Phase relations in the system MgO-NaCl-H₂O: The dehydroxylation of brucite in the presence of NaCl-H₂O fluids

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Abstract

The dehydroxylation of brucite was determined in the presence of NaCl-H₂O fluids containing 0, 2, 6, 11, 14, 18, 30, and 38 mol% NaCl (0.0, 5.5, 17.0, 28.8, 34.5, 41.7, 58.2, and 66.6 wt% NaCl) to ~2500 bars and ~700 °C by high-pressure differential thermal analysis (HP-DTA). At pressures below 150 bars, brucite dehydrates in two separate reactions involving at least one intermediate phase. The dehydroxylation reaction of brucite at pressure to ~2 kbars follows \(\ln P(\text{bars}) = 22.23 - 13620/T(\text{K})\). In the presence of NaCl-H₂O fluids, the dehydroxylation temperature is lowered because of the reduction of the activity of H₂O in these fluids. At 1 kbar pressure, mixing in the NaCl-H₂O fluids is virtually ideal, assuming a nearly complete association of NaCl, but at 2 kbars, the dissociation of NaCl is substantial. The phase relations in the system MgO-NaCl-H₂O show five univariant reactions emanating from an invariant assemblage, periclase + brucite + halite + liquid + vapor, located at 565 ± 5 °C and 440 ± 30 bars.

Introduction

Precise knowledge of the activity \(a_{H_2O}\) and the fugacity coefficient \(\Gamma_{H_2O}\) at elevated temperatures and pressures is important for studies of reactions involving H₂O. However, experimental information is limited, especially for concentrated electrolyte solutions at high temperatures and high pressures (Helgeson 1969; Helgeson et al. 1981; Bowers and Helgeson 1983; Oelkers and Helgeson 1991). Consequently, the activity and fugacity coefficients are simplified to unity in most thermodynamic calculations. Although this approach may be satisfactory for dilute fluids, it is not valid for concentrated fluids (e.g., Helgeson et al. 1981; Bowers and Helgeson 1983; Franz 1982). Using a theoretical approach, the activity and fugacity coefficients for the more concentrated fluids may be derived if some data are available. For example, Anderko and Pitzer (1993), using existing experimental data, obtained an equation of state for the system NaCl-H₂O, from which internally consistent values of \(a_{H_2O}\) and \(\Gamma_{H_2O}\) can be obtained for concentrated solutions. However, recent experimental results for this system (Aranovich and Newton 1996) indicate that the activity-composition relations may be much simpler than considered in previous models. Because no experimental data are available for many systems, further development of experimental methods to obtain information on the temperature-pressure-compositional \(PTX\) relations of aqueous systems remains essential.

In aqueous fluids, \(a_{H_2O}\) and \(\Gamma_{H_2O}\) may be determined experimentally at various \(P-T\) conditions by studying a univariant reaction in which H₂O is a participating component, by comparing the \(P-T\) conditions of this reaction in the presence of these fluids with the \(P-T\) conditions of the same reaction in the presence of pure H₂O. For example, Barnes and Ernst (1963), using the dehydroxylation reaction of brucite, determined the activity of H₂O in an H₂O-NaOH fluid. Likewise, Aranovich and Newton (1996) used the brucite dehydration reaction to determine \(a_{H_2O}\) of relatively concentrated NaCl-H₂O fluids at high temperatures and pressures to 15 kbars. More recently, \(\Gamma_{H_2O}\) in CaCl₂-H₂O fluids at elevated temperatures and pressures was obtained from a high-pressure differential thermal analysis (HP-DTA) of the dehydration of a Ca-exchanged montmorillonite in the presence of different CaCl₂-H₂O fluids (Wang et al. 1996). In the study presented here, we evaluate \(a_{H_2O}\) and \(\Gamma_{H_2O}\) in NaCl-H₂O fluids at pressures to 2500 bars using HP-DTA of the dehydroxylation reaction of brucite in the presence of these fluids. As in the work of Aranovich and Newton (1996), we selected the brucite dehydroxylation reaction because the solubility of MgO and Mg(OH)₂ in these fluids is very small (Walther 1986; Grabman and Popp 1991) and because the \(P-T\) conditions of this reaction are reasonably well established. Nevertheless, because we use this reaction as a baseline in this DTA study, it was necessary to assess the \(P-T\) relations of the brucite dehydroxylation at similar conditions.

Previous work

The reaction Mg(OH)₂ ⇌ MgO + H₂O has been investigated extensively, using quench methods (Kennedy 1956; Roy and Roy 1957; Fyfe 1958; Fyfe and Godwin 1962; Meyer and Yang 1962; Barnes and Ernst 1963; Aranovich and Newton 1996) and DTA techniques (We...