

## EFFECT OF CLATHRATE STRUCTURE AND PROMOTER ON THE PHASE BEHAVIOUR OF HYDROGEN CLATHRATES

Antonin Chapoy, Ross Anderson, Bahman Tohidi \*  
Centre for Gas Hydrate Research, Institute of Petroleum Engineering  
Heriot-Watt University, Edinburgh, EH14 4AS  
UNITED KINGDOM

### ABSTRACT

Hydrogen is currently considered by many as the “*fuel of the future*”. It is particularly favoured as a replacement for fossil fuels due to its clean-burning properties; the waste product of combustion being water. While hydrogen is relatively easy to produce, there is currently a lack of practical storage methods for molecular H<sub>2</sub>, and this is greatly hindering the use of hydrogen as a fuel. Gases are normally stored in vessels under only moderate pressures and in liquid form where possible, which yields the highest energy density. However, to store reasonable quantities of hydrogen in similar volume containers, cryogenic temperatures or extreme pressure are required. Many potential hydrogen storage technologies are currently under investigation, including adsorption on metal hydrides, nanotubes and glass microspheres, and the chemical breakdown of compounds containing hydrogen to release H<sub>2</sub>. Recent studies have sparked interest in hydrates as a potential hydrogen storage material. The molecular storage of hydrogen in clathrate hydrates could offer significant benefits with regard to ease of formation/regeneration, cost and safety, as compared to other storage materials currently under investigation. Here, we present new experimental hydrate stability data for sII forming hydrogen–water (up to pressures of 180 MPa) and hydrogen–water–tetrahydrofuran systems, the structure-H forming hydrogen–water–methylcyclohexane system, and semi-clathrate forming hydrogen–water–tetra-*n*-butyl ammonium bromide/tetra-*n*-butyl ammonium fluoride systems.

**Keywords:** gas hydrates, hydrogen, tetrahydrofuran, methylcyclohexane, tetra-*n*-butyl ammonium bromide, tetra-*n*-butyl ammonium fluoride, experimental data

### NOMENCLATURE

P	Pressure [MPa]
T	Temperature [K]
H	Hydrate
I	Ice
I1	Ice I
I3	Ice III
I4	Ice IV
I5	Ice V
L	Liquid
MCH	Methylcyclohexane
Q <sub>1</sub>	Quadruple point (I+V+L+H)
sI	Structure-I
sII	Structure-II
sH	Structure-H

TBAB	Tetra- <i>n</i> -butyl ammonium bromide
TBAF	Tetra- <i>n</i> -butyl ammonium fluoride
THF	Tetrahydrofuran
V	Vapour

### INTRODUCTION

It is now widely accepted that anthropogenic CO<sub>2</sub> emissions from the burning of fossil fuels are largely responsible for the rapid rise in global temperatures recorded over the past century. Worldwide concerns over the threat of global warming have provoked industrialised countries into working to reduce carbon emissions, with specific targets being laid out in the 1997 Kyoto Protocol agreement. To meet these goals, nations

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\* Corresponding author: Phone: +44(0)1314 513 672 Fax +44(0)1314 513 127 E-mail: [Bahman.Tohidi@pet.hw.ac.uk](mailto:Bahman.Tohidi@pet.hw.ac.uk)

must increase investment in 'clean', renewable sources of energy, and develop solutions for reducing CO<sub>2</sub> (and other greenhouse gases) emissions from existing and new fossil fuel usage.

There are a variety of renewable, carbon-free options for energy generation, including hydroelectric, wind, solar, and wave power. Hydroelectric and wind technology (e.g. wind farms) are well developed and commercially viable, but expansion can be hampered by the availability of suitable sites and local environmental/ecological concerns. Solar and wave power require further development before they become competitive, and face similar location/logistical problems. Nuclear is currently a favoured option for many governments, and is billed as 'clean' due to negligible carbon emissions. However, public concerns over safety present a considerable stumbling block to development; these in part being fuelled by the lack of a concrete consensus on long term radioactive waste disposal solutions. A further major problem with nuclear power, and probably the biggest hurdle to immediate expansion, is the high cost and long construction time of nuclear power plants.

