# Measurements of Solidification Kinetics for Benzene in Methane at High Pressures and Cryogenic Temperatures

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Production of liquefied natural gas (LNG) requires low temperatures (down to 111 K). At such conditions, low concentration impurities (100 ppm and below) in the process fluid can solidify (“freeze-out”), resulting in blockages and/or damage to downstream equipment. These impurities include BTEX compounds (including benzene), water and CO2. While tuned thermodynamic models can be used to predict solid-fluid equilibrium conditions, little is known about the kinetics of solid formation for LNG-relevant production conditions. To address this knowledge gap, a stirred, high-pressure, visual, microscopy-based apparatus has been developed and subsequently used to investigate solid-formation kinetics in LNG-relevant binary mixtures. The apparatus can detect solid crystals as small as 20 µm in a 3.5 mm field of view at temperatures down to 90 K and pressures up to 20 MPa, enabling measurement of solidification onset of low ppm impurities in LNG-relevant mixtures. In this presentation we will describe the apparatus and then present results focused primarily on solid benzene formation kinetics in a 100 ppm benzene-in-methane sample at pressures of (8 and 10) MPa. Benzene solid formation is demonstrated to be stochastic, with multiple repeat experiments demonstrating that formation onset occurs over a range subcooling values (from (4.4 to 11.0) K during cooling ramps of (0.5 – 1) K/min). From these results, a formation-probability distribution is generated and fit to a model based on Classical Nucleation Theory. This yields an estimate of 5 mJ/m2 for the effective surface free energy of solid benzene in liquid methane on the measurement cell’s copper base. We will also discuss the application of this apparatus to other systems and show how these results pave the way toward quantitative probabilistic risk estimates for solid formation in cryogenic heat exchangers.