

## Experimental Challenges to the Theory of High Pressure Geofluids

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Our group is undertaking systematic studies of the high-pressure thermodynamics of aqueous solutions, of salts (NaCl, Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, MgCl<sub>2</sub>), of ammonia and of carbon dioxide, as well as pure fluid water from 250 K to 700 K. Speeds of sound, phase boundaries, and miscibilities have all been determined with high accuracy. While much of the work has utilized the diamond anvil cell, at pressures up to 700 MPa high compressibilities necessitate the use of a conventional pressure vessels with suitably accurate pressure gauges. In this apparatus, speeds of sound are measured with a reproducibility of 0.02%, allowing the calculation of all thermodynamic properties, including chemical potentials of the solutes. A determination of the miscibility surface of the carbon dioxide/water system, and the observed departure from published equations of state, led to the hypothesis of a significant change in speciation at higher pressures. This has now been confirmed, with measurements showing a complete absence of the CO<sub>2</sub> molecule in these solutions. These measurements provide a new framework for modifying methods to describe aqueous solution chemistry at higher pressures. In particular, conventional notions for the behavior of the “standard state” and “excess” quantities can be revised.