Hydrogen is currently considered by many as the 'fuel of the future'. It is particularly favoured as a replacement for fossil fuels due to its clean-burning properties; the waste product of combustion being water. Many processes can be used to produce hydrogen (e.g. steam reforming of natural gas, catalytic decomposition of natural gas, partial oxidation of heavy oil, coal gasification, steam-iron coal gasification, water electrolysis, thermo-chemical, photochemical, photoelectrochemical and photo-biological processes). While hydrogen is relatively easy to produce, there is currently a lack of practical storage methods for molecular H<sub>2</sub>, and this is greatly hindering the use of hydrogen as a fuel. Gases are normally stored in vessels under only moderate pressures (for safety), and in liquid form where possible (e.g. propane, butane), which yields the highest energy density. However, to store reasonable quantities of hydrogen in similar volume containers, cryogenic temperatures (liquid H<sub>2</sub> T<20 K) or extreme pressures (100's of MPa) are required. As a result, the widespread use of hydrogen as a fuel, particularly for non-stationary applications (e.g. powering motor vehicles), is currently restricted.

Many potential hydrogen storage technologies are currently under investigation, including adsorption on metal hydrides, nanotubes and glass microspheres, and the chemical breakdown of compounds containing hydrogen to release H<sub>2</sub>. Hydrogen storage in carbon structures and metal hydrides are currently the leading areas of research. While these are promising technologies, both still have considerable limitations (Sandí, 2004 [1]). Metal hydrides provide a potential safe, stable storage media, yet incur a large weight penalty and require very high temperatures (> 200 °C) to trap/release hydrogen. Absorption of H<sub>2</sub> in carbon microstructures requires much less extreme conditions, however consistent and commercially viable H<sub>2</sub> contents have yet to be achieved.

Recent studies have sparked interest in gas (or clathrate) hydrates as potential hydrogen storage materials [2-3]. When compressed into the cages of a clathrate hydrate, the distance between gas molecules can approach that of the liquid state, making for very high compression ratios. For example, 1 m<sup>3</sup> of sI methane hydrate can hold up to 175 m<sup>3</sup> of gas at standard conditions. This has led to considerable research into gas hydrates as a potential means for the storage and transportation of gases. However, for common sI and sII hydrates, either high pressures (10's of MPa) or low temperatures (subzero) are needed for stability, which introduces significant technical and operational costs. There have been various attempts to increase hydrate stability to lower pressures by employing hydrate 'promoters' (e.g., THF, propane). However, these 'promoters' occupy most of the large cavities, reducing the storage capacity. Until recently (and for the largely forgotten study of Villard, 1887 [4]), hydrogen was considered not to form gas hydrates due to its molecular diameter being too small to stabilise cavities. However, Mao et al. (2002) [2] demonstrated that pure hydrogen can form sII clathrate hydrates at very high pressures and low temperatures, sparking interest in hydrates as a potential hydrogen storage material. Florusse et al. (2004) [5] have subsequently shown that the pressure required to stabilise hydrogen in clathrates can be greatly reduced by adding a second guest 'promoter', namely tetrahydrofuran/THF (~5 MPa at 7 °C). The molecular storage of hydrogen in clathrate hydrates could offer significant benefits with regard to ease of formation/regeneration, cost and

safety, as compared to other current storage materials currently under investigation. However, it is now widely accepted that common clathrate structures (sI, sII, sH) cannot achieve H<sub>2</sub> storage goals. This leaves the option of investigating alternative new clathrate structures and their potential uses for H<sub>2</sub> storage and/or separation.

Here, we present new experimental hydrate stability data for sII forming hydrogen–water (up to pressures of 180 MPa) and hydrogen–water–tetrahydrofuran systems, the structure-H forming hydrogen–water–methycyclohexane system, and semi-clathrate forming hydrogen–water–tetra-*n*-butyl ammonium bromide/tetra-*n*-butyl ammonium fluoride systems.

## EXPERIMENTAL

Clathrate dissociation and/or ice melting PT conditions were determined by standard constant volume cell isochoric equilibrium step-heating techniques. This method, which is based upon the direct detection (from pressure) of bulk density changes occurring during phase transitions, produces very reliable, repeatable phase equilibrium measurements. [6]. Two set-ups were used; one for pressures up to 40 MPa and a second for pressures up to 200 MPa.

