



Isothermal method for hydrate studies using a transparent variable volume cell

P. T. Ngema,¹ W. M. Nelson,¹ P. Naidoo,¹ D. Ramjugernath,¹ and D. Richon^{1,2,a)}

¹*School of Engineering, Thermodynamics Research Unit, University of KwaZulu Natal, ZA-4041 Durban, South Africa*

²*School of Science and Technology, Department of Biotechnology and Chemical Technology, Aalto University, Aalto 00076, Finland*

(Received 7 January 2014; accepted 6 April 2014; published online 29 April 2014)

The measurements of hydrate dissociation points are generally achieved using the well-established isochoric method. This method implies determination of the total pressure of the system under study, as a function of temperature. It is quite time consuming, especially at higher pressures. Working at higher pressures requires equilibrium cells with thicker walls, which compromises on fast heat exchange. The use of a variable volume cell is therefore quite attractive as it allows for the measurements of hydrate dissociation pressure under isothermal conditions. This paper describes a transparent variable volume cell used for efficient and rapid measurements via the isothermal procedure. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4871587>]

I. INTRODUCTION

Gas hydrate technology is a reversible approach in which pressurized gas and water are combined forming a solid, called a gas hydrate or clathrate hydrate.¹ In gas hydrates, the gas molecules are trapped inside water cavities that are composed of hydrogen-bonded water molecules. During the last few decades, potential industrial applications of gas hydrate technology have gained considerable attention.¹⁻⁴ Examples are natural gas processing, storage and transportation, CO₂ sequestration, carbon dioxide (CO₂) capture from industrial/flue gases, steam reforming processes, hydrogen (H₂) storage, water desalination, etc. In order to reliably predict hydrate thermodynamic properties regarding potential industrial applications, engineers need reliable thermodynamic models based on accurate experimental equilibrium data. To date, the majority of existing models have been developed to cope with petroleum industry requirements (hydrocarbon systems). Consequently, model parameters must be reconsidered for hydrates containing other gas molecules using reliable phase equilibrium data.¹⁻⁵ It is necessary to keep in mind that any deviation in the measurement of hydrate phase equilibrium properties will lead to significant errors in model predictions. Therefore, measuring numerous and accurate experimental data on the phase behavior of pure and mixed clathrate hydrates is of utmost importance. A number of experimental devices and methods for measuring hydrate phase equilibrium for various systems reported in the literature have been reviewed by Sloan and Koh.¹ Classically, experimental methods involve measuring hydrate phase boundaries. For these purposes an isochoric pressure-search method⁶⁻⁸ is used to determine the hydrate temperature and pressure dissociation conditions. The drawback of this particular method is the time required to obtain P vs T graphs through temperature incremental steps (for full temperature decrease and increase). At

constant temperature, changing the volume of the system using a variable volume cell is much faster allowing rapid determination of hydrate pressure dissociation.

II. EXPERIMENTAL

A. Materials

The carbon dioxide (CO₂) used in this study was purchased from Afrox, with a manufacturer stated purity of 99.9%. Ultrapure Milli-Q water was used in this experiment. It had an electrical resistivity of 18 MΩ cm at 298.15 K.

B. Equipment

Figure 1 shows a schematic diagram of the new variable volume cell apparatus incorporating a novel stirring device used in this study. The equilibrium cell consists of a hollow cylindrical sapphire tube (manufactured by Rayotek Scientific) compressed and sealed, using nitrile o-rings, between two SS 316L metal flanges. The sapphire tube is 70.0 mm in height, with an outer diameter of 35.6 mm and an internal diameter of 17.8 mm. The thick walled design and the small internal diameter of the equilibrium cell allow it to withstand pressures up to approximately 200 bars (at 373 K). Observation of the liquid level and the gas hydrate formation and dissociation inside the equilibrium cell is easy due to the transparent nature of the sapphire cell. The maximum volume within the equilibrium chamber is roughly 10 cm³, due to displaced volumes (piston, mixing device, etc.). A Heidolph RZR 2041 overhead stirring device was used to drive the internal stirring mechanism. The top and bottom stirring devices were made using polytetrafluoroethylene (PTFE) and Neodymium magnets (manufactured by Supermagnete, Germany). The upper cylindrical PTFE mixer is magnetically coupled with the internal stirring shaft which passes through the upper part of the cell piston (see Figure 1). The internal stirring shaft is driven by the overhead

^{a)} Author to whom correspondence should be addressed. Electronic mail: richon.dominique@gmail.com.

