e.m.f. measurements using yttria stabilised zirconia as solid electrolyte

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Abstract

The equilibrium reactions: $4CaKPO_4(s) + 6Ni(s) \rightleftarrows CaK_4(PO_4)_2(s) + 3CaO + 2Ni_3P(s) + 5/2O_2(g)$, $4CaKPO_4(s) + 3K_4P_2O_7(s) + 6Ni(s) \rightleftarrows 4CaK_4(PO_4)_2(s) + 2Ni_3P(s) + 5/2O_2(g)$, $4CaK_2P_2O_7(s) + 6Ni(s) \rightleftarrows 4CaKPO_4(s) + K_4P_2O_7(s) + 2Ni_3P(s) + 5/2O_2(g)$ and $Ca_{10}K(PO_4)_7(s) + 9CaK_2P_2O_7(s) + 18Ni(s) \rightleftarrows 19CaKPO_4(s) + 6Ni_3P(s) + 15/2O_2(g)$ were studied in the temperature range from 880 to 1125 K. The oxygen equilibrium pressures were determined using galvanic cells incorporating yttria stabilised zirconia as solid electrolyte. From the measured data and using literature values of standard Gibbs free energy of formation for CaO, Ni_3P and $K_4P_2O_7$, the following relationship of the standard Gibbs free energy of formation for $CaKPO_4$, $CaK_4(PO_4)_2$, $CaK_2P_2O_7$, and $Ca_{10}K(PO_4)_7$ were calculated:

$$\Delta_f G^\circ(CaKPO_4) \pm 5.2/(kJ \cdot mol^{-1}) = -1506.6 - 3.2933(T/K) + 0.4603(T/K) \cdot \ln(T/K)\ 890 < (T/K) < 1125$$
$$\Delta_f G^\circ(CaK_4(PO_4)_2) \pm 8.9/(kJ \cdot mol^{-1}) = -3498.2 - 2.1339(T/K) + 0.3661(T/K) \cdot \ln(T/K)\ 930 < (T/K) < 1125$$
$$\Delta_f G^\circ(CaK_2P_2O_7) \pm 7.2/(kJ \cdot mol^{-1}) = -2690.0 - 3.7820(T/K) + 0.5599(T/K) \cdot \ln(T/K)\ 940 < (T/K) < 1100$$
$$\Delta_f G^\circ(Ca_{10}K(PO_4)_7) \pm 133/(kJ \cdot mol^{-1}) = -5988.3 - 57.063(T/K) + 7.4407(T/K) \cdot \ln(T/K)\ 880 < (T/K) < 1015.$$

Keywords: e.m.f. Measurements; Gibbs free energy of formation; Solid electrolyte; Calcium potassium phosphates

1. Introduction

During combustion and gasification of biomass fuels, condensed phases consisting of various different elements are formed. Besides the traditionally studied major ash forming elements (Ca, K, Na, Si), significant amounts of phosphorous are contained in many biomass fuels and sludges. Such phosphorous containing ash products typically appear in the ternary system $CaO–K_2O–P_2O_5$. However, reliable thermodynamic data for ternary phases in this system are lacking. Work is now being carried out at our department to structurally characterise and to determine stabilities of a number of phases in the $CaO–K_2O–P_2O_5$ system [1–6]. Recently, solid state e.m.f. measurements were carried out to determine Gibbs free energies in the subsystem $CaO–P_2O_5$ [4]. The present work was undertaken to determine thermodynamic stabilities of a number of ternary phases using the solid electrolyte galvanic cell technique.

2. Materials and methods

2.1. Equilibria considered

The stability regions in part of the $CaO–K_2O–P_2O_5$ system are illustrated in figure 1. Besides CaO and $K_4P_2O_7$, the intermediate phases $CaKPO_4$, $CaK_4(PO_4)_2$, $CaK_2P_2O_7$,

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and $Ca_{10}K(PO_4)_7$ appear in the various three phase areas. Based on these phase relations and by using the auxiliary solid couple Ni/Ni_3P, the following equilibrium reactions are derived:

$$4CaKPO_4(s) + 6Ni(s) \rightleftarrows CaK_4(PO_4)_2(s) + 3CaO + 2Ni_3P(s) + 5/2O_2(g) \tag{I}$$

$$4CaKPO_4(s) + 3K_4P_2O_7(s) + 6Ni(s) \rightleftarrows 4CaK_4(PO_4)_2(s) + 2Ni_3P(s) + 5/2O_2(g) \tag{II}$$

$$4CaK_2P_2O_7(s) + 6Ni(s) \rightleftarrows 4CaKPO_4(s) + K_4P_2O_7(s) + 2Ni_3P(s) + 5/2O_2(g) \tag{III}$$

$$Ca_{10}K(PO_4)_7(s) + 9CaK_2P_2O_7(s) + 18Ni(s) \rightleftarrows 19CaKPO_4(s) + 6Ni_3P(s) + 15/2O_2(g) \tag{IV}$$

The discussion regarding the galvanic cell technique and the involvement of the auxiliary solid couple, Ni/Ni_3P, has previously been addressed by Sandström *et al.* [4]. The oxygen pressures obtained in these equilibria can be determined by e.m.f. measurements using YSZ as solid electrolyte.

