Comparison of Experimental Gas Hydrate Equilibrium Data Obtained from an Isochoric Method and High-Pressure Calorimetry for Pressures Up to 100 MPa

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Gas hydrates are solid structures formed by low molecular weight gas molecules and water that associate under certain conditions of pressure and temperature. The interest in studying the formation and dissociation mechanisms of these compounds lies on different areas, such as flow assurance of oil and gas production, water purification, capture and sequestration of CO2, or even also in the possible use of these hydrates as an alternative energy resource. Although there are many studies in the literature involving phase equilibrium of hydrates, there are limited experimental data at extreme conditions of pressure and considering a wide range of gas composition, mainly due to equipment limitations. The two most applied methodologies to study hydrate phase equilibrium are with the isochoric method and calorimetry. This work presents new equilibrium data and compares hydrate dissociation temperatures obtained from both methodologies for pressures up to 100 MPa, using a high pressure PVT cell and a calorimetric configuration based on HP- μ DSC. Drawbacks for each one are highlighted, and results are also compared to predictions from the van der Waals and Platteeuw model. Two different systems were studied: pure methane and a gas mixture of methane and propane. For the gas mixture system, results from both methodologies showed evidences of simultaneous formation of structures sI (methane hydrate) and sII (methane-propane hydrate), most likely due to the excess methane. This phenomenon is not predicted by the thermodynamic models but likely could occur on hydrate reservoirs and oil pipelines.