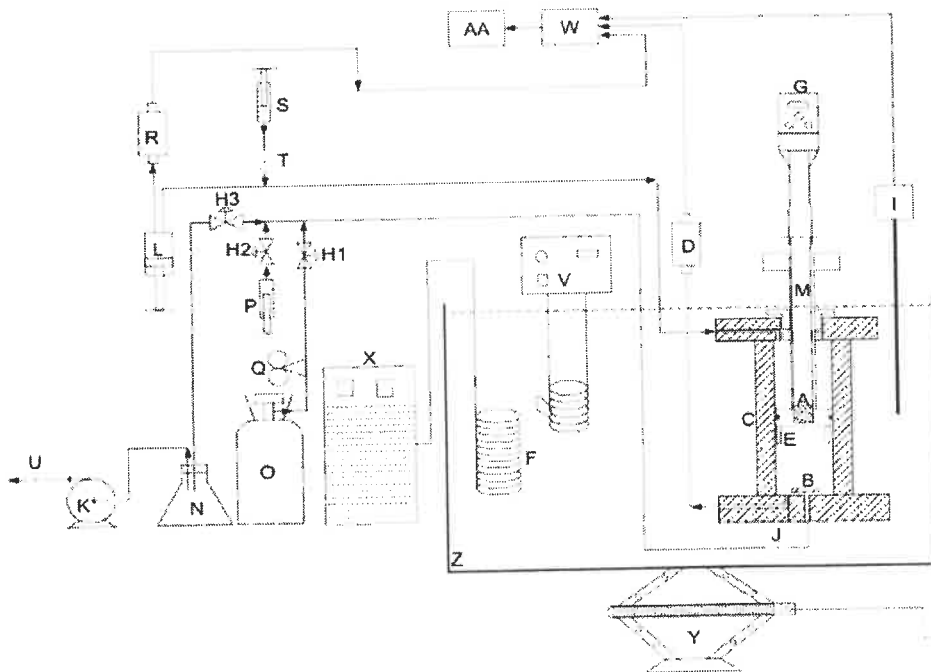


FIG. 1. Schematic flow diagram for new variable volume equilibrium cell; A, Neodymium magnet; B, magnetic stirrer bar; C, variable volume cell; D, pressure transducer for the cell; E, impeller; F, cooling coil; G, overhead mechanical stirrer; H₁, shut-off valve; I, Pt-100; J, drain or loading valve; K, vacuum pump; L, hydraulic cylinder; M, mechanical shaft; N, vacuum flask; O, refrigerant gas cylinder; P, liquid syringe with aqueous solution; Q, pressure regulator; R, pressure transducer for the hydraulic cylinder; S, hydraulic liquid; T, inlet valve for the hydraulic liquid; U, vent valve to atmosphere; V, temperature programmable circulator; W, data acquisition unit; X, cold finger; Y, mechanical jack; Z, water bath; AA, computer.

stirrer, which in turn drives the upper and lower cell mixers, see Figure 2 for stirrer details.

