

Development of a novel experimental apparatus for hydrate equilibrium measurements



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ABSTRACT

A novel experimental apparatus was designed and constructed for measuring the three-phase equilibrium conditions of pure gas and gas mixture hydrates. The experimental apparatus can operate at pressures up to 20 MPa. The different parts of the experimental set-up are discussed and analyzed. Calibration issues are addressed and validation experimental measurements are reported at pressure conditions below 10 MPa for the case of pure gas hydrates. In addition to measuring the three-phase equilibrium pressure and temperature conditions with the current experimental apparatus, liquid phase analysis measurements are reported. In particular, the solubility of the gas in the aqueous phase is measured under three-phase equilibrium conditions. Gases of interest to the current study include CH₄ and CO₂. Both gases are of significant importance in industrial gas-storage and transportation applications, as well as gas-mixture separation applications.

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1. Introduction

The accurate knowledge of the pressure/temperature and composition conditions under which three-phase hydrate equilibrium can occur for hydrate-forming pure gases or gas mixtures is of significant importance [1,2] for a number of applications of practical interest (i.e., flow assurance [3,4], gas storage and transportation of “energy-carrier” gases [5–7] or “greenhouse” gases [8,9], gas-mixture separation [10–12], exploitation of future energy sources [13–16]), climate change [17,18], and geologic hazard [19,20]).

Such information can be acquired following a number of approaches [1]. In particular, simulations at the molecular (atomistic/microscopic) scale [21], including Molecular Dynamics (MD) [22–26] and Monte Carlo (MC) [27,28] simulations can be used. Note however, that such approaches require significant computational power and are not recommended for routine applications. On the other hand, at the macroscopic (continuum) scale, equations of

state (EoS), coupled with the van der Waals – Platteeuw statistical theory [29] have been used routinely to perform engineering calculations for practical industrial applications [30–38]. This type of approach is computationally much faster than performing molecular simulations; however, in order to increase its accuracy it requires the existence of experimental measurements that are used for model-calibration purposes (i.e., in order to calculate accurately hydrate equilibrium pressures or temperatures it is required to optimize the Kihara parameters using three-phase hydrate equilibrium experimental data). Finally, experimental measurements can be performed [1] in order to obtain the three-phase hydrate equilibrium conditions which are time-consuming, as well as costly processes, given the range of conditions and the possible number of mixtures that can be of practical interest.

When hydrate-forming systems are under three-phase equilibrium conditions (i.e., H–L_w–V or H–I–V) the following three phases are present: solid hydrate (H), vapor (V), and liquid (L_w) H₂O or ice (I). For some particular cases that exhibit an upper quadruple point (Q₂) the three-phase equilibrium conditions can be of the following type H–L_w–L_g where the vapor phase (V) is now replaced by a second liquid phase (L_g). Such an example is the case of CO₂ [1] (in that case subscript g is replaced by CO₂). In either case, the presence of the third solid phase (H) is a source of additional

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difficulties during experimental measurements when compared to the simple case of fluid phase equilibria, either vapor–liquid (VLE) or liquid–liquid (LLE) equilibria.

The main objective of the current study is to design, construct, and test/validate an experimental apparatus that can successfully perform the following two tasks:

- Measure the pressure (P) and temperature (T) conditions during three-phase ($H-L_w-V$ or $H-L_w-L_g$) equilibria of pure gases, and
- Perform quantitative analysis of the liquid phase (i.e., solubility measurements) that is under three-phase ($H-L_w-V$ or $H-L_w-L_g$) equilibrium conditions.

Experimental data that are related to the first task are routinely reported in the literature by standard experimental studies. For example, Sloan and Koh [1] provided a detailed list of experimental measurements and techniques, and a detailed archive of hydrate experimental measurements is presented by NIST [39]. Eslamimaneh et al. [40] reported an extensive review of experimental hydrate studies that are of interest to applications related to gas mixture separation.

On the other hand, the second task is significantly more complicated and, therefore, only a limited number of studies (i.e., when compared to those related to the first task) have been reported that proceed to address the particular issue of measuring the hydrate guest solubilities in the liquid phase [41–57]. While the majority of those experimental studies focus on the measurement of the guest–gas solubilities of pure gas hydrate systems [41–51], a limited number of studies focus on the measurement of solubilities of gas–mixture hydrate systems [52–57].

In a related context, Belandria et al. [58,59] determined the hydrate temperature and pressure dissociation conditions of binary gas mixtures (i.e., $CO_2 - CH_4$ [58], and $CO_2 - N_2$ [59]), and obtained the gas-phase composition using gas chromatography (GC). Finally, the composition of the liquid and hydrate phases were calculated using the material balance approach that was proposed by Ohgaki et al. [60]. In a recent study by Tsimpanogiannis et al. [61], the computational aspects of calculating solubilities under hydrate-forming conditions of pure gases and the related theoretical studies were reviewed.

