Molecular Hydrogen Storage in Novel Binary Clathrate Hydrates at Near-Ambient Temperatures and Pressures

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2006 DOE H_2 Program Review

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Agenda

- Introduction & Motivation
- H_2/THF Binary Hydrate Measurements
- H_2/Cyclohexanone Binary Hydrate Measurements
- H_2 Storage in Semi-Clathrate Materials
- Hydrotropes Effect on H_2 Hydrate Formation
- Future Work

Accomplishments

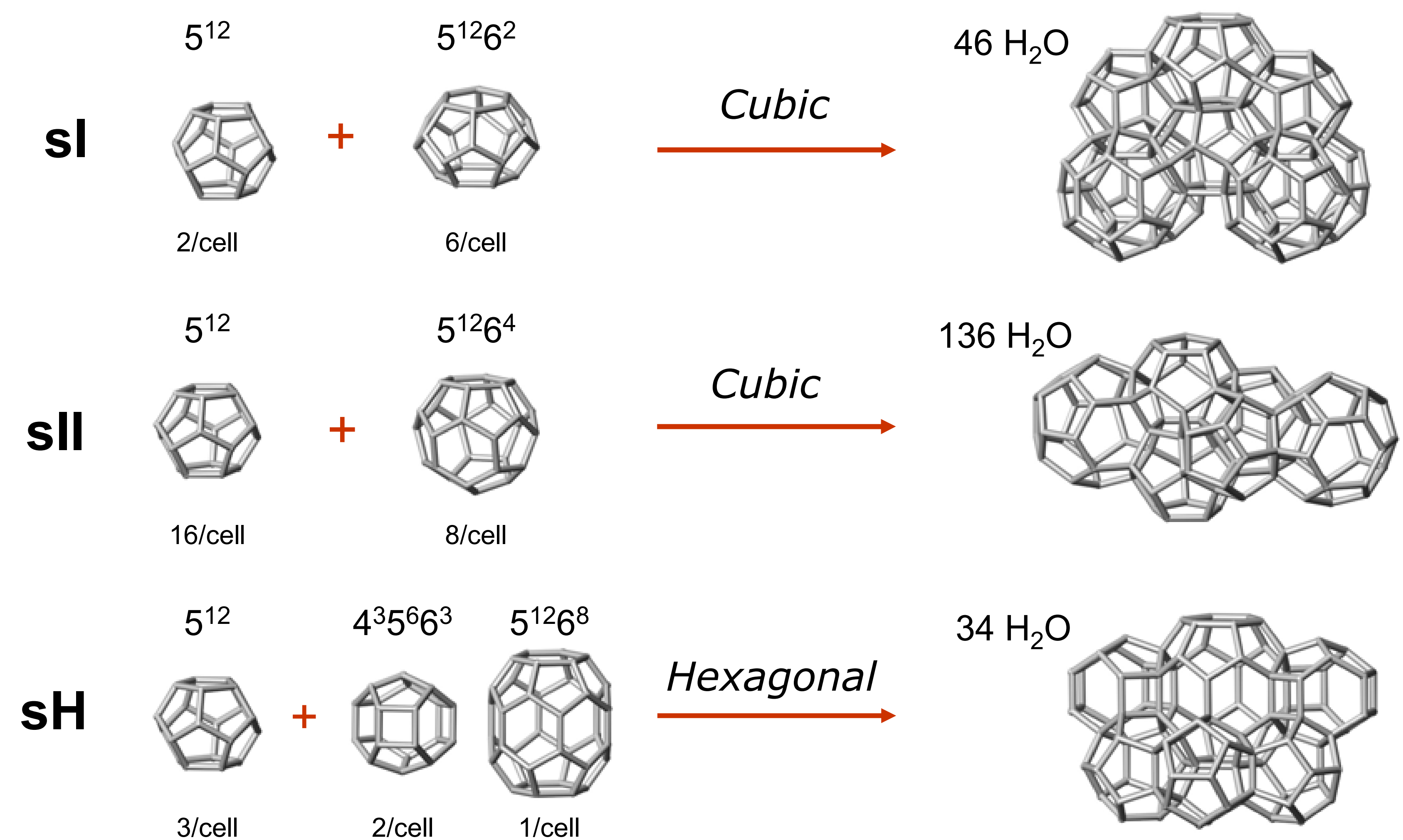
- H_2 hydrate pressure reduced by 2 orders of magnitude with THF
  - H_2 is enclathrated in sII hydrate
- Storage capacity confirmed
  - Up to one H_2 per 5^{12} of sII binary clathrate
  - H_2 storage independent of xTHF (at tested conditions)