The temperature of the equilibrium cell is measured by two three-wire Pt-100s. The probes are inserted into the wells drilled into the top and bottom flanges that support and seal the sapphire tube. The probe tips are in very light contact with the metal flange just short of the equilibrium cell, thus, providing excellent representation of the equilibrium cell tem-

perature, and allowing for potential temperature gradients to be captured. The two Pt-100 temperature probes were calibrated using a thermo-regulated water bath and a WIKA primary temperature probe connected to a WIKA CTH 6500 multi-meter. The calibration uncertainty was ± 0.05 K. The combined uncertainties in the temperature measurements are ± 0.07 K and ± 0.074 K ($k = 2$), respectively. The pressure in the equilibrium cell was measured using a 0–10 MPa gauge

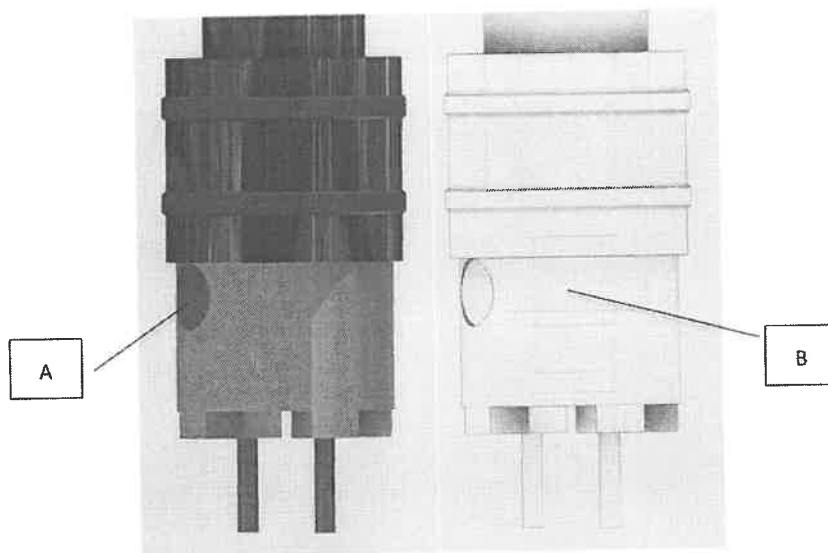


FIG. 2. Details of the stirrer: A, external magnet; B, internal magnet.

pressure transmitter (WIKA; model P10). The P10 pressure transmitter was calibrated against a 0–25 MPa WIKA CPT 6000 pressure transducer (stated accuracy of 0.025%). The combined uncertainty in the pressure measurement is estimated as ± 0.009 MPa ($k = 2$).

C. Experimental method

The dissociation conditions reported in this study were measured using an isothermal method. Prior to measurements the equilibrium cell was washed with acetone and evacuated to 0.2 kPa for a period of 30 min to ensure the removal of trace impurities. A volume of 9 cm³ of water was filled into the cell. The variable volume cell was immersed into the temperature-controlled bath and the CO₂ transferred into the equilibrium cell. The contents within the cell were agitated by adjusting the speed overhead stirrer to 500 rpm. The cell contents were rapidly mixed to ensure that thermodynamic equilibrium was obtained. When the temperature and pressure readings were stable, within the uncertainties of their measurements, the equipment was ready for the first experiment. The fluid within the equilibrium cell was compressed by a hydraulic piston driven by a hand-pump (WIKA, model HD 250), see Figure 1. The pressure within the equilibrium cell was recorded as a function of system volume at constant temperature.^{9,10} The pressure was incrementally increased, by 100 kPa, every 2 min until the hydrate was formed. After the formation of hydrate, the pressure of the system was very carefully decreased using the hand-pump until complete dissociation of the hydrate crystals was achieved. This pressure was recorded at that point as dissociation pressure. To test for repeatability the measurement was repeated three times.

III. RESULTS AND DISCUSSION

The binary test system of CO₂ + water was studied at the pressure range between 1.746 and 3.788 MPa. A photograph of CO₂ hydrate as formed in the variable volume cell is shown in Figure 3.

The results reported in Table I are compared to literature data: Englezos and Hall,¹¹ Chun *et al.*,¹² Mohammadi *et al.*,¹³ and Strydom¹⁴ in Figure 4.

This was done to verify the reliability of the variable volume cell and the isothermal method used to obtain the gas hydrate phase data. The data for the binary test system for the CO₂ + water agree very well with the existing literature values, which confirms and provides confidence that the variable volume cell can be used to rapidly perform measurements for unpublished gas hydrate systems.