In this work, a new experimental apparatus was designed and built for measurements of hydrate phase equilibria. The paper is organized as follows: Initially, the design of the experimental apparatus is presented and the various parts are described in detail. Subsequently, we describe the experimental procedure that is followed during the experiments, along with the methodology to calculate the gas solubilities in the liquid phase. Finally, we present the experimental measurements for the case of pure CO_2 and CH_4 hydrates and comparison with available experimental values from the literature (Sloan and Koh [1] in their review book report a detailed list of experimental measurements for the case of pure CH_4 or CO_2 hydrates). The good agreement of the measurements and the reported values validate the new experimental apparatus.

2. Experimental

2.1. Apparatus design

A detailed schematic diagram of the constructed high pressure PTV apparatus inside the air bath, along with the gas preparation manifold is shown in Fig. 1, while Fig. 2a shows an overview picture of the actual equipment. In the subsequent sections a more detailed discussion of the various parts of the experimental apparatus is presented.

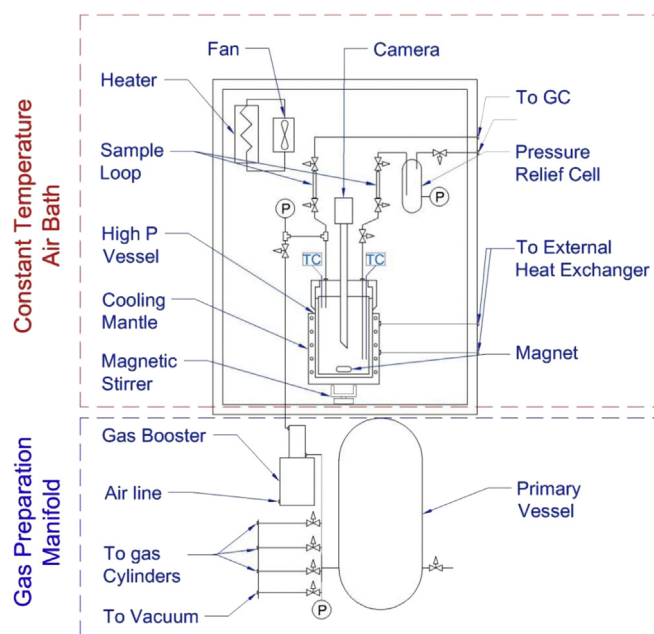


Fig. 1. Schematic diagram of the designed high pressure PVT device and the gas preparation manifold. The top part of the diagram shows the design of the equipment inside the constant-temperature air bath, while the bottom part shows the design of the gas-mixture preparation manifold.

2.1.1. Gas preparation manifold

The manifold of the device (see the bottom part of Fig. 1 for a schematic diagram, and Fig. 2a for an overview picture), is the system where a gas mixture of the desired composition can be prepared. It consists of 4 toggle valves (HOKE), one reservoir vessel (Primary vessel) having a volume of 24 L and maximum operating pressure of 1.2 MPa, one electronic pressure transducer (WICA D-10) for low pressures (PT1) up to 2 MPa (with a measurement precision of $\delta P = \pm 0.002$ MPa), the pilot air valve (Swagelok) for the gas booster, and the gas booster (JULY GB25) with a pressure-multiplying ratio of 20. One of the toggle valves is connected to a turbomolecular pump (Edwards EXT250) assisted by a rotary pump (Edwards E2M2) and facilitates the evacuation of the reservoir vessel down to a pressure of 10^{-9} MPa. The 3 additional toggle valves are connected to the gas cylinders equipped with pressure regulators (Linde) up to 1 MPa. With the aid of the pressure transducer, a gas phase of known composition consisting of 1, 2, or 3 gases can be prepared in the primary vessel. Taking into account the volumes of the PVT cell and the Primary vessel, the required starting pressure of the vessel (P_{fill}) can be calculated in relation to the desired equilibrium pressure in the PVT cell (P_{cell}) as follows: $P_{fill} = P_{cell} \times 0.0125 + 0.75$ (MPa). This implies that if the desired equilibrium pressure is 20 MPa, the required starting pressure in the Primary vessel is 1 MPa. The booster receives the feed pressure from the vessel and has the capacity to multiply it by a factor of 20 in relation to the pressure of the pilot air.

2.1.2. Thermostated air cabinet

The PVT cell, 7 high pressure (24 MPa) diaphragm valves (Swagelok), 2 additional electronic pressure transducers (WICA D-10), namely a high pressure transducer (PT2) for pressures in the range 0–20 MPa (with a measurement precision of $\delta P = \pm 0.02$ MPa), and a low pressure transducer (PT3) for pressures in the range 0–1 MPa (with a measurement precision of $\delta P = \pm 0.001$ MPa), the gas and liquid sampling loops (SL) having accurately defined volumes, and one pressure relief cell for the

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