

# Determination of standard Gibbs free energy of formation for $\text{Ca}_2\text{P}_2\text{O}_7$ and $\text{Ca}(\text{PO}_3)_2$ from solid-state EMF measurements using yttria stabilised zirconia as solid electrolyte

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## Abstract

The equilibrium reactions:  $3\text{Ca}_2\text{P}_2\text{O}_7(\text{s}) + 6\text{Ni}(\text{s}) \rightleftharpoons 2\text{Ca}_3(\text{PO}_4)_2(\text{s}) + 2\text{Ni}_3\text{P}(\text{s}) + \frac{5}{2}\text{O}_2(\text{g})$  and  $2\text{Ca}(\text{PO}_3)_2(\text{s}) + 6\text{Ni}(\text{s}) \rightleftharpoons \text{Ca}_2\text{P}_2\text{O}_7(\text{s}) + 2\text{Ni}_3\text{P}(\text{s}) + \frac{5}{2}\text{O}_2(\text{g})$  were studied in the temperature range 890 K to 1140 K. The oxygen equilibrium pressures were determined using galvanic cells incorporating yttria stabilized zirconia as solid electrolyte. From the measured data and using the literature values of standard Gibbs free energy of formation for  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{Ni}_3\text{P}$ , the following relationship of the standard Gibbs free energy of formation for  $\text{Ca}_2\text{P}_2\text{O}_7$  and  $\text{Ca}(\text{PO}_3)_2$  were calculated:

$$\Delta_f G^\circ(\text{Ca}_2\text{P}_2\text{O}_7) \pm 11/(\text{kJ} \cdot \text{mol}^{-1}) = -3475.9 + 1.5441(T/\text{K}) - 0.1051(T/\text{K}) \cdot \ln(T/\text{K}) \text{ and}$$

$$\Delta_f G^\circ(\text{Ca}(\text{PO}_3)_2) \pm 12/(\text{kJ} \cdot \text{mol}^{-1}) = -3334.8 + 6.1561(T/\text{K}) - 0.6950(T/\text{K}) \cdot \ln(T/\text{K}).$$

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**Keywords:** EMF measurements; Gibbs free energy of formation; Solid electrolyte; Auxiliary solid couple; Calcium phosphates

## 1. Introduction

A number of different elements constitute the condensed phases formed during combustion and gasification of biomass fuels. In addition to the traditionally studied major ash forming elements (Ca, K, Na, and Si), significant amounts of P is contained in many biomass fuels and sludges. However, often reliable thermodynamic data for ash species containing P are frequently lacking. To remedy this situation, we have initiated thermochemical studies of a number of phases in the system  $\text{CaO-K}_2\text{O-P}_2\text{O}_5$  by solid state EMF-measurements.

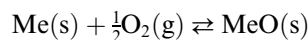
In the binary subsystem  $\text{CaO-P}_2\text{O}_5$ , reliable thermodynamic data are available in the literature for  $\text{CaO}$  [1],

$\text{Ca}_3(\text{PO}_4)_2$  [2] and  $\text{P}_2\text{O}_5$  [1]. Concerning the phases  $\text{Ca}_2\text{P}_2\text{O}_7$  and  $\text{Ca}(\text{PO}_3)_2$ , there are data in the literature [1,3–6] but of less certainty. The purpose of the measurements performed in this study was to provide improved Gibbs free energies of formation ( $\Delta_f G$ ) for  $\text{Ca}_2\text{P}_2\text{O}_7$  and  $\text{Ca}(\text{PO}_3)_2$ .

## 2. Experimental

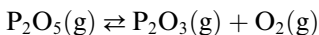
### 2.1. Method

At our department EMF-measurements of galvanic cells, involving yttria stabilised zirconia (YSZ) as solid electrolyte, have successfully been utilised in order to determine thermodynamic data for a large number of phases in metal oxide systems. A prerequisite is, however, the presence of oxygen participating in a redox-system, e.g.:

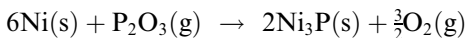


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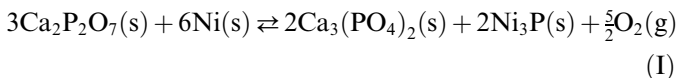
It is evident from equilibrium model calculations in the system P–O, that the following gas-phase reaction:



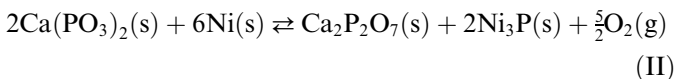
is ubiquitous at high temperatures. It was also found that  $\text{P}_2\text{O}_3(\text{g})$  would be the dominating species at low oxygen pressures (less than  $\sim 10^{-15}$  bar). When  $\text{Ni}(\text{s})$  is added to this system,  $\text{P}_2\text{O}_3(\text{g})$  is extracted from the gas phase to form  $\text{Ni}_3\text{P}(\text{s})$  according to the reaction:



Thus, if the solid phases  $\text{Ca}_2\text{P}_2\text{O}_7$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{Ni}$ , and  $\text{Ni}_3\text{P}$  are mixed and heated to higher temperatures, then the following equilibrium reaction will occur:



Analogously, the following equilibrium reaction involving the solid phases  $\text{Ca}_2\text{P}_2\text{O}_7$ ,  $\text{Ca}(\text{PO}_3)_2$ ,  $\text{Ni}$ , and  $\text{Ni}_3\text{P}$  can be derived:



The oxygen pressures ( $p_{\text{O}_2}$ ) obtained in these equilibria can be determined by EMF-measurements using YSZ as solid electrolyte. Once  $\lg(p_{\text{O}_2})$  values have been determined, the  $\Delta_r G^\circ$ -values can be calculated for equilibria (I) and (II) and subsequently the desired  $\Delta_r G^\circ$ -values, provided that two of the  $\Delta_r G^\circ$ -values in each equilibrium reaction are available.