The total time to complete the formation and dissociation using isochoric equilibrium cell of Strydom¹⁴ was on average around 20 h. With the isothermal equilibrium cell incorporating the new stirring device the **total time can be reduced to 30 min** in order to obtain one dissociation pressure. This shows an impressive improvement compared to the isochoric equipment of Strydom.¹⁴

For best accuracy and time saving it is recommended to work in a small pressure range as close as possible to the



FIG. 3. Photograph of CO₂ hydrate.

dissociation pressure point through several small pressure increase and decrease around this point. Data points for the CO₂ + water test system were repeated at different stirrer speeds of 500, 700, 900, 1100, and 1500 rpm. This was done in order to obtain the optimum stirrer speed that can be used to operate the variable volume cell. It was found that the stirrer speed of 500 rpm was quite convenient. Therefore, all hydrate dissociation points for the CO₂ + water test system were studied at 500 rpm.

TABLE I. Hydrate dissociation data for the CO₂ + water system.

T (K)	P (MPa)
276.07	1.746
276.07	1.753
276.07	1.730
277.08	2.029
277.08	2.001
277.08	2.012
278.05	2.256
278.05	2.243
278.05	2.303
279.13	2.676
279.13	2.607
279.13	2.631
280.11	2.903
280.11	2.933
280.11	2.913
281.10	3.370
281.10	3.343
281.10	3.311
282.14	3.767
282.14	3.733
282.14	3.788

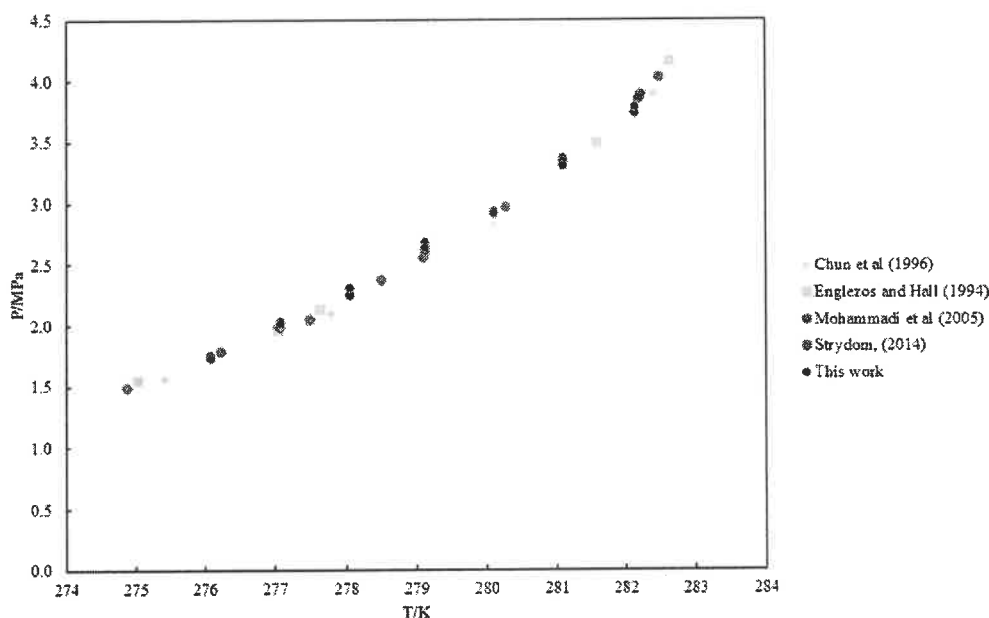


FIG. 4. Comparison of hydrate dissociation conditions for CO₂ + water system with respect to literature data.

IV. CONCLUSIONS

A new technique has been developed and successfully tested to measure hydrate dissociation pressures in the isothermal mode. The corresponding equilibration times are at least ten times shorter than that for the isochoric mode. Consequently, the isothermal method is much preferable provided a satisfactory variable cell is available in the operating conditions.

ACKNOWLEDGMENTS

D. Richon acknowledges the financial support of the University of Kwa-Zulu Natal (South Africa) and Aalto University (Finland).

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