Accomplishments

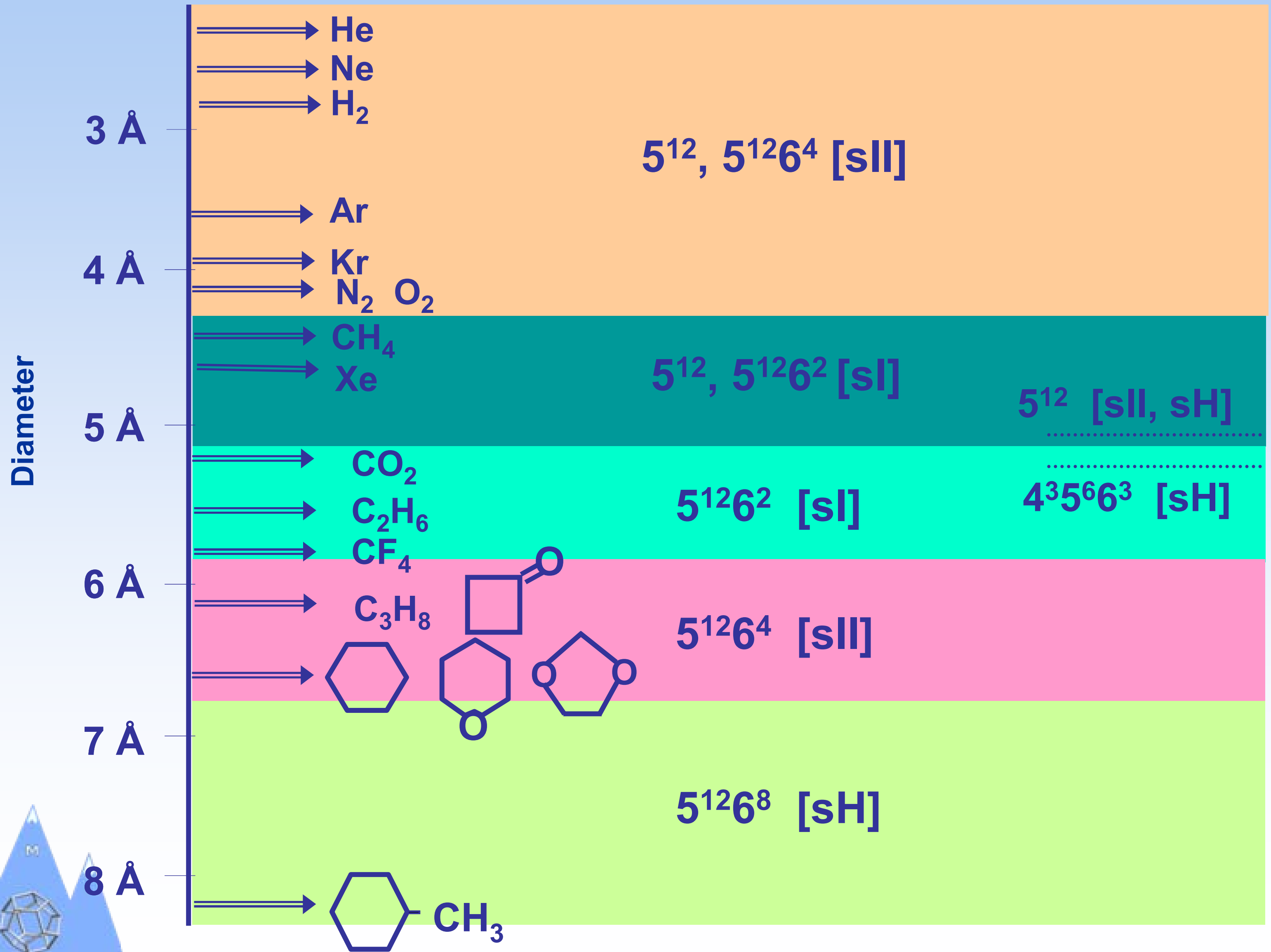
- H_2 can stabilize a hydrate structure otherwise unstable
  - H_2/cyclohexanone hydrate
- First semi-clathrate formed with H_2
- No thermo promotion from hydrotropes

INTRODUCTION & MOTIVATION

What are Clathrate Hydrates…?

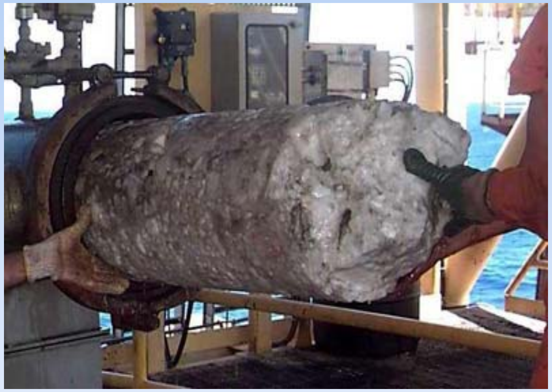


Molecular Sizes and Hydrate Structures



Gas Clathrate Hydrates

- Encapsulate small gas molecules (CH_4, C_2H_6, etc.)



