Nucleation Rates of Carbon Dioxide Gas-Hydrates

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The formation of gas hydrates is one of the challenges in plant operation under conditions of elevated pressures, humidity, and low temperatures. Furthermore, applications like the sequestration of carbon dioxide, basic understanding of processes in the oil industry and natural gas processing are the most prominent applications, which urgently require a profound knowledge of the physico-chemical aspects of the underlying mechanisms. Unfortunately, basic research on the kinetics of hydrate formation taking into account the different aspects of equilibrium thermodynamics and the kinetics of phase transitions is scarce. This contribution summarizes different experimental approaches to determine the formation of gas hydrates. Advantages and disadvantages of these techniques are explicated and discussed in the light of investigations on nucleation. Against this background, we have characterized onset conditions of the formation of gas hydrates from carbon-dioxide saturated water and have determined characteristic times and nucleation rates for different degrees of supersaturation. Such specific types of experiments should contribute to the understanding of the basics of hydrate formation. For this purpose, a set of experiments has been performed using a high pressure apparatus suitable up to pressures of p = 700 bar. The setup consists of two independent parts, which allow for a preparation of binary mixtures under defined conditions and rapid kinetic studies of phase transitions induced by fast pressure changes, respectively. This concept allows an independent control of temperature and pressure without a change of the composition of a sample. Results indicate a strong variation of induction times or even nucleation rates of hydrate formation at different degrees of supersaturation and are discussed in terms of classical nucleation theories.