

Redefining the phase diagram of carbon dioxide within the quasi-harmonic approximation

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The experimental study of the CO₂ phase diagram is hampered by strong kinetic effects leading to wide regions of metastability and to large uncertainties in the location of phase boundaries. Here we determine the CO₂ phase boundaries by means of ab-initio calculations of the Gibbs free energy of several molecular and non-molecular solid phases of CO₂. Temperature effects are included in the quasi-harmonic approximation. Contrary to previous results, we find that the boundary between non-molecular phases and phase V has a positive slope and starts at 21.5 GPa at T = 0 K. A triple point between phase IV, V, and the liquid phase is found at 35 GPa and 1600 K, indicating a broader region of stability for the non-molecular phases than previously thought. The experimentally determined boundary line between CO₂-II and CO₂-IV is reproduced by our calculations, indicating that kinetic effects are not relevant in that transition.

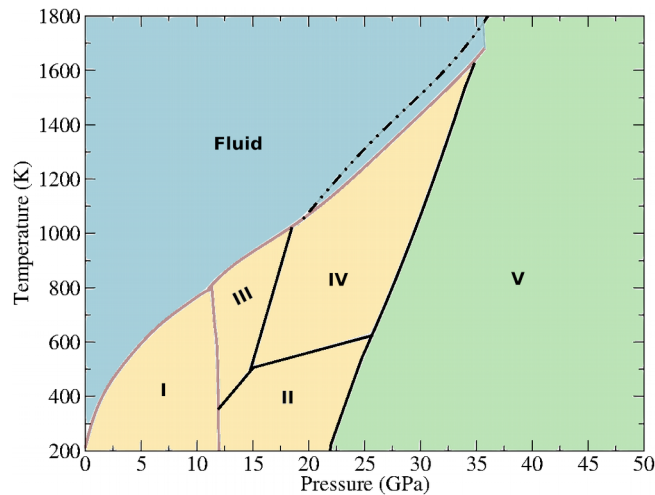


Fig. 1. Theoretical phase diagram for carbon dioxide at high pressure and temperature.

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