- Cause of pipeline blockage in natural gas/oil production

- Potential future energy source (CH_4)

- Concentrate large volume of gas
  - sII → ~170 m^3 of gas (STP) per m^3 of hydrate

SCHOOL OF MINES COLORADO 1874

H_2 in Hydrates

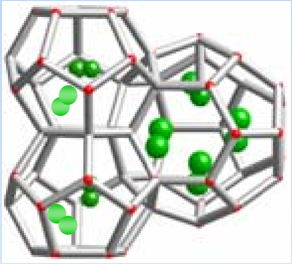
- ’83 – Holder et al.: H_2 Rich Gases
  - H_2 too small to contribute to hydrate stability
- ’84 – Ng & Robinson: < 40% H_2 in gas
  - predicted H_2 enters the hydrate structure
- ’99 – Dyadin: H_2 and noble gases
  - experimental hydrate decomposition P = 100-360 MPa
- ’00 – Guo et al.: H_2 and gas mixtures
  - Assumes H_2 to be a hydrate non former

Clathrate Hydrates Can Store H_2

⇨ 2002 - Mao W. et al.: Pure H_2 hydrate . *Science* **2002**, *297*, 2247.

$2\ H_2 \rightarrow 5^{12}$
$4\ H_2 \rightarrow 5^{12}6^{4}$

P=200 MPa
T=280 K
5.0 wt%
~ 460 m^3gas(STP)/m^3



Potential storage medium for hydrogen

⇩

- ⇨ H_2O only by-product
- ⇨ H_2 is not bonded to the hydrate structure
- ⇨ No need of chemical reaction for gas release
- ⇨ Complete reversible
- ⇨ Fast Kinetics (formation and decomposition)
- ⇨ *Extreme formation pressures*

THF/H_2 Hydrate Stable at Much Lower P than Pure H_2 Hydrate

⇨ 2004 - Florusse L. et al.: Binary THF-H_2 hydrate

Science **2004**, *306*, 469.