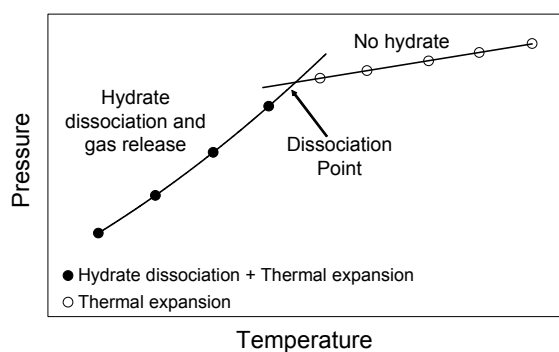


Figure 1 Dissociation point determination from equilibrium step-heating data. The equilibrium dissociation point is determined as being the intersection between the hydrate dissociation (gas release related pressure rise with increasing temperature) and the linear thermal expansion (no hydrate) curves

## Materials

Hydrogen was purchased from BOC gases with a certified purity greater than 99.995 vol. %. THF, from Prolabo, had a certified purity of 99.975 % min. Methylcyclohexane from Sigma-Aldrich had a certified purity 99.5%. Tetra-*n*-butyl ammonium

bromide (50 wt%) in water and tetra-*n*-butyl ammonium fluoride (75 wt%) in water were purchased from Sigma-Aldrich. Deionised water was used to dilute tetra-*n*-butyl ammonium bromide, dilute tetra-*n*-butyl ammonium fluoride and tetrahydrofuran to the different desired aqueous mass fractions used in experiments.

## Ultra-High Pressure Apparatus

The ‘ultra-high pressure’ hydrate set-up was used for tests up to 200 MPa. It comprises of a 45ml cell constructed of AISI 660 steel, which is compatible with many oilfield chemicals, including aqueous solutions containing salts and/or organic hydrate inhibitors. A schematic of the set-up is shown in Figure 2, which is pressure tested to 200 MPa. Cell temperature is monitored with a PRT (Platinum Resistance Thermometer) with the sensing part in contact with test fluids. Cell pressure is measured using a *Quartzdyne* pressure transducer accurate to 0.05 MPa. System temperature is controlled by circulating coolant from a cryostat through a jacket surrounding the cell. Mixing is achieved by rocking the cell through 180° using a compressed air-driven mechanism. To aid mixing, steel ball-bearings are placed inside the cell.

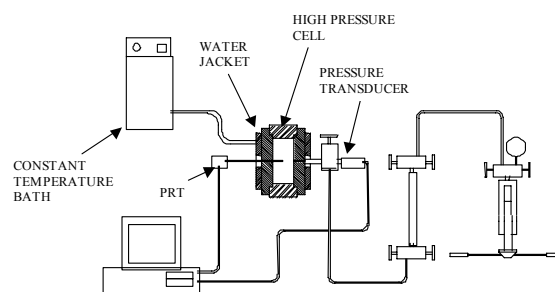


Figure 2 Schematic of ultra high pressure rig

## High Pressure Apparatus

Figure 3 shows the apparatus used to determine phase equilibrium conditions at pressures lower than 40 MPa. The set-up comprises of a 500 ml stainless steel cylindrical autoclave cell. Temperature control (0.1 K) is again provided by a circulating coolant/jacket system. A PRT determines cell temperature, while pressure is measured by means of a strain gauge transducer. To achieve rapid thermodynamic equilibrium through good mixing of the fluids, a magnetic

motor driven stirrer was used for agitation of fluids.

