

Thermodynamic study of the $\text{CaSO}_4\text{-H}_2\text{O}$ solid-gas transformations: How much water does calcined gypsum contain?

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Gypsum is the mineralogical used term to describe materials that are mainly constituted of calcium sulfate dihydrate ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$). The calcination of gypsum, i.e. the dehydration of gypsum under solid-gas conditions, is of great technological importance because it represents the main industrial process for the production of plaster, the inorganic material with the largest production in the world. Plaster, in turn, is mainly constituted of calcium sulfate hemihydrate ($\text{CaSO}_4\cdot 0.5\text{H}_2\text{O}$). In spite of the significance of these materials for this and other scientific fields, some important aspects of the chemical system $\text{CaSO}_4\text{-H}_2\text{O}$ are still unknown. In particular, the water content within the gypsum calcination products is only partially described in the literature. [1,2].

This absence of a complete understanding of this system despite its importance and the fact that these materials have been used since antiquity can be attributed to several phenomena that contribute to its complexity. First of all, the literature acknowledges the existence of several calcium sulfate polymorphs. For instance, the dehydration of gypsum can lead to different calcium sulfate hydrates of the form $\text{CaSO}_4\cdot \varepsilon\text{H}_2\text{O}$, where ε can be 0.625, 0.5, or 0, depending on the temperature (T) and water vapor partial pressure (P) under which the reaction takes place. [3,4] Moreover, these compounds can also present zones of divariance, i.e., domains where the overall water content of these hydrates can change continuously with T and P. [5] The fine knowledge of the stability domain of each species throughout successive thermal transformations of the $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ is still debatable.

In this context, the objective of the present work is to determine the stability conditions and domains for the $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ dehydration products. Furthermore, the nature of the divariant behavior is also investigated. Thermogravimetric analysis under isotherm and isobaric conditions using different protocols with temperature ranges of 30°C to 250°C and water vapor partial pressure ranges of 5 hPa to 60 hPa was performed. The results allowed the determination of two zones of divariance and one univariant domain. The variations of the measured water contents in contrast with the stoichiometry of each polymorph were interpreted with models adapted for each zone. Finally, a phase diagram P-T is proposed based on the stability domain of each phase, and values of change in enthalpy and entropy of reaction were obtained for each transformation and compared with previously published values. [6]

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