

"Cenotectic": On the Equilibrium Limit of Liquid Stability in Aqueous Systems

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Phase stability, and the limits thereof, are a central concern of materials thermodynamics. However, the temperature limits of equilibrium liquid stability in chemical systems have only been widely characterized under constant (typically atmospheric) pressure conditions, whereunder the limit is represented by the eutectic. At higher pressures, this limit will shift in both temperature and chemical composition, opening a wide thermodynamic parameter space over which the absolute limit, i.e., the limit under arbitrary values of the thermodynamic forces at play, might exist. In this work, we use isochoric freezing to measure this absolute limit for the first time in several binary aqueous brines, and, nodding to the etymology of “eutectic”, we name this limit the “cenotectic” (from Greek “κοινόζ-τηξιζ”, “universal-melt”). We observe that when no solute-bearing high-pressure phases exist, the cenotectic occurs consistently $22 \pm 2\text{K}$ below the 1 bar eutectic and at approximately $213 \pm 3\text{ MPa}$, suggesting domination by the liquidus behaviors of the icy phases present. In charting the T-P evolution of each eutectic configuration, we also encounter several unreported high-pressure hydrates of NaHCO_2 , MgCl_2 , and NaCl , and we find that these high-pressure phases can produce complex multi-phase configurations involving the liquid that may remain metastable to significantly lower temperatures. We discuss the implications of these findings for ocean worlds of our solar system and cold ocean exoplanets; estimate thermodynamic limits on ice crust thickness and final ocean depth (“end-game”) using the cenotectic pressure; and finally provide a generalized thermodynamic perspective on (and definition for) this new fundamental thermodynamic invariant point.