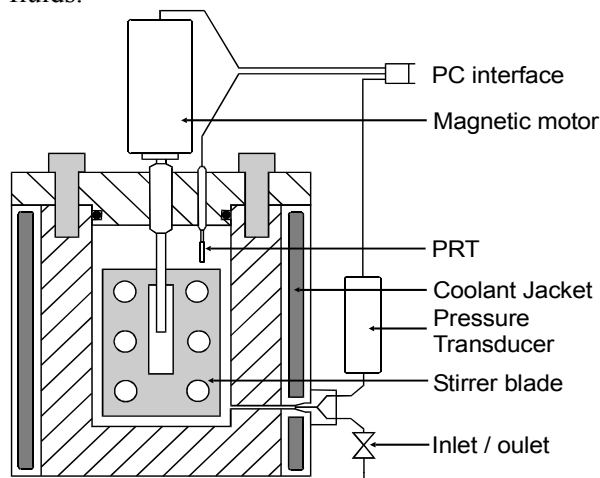


Figure 3 Schematic of high pressure rig

### Experimental Procedures

For the  $\text{H}_2\text{-H}_2\text{O}$  and  $\text{H}_2\text{-MCH-H}_2\text{O}$  systems, the ultra high pressure rig (200 MPa) was used. For all other systems, the high pressure autoclave set-up (40 MPa) was used. A typical test to determine the hydrate dissociation point of a system was as follows:

The equilibrium cell was first cleaned and vacuumed, then charged with the desired components. For the  $\text{H}_2\text{-THF-H}_2\text{O}$ ,  $\text{H}_2\text{-TBAB-H}_2\text{O}$  and  $\text{H}_2\text{-TBAF-H}_2\text{O}$  systems, the aqueous liquid solutions were first prepared to the desired concentration (19 mass%, 43 mass% and 35 mass%, respectively), loaded into the cell, then hydrogen injected directly from a high pressure cylinder to achieve the desired starting pressure.

For the  $\text{H}_2\text{-H}_2\text{O}$  system, half of the volume of the cell was initially preloaded with water, then hydrogen injected to achieve a pressure of 70 MPa. To attain higher pressures, water was subsequently injected using a high pressure hand pump. For  $\text{H}_2\text{-MCH-H}_2\text{O}$  tests, procedures were similar; water injection to pre-loaded systems being used increase pressures beyond 70 MPa.

For all systems, the cell temperature was set to a point well outside the expected hydrate stability zone for the system under study during loading. Temperature was then lowered to form hydrates; growth being detected by an associated drop in cell pressure (as gas becomes trapped in hydrate structures). Cell temperature was then raised step-

wise (usually  $0.5^\circ\text{C}$  intervals), allowing enough time at each temperature step for equilibrium to be reached (sometimes in excess of 24h for the  $\text{H}_2\text{-H}_2\text{O}$  system). At temperatures below the point of complete dissociation, gas is released from decomposing hydrates, giving a marked rise in the cell pressure with each temperature step (Figure 1). However, once the cell temperature has passed the final hydrate dissociation point, and all clathrates have disappeared from the system, a further rise in the temperature will result only in a relatively small pressure rise due to thermal expansion. This process results in two traces with very different slopes on a pressure versus temperature (P/T) plot; one before and one after the dissociation point. The point where these two traces intersect (i.e., an abrupt change in the slope of the P/T plot) is taken as the dissociation point (see Figure 1).

Following measurement of a single dissociation point, cell pressure was increased by injection of water (for the  $\text{H}_2\text{-H}_2\text{O}$  and  $\text{H}_2\text{-MCH-H}_2\text{O}$  systems) or hydrogen to reach the next desired condition, before the cycle was repeated to determine a further point on the phase boundary for the system.

### RESULTS AND DISCUSSION

Experimental clathrate hydrate dissociations were obtained for the binary system  $\text{H}_2\text{-H}_2\text{O}$  and for the ternary systems  $\text{H}_2\text{-MCH-H}_2\text{O}$ ,  $\text{H}_2\text{-THF-H}_2\text{O}$ ,  $\text{H}_2\text{-TBAB-H}_2\text{O}$  and  $\text{H}_2\text{-TBAF-H}_2\text{O}$ . Measured equilibrium hydrate dissociation conditions are reported in Tables 1-5, and plotted in Figure 4.

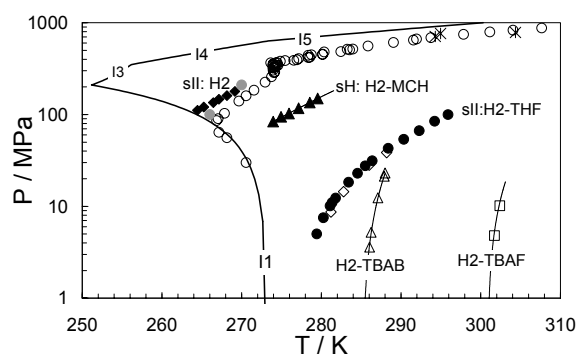


Figure 4 Effect of clathrate structure and promoter on the phase behaviour of hydrogen clathrates.