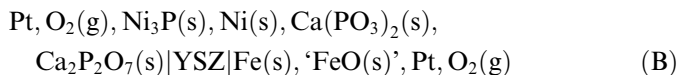
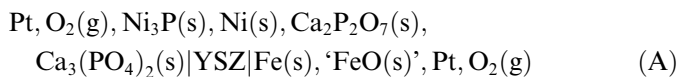
## 2.2. Materials and preparations

The chemicals used in the experiments were:  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  (Sigma 98%),  $\text{CaCO}_3$  (Riedel-de-Haën, 98%),  $\text{Fe}$  (Merck p.a.),  $\text{Fe}_2\text{O}_3$  (Fischer Scientific, Pittsburgh, PA),  $\text{Ni}$  (Merck) and  $\text{Ni}_3\text{P}$  (Aldrich). The reference system  $\text{Fe}/\text{FeO}'$  ( $\text{FeO}'$  denotes nonstoichiometric wüstite in equilibrium with solid iron) was synthesised by mixing powders of  $\text{Fe}$  and  $\text{Fe}_2\text{O}_3$ , in a ratio of 4:1 to achieve an equimolar ratio between  $\text{Fe}$  and  $\text{FeO}'$ . The reference mixture was placed in an alumina tube that was evacuated and heated to 1073 K.  $\text{Ca}(\text{PO}_3)_2$  was synthesised by dehydrating  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  at 673 K, whereas  $\text{Ca}_2\text{P}_2\text{O}_7$  was synthesised by dehydrating  $\text{CaHPO}_4$  at 1073 K.  $\text{CaO}$  was synthesised by calcinating  $\text{CaCO}_3$  at 1343 K.  $\text{Ca}_3(\text{PO}_4)_2$  was synthesised by mixing stoichiometric amounts of  $\text{Ca}(\text{PO}_3)_2$  and  $\text{CaO}$ , and heated at 1343 K for about 18 h.

All chemicals were analysed by X-ray diffraction (Bruker, D8Advance), verified against the Powder Diffraction File (PDF-2) [7], and were found to be pure within the limits of the diffractometer resolution ( $\leq 1\%$ ).

## 2.3. EMF cells and experimental procedure

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



The cell design used was a so-called closed “double-tube cell” (figure 1). The YSZ tube containing the sample was enclosed in an  $\text{Al}_2\text{O}_3$  tube containing the reference system  $\text{Fe}/\text{FeO}'$ , which was then evacuated. On top of the YSZ tube, a two-way valve was mounted to facilitate evacuation of the sample during the early stages of heating. The EMF potentials were measured between the inner electrode and the electrode wound around the outside of the YSZ tube. The outer electrode was always connected to the positive pole of the voltmeter. In a typical run, the cell was evacuated during an initial stage of heating up to 700 K, while measurements were performed between 900 K and 1140 K. The lower temperature value was chosen on the basis that below 900 K the reactions were too sluggish to reach equilibrium within a reasonable time while the choice of higher temperature was based on the eutectic/peritectic point, 1153 K, in the  $\text{Ni}$ – $\text{Ni}_3\text{P}$  subsystem. The measurements started at the higher temperature since equilibrium was faster achieved at that temperature. The measurements were performed by changing  $T$  stepwise, equilibrated for a minimum of 8 h for each step. After the run, the cells were

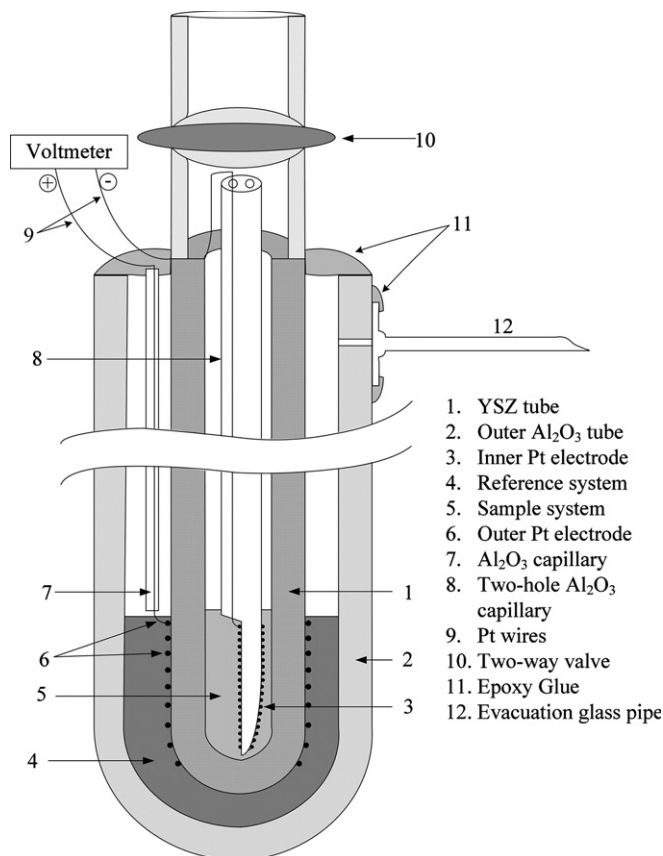


FIGURE 1. Schematic illustration of the closed “double-tube cell” arrangement.

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