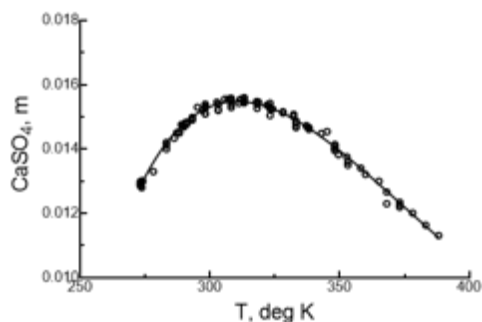


Establishing a reliable base for an internally consistent set of aqueous mineral thermodynamic properties: the system $\text{CaSO}_4\text{—H}_2\text{O}$

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The reliability of geochemical codes depends on the quality of the database for equilibrium constants, activity coefficients, and temperature and pressure dependent parameters. There are numerous compilations of thermodynamic data, but only a few have incorporated critical evaluations of the original papers (e.g. NBS tables, JANAF tables, CODATA, NEA/TDB). Thermodynamic properties encompass large networks of interconnected data such that an improvement in any one property will affect several others. Rarely has the starting point(s) for the network been adequately addressed in these assessments. I have chosen the system $\text{CaSO}_4\text{—H}_2\text{O}$ as a base or anchor for aqueous mineral reactions because there are some 300 papers on the gypsum, anhydrite, and bassanite solubilities as a function of temperature, many of them are of high quality, and there are direct pathways to other minerals to form an internally consistent network. Currently we have fit the gypsum solubility data as a function of temperature to a thermodynamic function by a nonlinear weighted multiple regression.



High-quality conductivity measurements have also been fit for 0-75°C from which the stability constant for the neutral ion pair was derived. The temperature-dependence of the activity coefficients for Ca^{2+} and SO_4^{2-} ions was derived from dilution enthalpies to derive a more reliable K_{sp} for gypsum solubility. From the carefully evaluated portlandite solubility, the thermodynamic properties of the Ca^{2+} ion can be derived. CODATA is the best source of properties for the SO_4^{2-} ion. From these the properties of gypsum are derived with greater accuracy and precision than from calorimetric measurements.