This work:  $\blacklozenge$ :  $\text{H}_2$ ;  $\blacktriangle$ :  $\text{H}_2\text{-MCH}$ ;  $\diamond$ :  $\text{H}_2\text{-THF}$ ;  $\triangle$ :  $\text{H}_2\text{-TBAB}$ ;  $\square$ :  $\text{H}_2\text{-TBAF}$ .  $*$ :  $\text{H}_2$ , data from Vos et al. [7]  $\circ$ :  $\text{H}_2$ , data from Dyadin et al. [8]  $\bullet$ :  $\text{D}_2$ , data from Lokshin and Zhao [9] ( $\text{D}_2\text{-D}_2\text{O}$  system);  $\bullet$ :  $\text{H}_2\text{-THF}$  data from Florusse et al. [5].

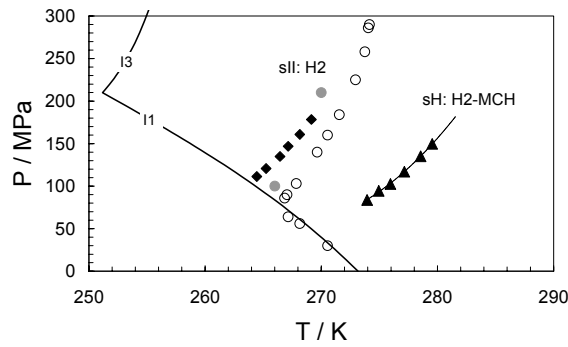


Figure 5 Experimental clathrate hydrate dissociation for the binary system  $\text{H}_2\text{-H}_2\text{O}$  (◆: this work; ○:  $\text{H}_2$ , data from Dyadin et al. [8] ●:  $\text{H}_2$ , data from Lokshin and Zhao [9]) and for the ternary system  $\text{H}_2\text{-MCH-H}_2\text{O}$  (◇: this work).

### $\text{H}_2\text{-H}_2\text{O}$ binary system

For the binary system  $\text{H}_2\text{-H}_2\text{O}$ , there is an obvious scattered in the clathrate hydrate dissociation point reported from different authors, deviations sometimes being in excess of 3 K (Figure 5). Dyadin et al. [8] stated that in some experiments, equilibrium states were not actually achieved, whereas Lokshin and Zhao [9] studied the  $\text{D}_2\text{-D}_2\text{O}$  system. In Figure 6, a typical dissociation point measurement is shown, hydrate dissociation is characterised by essentially congruent decomposition on the phase boundary.

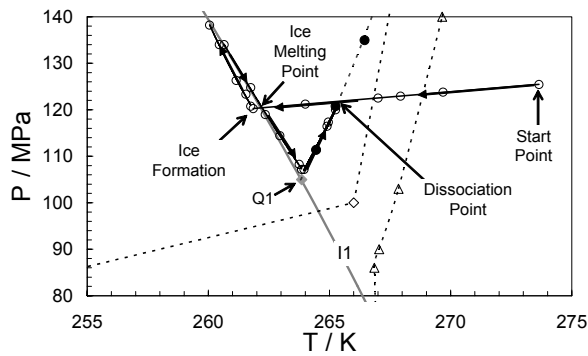


Figure 6 Typical clathrate hydrate dissociation point measurement for the binary system  $\text{H}_2\text{-H}_2\text{O}$  (○: equilibrium points; ◆: estimated  $Q_1$ ).

Experimental clathrate hydrate dissociation points:  
●: this work; △:  $\text{H}_2$ , data from Dyadin et al. [8]  
◇:  $\text{H}_2$ , data from Lokshin and Zhao [9].

The quadruple point,  $Q_1$  – where ice, vapour, liquid and hydrate coexist for this system ( $\text{I}+\text{V}+\text{L}+\text{H}$ ) – has been estimated. The point where the best fitted curve to our experimental data and

the ice I curve intersect is taken as the quadruple point (Figure 6).

