

# High-Pressure Phase Equilibria: Current State, Gaps, and Research Perspectives

## 1. Experimental Techniques and Measurements

The accurate determination of phase equilibria under high-pressure (HP) conditions remains a cornerstone of thermodynamics applied to chemical engineering and energy systems. Several experimental methodologies have been developed and refined:

- **Static analytical cells** provide reliable measurements by filling a cell with known composition and sampling after equilibrium is reached. Despite their robustness, these methods are time-consuming and prone to sampling errors (Griffiths, 2003; Kolstad & Goodwin, 2016).
- **Dynamic and recirculation methods** allow faster attainment of equilibrium, particularly for multicomponent systems, through controlled flow and mixing (Dohrn & Gillespie, 2002).
- **Synthetic and optical methods**, based on visual or spectroscopic detection of phase boundaries, are increasingly automated and suitable for HP conditions (Dohrn & Nagy, 1999).
- **Density measurements**, often performed with vibrating-tube densimeters, are essential for  $P$ - $\rho$ - $T$  characterization and for supporting EOS development (Wagner & Pruss, 2002).
- **In-situ spectroscopy** (Raman, FTIR) is gaining traction to directly analyze phase compositions without sampling biases (Vega-Maza et al., 2013).
- At extreme pressures and temperatures, **diamond-anvil cells combined with synchrotron or neutron diffraction** are used in geoscience and materials science (Hemley & Mao, 1998).

Recent trends include **integrated platforms** combining VLE, density, and transport property measurements, as well as increasing automation for higher data throughput.

## 2. Modeling Approaches

The modeling of HP phase equilibria is dominated by several families of equations of state (EoS):

- **Cubic EoS** (Peng-Robinson, SRK and variants) remain widely applied in industry due to their robustness and computational efficiency, despite limitations for strongly associating or polar systems (Peng & Robinson, 1976).
- **SAFT-based EoS** (PC-SAFT, CPA) provide improved molecular-level descriptions, especially for associating and polar fluids (Gross & Sadowski, 2001; Hendriks et al., 2010).
- **Multi-parameter EoS** such as Span-Wagner for  $\text{CO}_2$  (Span & Wagner, 1996) and GERG-2008 for natural gas mixtures (Kunz & Wagner, 2008) are used when high accuracy is required.
- **Molecular simulations** (GCMC, MD) are increasingly applied for systems lacking experimental data, offering molecular-level insights into solvation, association, and phase separation (Frenkel & Smit, 2001; Vrabec et al., 2009).
- **Hybrid physics-machine learning approaches** are emerging, coupling EoS with data-driven corrections and uncertainty quantification (Young & Tiwary, 2022; von Solms et al., 2022).

# Current Perspectives In High Pressure Biology

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