2.2. Materials and preparations

The chemicals used in the experiments were: $CaCO_3$ (Riedel-de-Haën, 98%), $Ca(H_2PO_4)_2$ (Sigma, 98%), $CaHPO_4$ (Mallinckrodt, analytical reagent), K_2CO_3 (Merck, p.a.), K_2HPO_4 (Merck, p.a.), Fe (Merck p.a.), Fe_2O_3 (Fischer Scientific, Pittsburgh, PA), Ni (Merck) and Ni_2P (Aldrich). $CaK_2P_2O_7$ was synthesised by mixing $Ca(PO_3)_2$ and K_2CO_3 in equimolar amounts and keeping the mixture at 1073 K for ~18 h. $CaKPO_4$ was synthesised by mixing $Ca_2P_2O_7$ and K_2CO_3 in equimolar amounts and maintaining the mixture at 1273 K for ~18 h. $CaK_4(PO_4)_2$ was synthesised by mixing $Ca(PO_3)_2$ and K_2CO_3 in a 1:2 ratio, heated to 1273 K and kept at that temperature for ~18 h. $K_4P_2O_7$ was synthesised by dehydrating K_2HPO_4 at 673 K. $Ca_3(PO_4)_2$ was used as starting material in equilibrium (IV) and its synthesis has been described by Sandström *et al.* [4]. The syntheses of CaO, $Ca(PO_3)_2$, $Ca_2P_2O_7$, and the reference system Fe/'FeO' have also been described by Sandström *et al.* [4].

All chemicals were analysed by X-ray diffraction (Bruker, D8Advance), verified against the Powder Diffraction File (PDF-2) [8], and were found to be pure within the limits of the diffractometer resolution ($\leqslant 1\%$).

2.3. e.m.f. Cells and experimental procedure

The cell-schemes for the measured equilibria can be written as:

$$\text{Pt, } O_2(g)\text{, } Ni_3P(s)\text{, } Ni(s)\text{, } CaKPO_4(s)\text{, } CaK_4(PO_4)_2(s)\text{, } CaO(s)|YSZ|\text{Pt, } O_2(g)\text{, } Ni_3P(s)\text{, } Ni(s)\text{, } CaKPO_4(s)\text{, } CaK_4(PO_4)_2(s)\text{, } CaO(s)\text{, Pt}|YSZ|Fe(s)\text{, 'FeO(s)', Pt, } O_2(g) \tag{A}$$

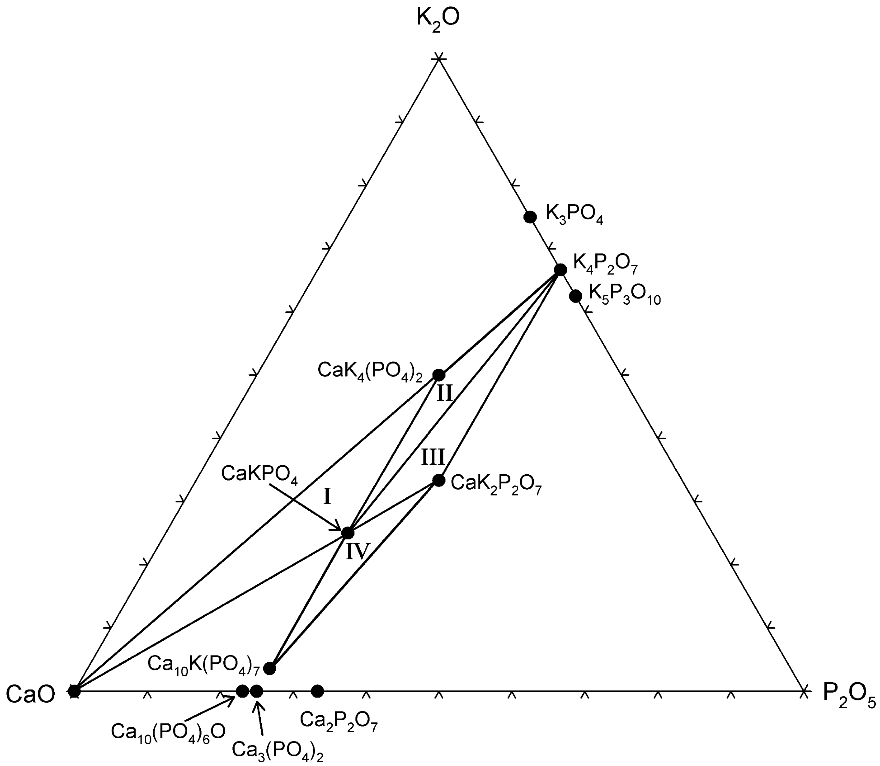

FIGURE 1. Phase relations in part of the $CaO–K_2O–P_2O_5$ system. The roman numerals represent the measured equilibria (I) to (IV). The phase areas (I) and (IV) were obtained in this work, while the phase areas (II) and (III) were established by Znameriowska [7].