$T_{\text{exp}} / \text{K}$ ( $\pm 0.1$ )	$P_{\text{exp}} / \text{MPa}$ ( $\pm 0.05$ )
269.15	178.41
268.15	160.76
267.15	146.80
266.45	134.97
265.25	120.75
264.45	111.38
$Q_1^\dagger$ : 263.85	105.00

Table 1. Experimental clathrate hydrate dissociation ( $\text{H}+\text{L}+\text{V} > \text{L}+\text{V}$ ) for the binary system  $\text{H}_2\text{-H}_2\text{O}$  ( $^\dagger$ Estimated)

The cage occupancy for this system has also been the subject of some debate. Mao et al. [2] were the first to report that hydrogen could form simple cubic structure-II clathrate hydrates at high pressures (200 MPa at 280 K) and/or cryogenic temperatures (145 K). Authors estimated a clathrate stoichiometry of  $\text{H}_2.2\text{H}_2\text{O}$  based on double  $\text{H}_2$  occupancy of all sixteen small pentagonal dodecahedral ( $5^{12}$ ) cavities, and quadruple occupancy of larger hexakaidecahedral ( $5^{12}6^4$ ) cavities, giving a maximum hydrogen storage capacity of 5 mass%. Subsequently, in 2004, Lovskin et al. [3] demonstrated that the hexakaidecahedral cage can hold up to four hydrogen molecules (2 to 4 depending on T and P), but the small pentagonal dodecahedral cage can hold only one hydrogen molecule, leading to a maximum hydrogen capacity of 3.77 mass%.

### $\text{H}_2\text{-MCH-H}_2\text{O}$ ternary system

By adding a second guest – the well-known structure-H former methylcyclohexane – it is possible to stabilize hydrogen in a clathrate structure at significantly lower pressures than those for pure structure-II hydrogen clathrate hydrates (Figure 5). Measured experimental equilibrium hydrate dissociation conditions for this system are reported in Table 2.

The structure-H unit crystal is made up of three small dodecahedron cages ( $5^{12}$ ), two medium irregular dodecahedron cages ( $4^35^66^3$ ), and one large icosahedral cage ( $5^{12}6^8$ ), in total requiring 34 water molecules. A theoretical  $\text{H}_2$  storage capacity can be estimated for this system assuming single occupancy of the small and medium cages by



hydrogen, and full occupancy of the large cage by MCH. The maximum hydrogen capacity for this guest configuration would be 1.38 mass%.

$T_{\text{exp}} / \text{K}$ ( $\pm 0.1$ )	$P_{\text{exp}} / \text{MPa}$ ( $\pm 0.05$ )
279.55	149.66
278.55	135.17
277.15	117.08
275.95	102.62
274.95	94.48
273.95	83.72

Table 2. Experimental clathrate hydrate dissociation ( $H+L+L_{\text{HC}}+V > L+L_{\text{HC}}+V$ ) for the ternary system  $H_2$ -MCH- $H_2O$

### $H_2$ -THF- $H_2O$ ternary system

Experimental clathrate hydrate dissociation for the ternary system  $H_2$ -THF- $H_2O$  has been measured with a stoichiometric THF to water ratio of 1:17 (Table 3).

The hydrogen content of binary  $H_2$ -THF hydrates has been the subject of some controversy. Lee et al. [10] claimed that the hydrogen content of sII  $H_2$ -THF clathrates could be greatly increased (up to ~4 mass%  $H_2$ ) at modest pressures (12 MPa) by “tuning” THF contents. Based on Raman, MAS NMR and volumetric measurements, authors argued that clathrate dodecahedral cavities could accommodate two  $H_2$  molecules, and, at initial aqueous THF concentrations below the atmospheric eutectic composition (~1.0 mole%), in the hydrate-ice-vapour region ( $H+I+V$ ) region, clusters of four hydrogen molecules could replace THF in large hexakaidecahedral cavities, whereby greatly increasing  $H_2$  content. However the most recent detailed study of  $H_2$ -THF clathrate hydrogen contents directly contradicts the findings of these authors; Strobel et al. [11], using volumetric measurements in conjunction with Raman and MAS NMR data, concluded that small cavities can only accommodate single  $H_2$  molecules, and that, irrespective of initial aqueous THF concentration and/or formation conditions, large cavities are always fully occupied by THF. A maximum hydrogen content of around 1 mass% was reported. Similarly, Anderson et al. [12] tried to replicate the work of Lee et al., and confirmed the findings of Strobel et al. [11], i.e. that no evidence for  $H_2$  entering and stabilising the large sII cavity under tested conditions was found.

These conclusions were also supported by the more recent work of Talyzin [13]. To date, the results of Lee et al. [10] have not been independently replicated.

$T_{\text{exp}} / \text{K}$ ( $\pm 0.1$ )	$P_{\text{exp}} / \text{MPa}$ ( $\pm 0.05$ )
281.20	8.69
282.80	14.46
286.00	28.15
288.20	38.58

Table 3. Experimental clathrate hydrate dissociation ( $H+L+V > L+V$ ) for the ternary system  $H_2$ -THF- $H_2O$  ( $w=19$  wt%)

### Semi-clathrate hydrates

Semi-clathrate hydrates share many of the physical and structural properties of classical clathrate hydrates (sI, II and H). Both hydrate classes comprise of a hydrogen-bonded water latticework based primarily around the pentagonal dodecahedra ( $5^{12}$ ) unit of structure. Structural variety arises from the way dodecahedra associate; face sharing or bonding between vertices adjusting to create a variety of interstitial multifaceted polyhedra for accommodation of (guest) gas molecules or ion pairs without significantly disrupting the hydrogen-bonding scheme of the water framework [14]. The principal difference between the two classes is that, in true clathrate hydrates, guest molecules are not physically bonded to the water lattice, rather they are stabilised within and lend stability to cavities through van der Waals interactions. In contrast, in semi-clathrates, guest molecules can both physically bond with the water structure and occupy cavities; for the quaternary (or peralkyl) ammonium salt semi-clathrates, the QAS hydrophobic cation takes a cage filling role, whilst the negatively charged anion is hydrogen bonded with water latticework [14,15]. Although semi-clathrates are primarily composed of water (often >95 mole%  $H_2O$ ), this configuration lends great thermal stability to structure, giving some semi-clathrates melting temperatures in excess of 303.15 K at atmospheric pressure.

<b>T<sub>exp</sub> / K (±0.1)</b>	<b>P<sub>exp</sub> / MPa (±0.05)</b>
286.05	3.60
286.25	5.23
287.10	12.41
287.90	21.29
288.00	23.07

Table 4. Experimental semi-clathrate hydrate dissociation ( $H+L+V > L+V$ ) for the ternary system  $H_2$ -TBAB- $H_2O$  ( $w=43$  mass%)

In this work, semi-clathrate hydrate phase equilibria were determined experimentally for  $H_2$ -TBAB- $H_2O$  and  $H_2$ -TBAF- $H_2O$  systems under hydrogen pressures up to 25 MPa over the temperature range 286 to 303 K (Tables 4 and 5). Figure 4 shows that binary  $H_2$ -QAS semi-clathrate hydrates demonstrate greatly increased thermal and low pressure stability when compared with  $H_2$  and binary  $H_2$ -THF clathrate hydrates. However, assuming full occupancy of the small-sized cage by hydrogen, the theoretical storage capacity is only 0.6 wt%.

<b>T<sub>exp</sub> / K (±0.1)</b>	<b>P<sub>exp</sub> / MPa (±0.05)</b>
301.73	4.81
302.40	10.13

Table 5. Experimental semi-clathrate hydrate dissociation ( $H+L+V > L+V$ ) for the ternary system  $H_2$ -TBAF- $H_2O$  ( $w=35$  mass%)

## CONCLUSIONS

We have presented new experimental hydrate stability data for sII forming hydrogen–water (up to pressures of 180 MPa) and hydrogen–water–tetrahydrofuran systems, the structure-H forming hydrogen–water–methycyclohexane system, and semi-clathrate forming hydrogen–water–tetra-*n*-butyl ammonium bromide/tetra-*n*-butyl ammonium fluoride systems. This data provides better delineation of hydrogen stability fields, for which there is notable scatter for some systems (notably the  $H_2$ - $H_2O$ ).

The theoretical hydrogen storage potential of these structures has also been assessed, and it is concluded that data to date indicate that the more favourable the thermodynamic stability of binary  $H_2$ -promoter clathrate is, the lower the hydrogen content.

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