1 H_2 → 5^{12}

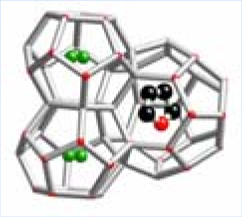
1 THF → $5^{12}6^4$

P=6 MPa

T=280 K

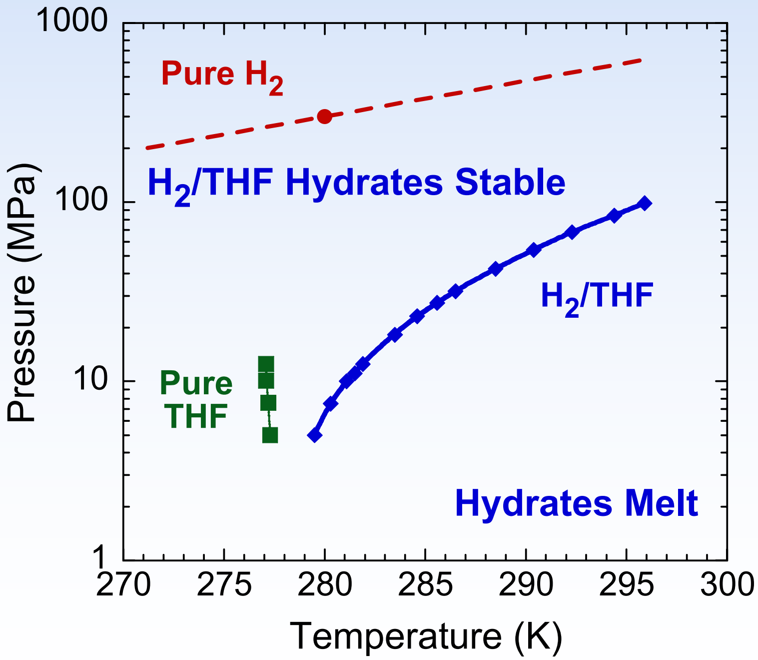
1.0 wt%

~ 115 m^3gas(STP)/m^3



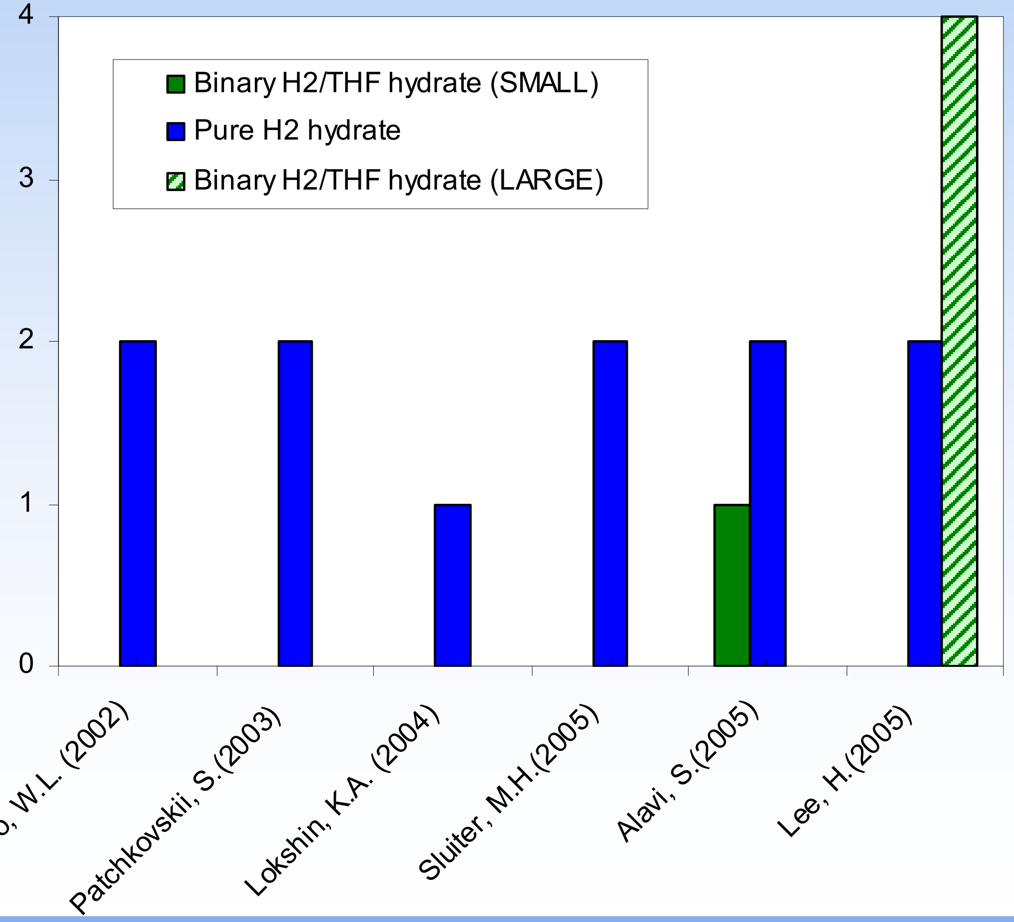
Pressure reduction

2 orders of magnitude



Scientific Impact

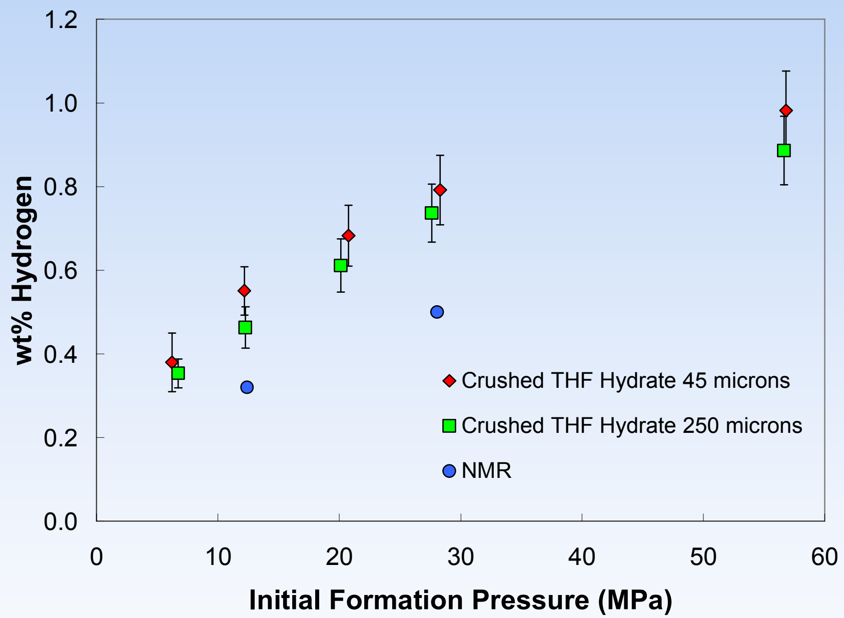
⇨ Discrepancy on cage occupancy

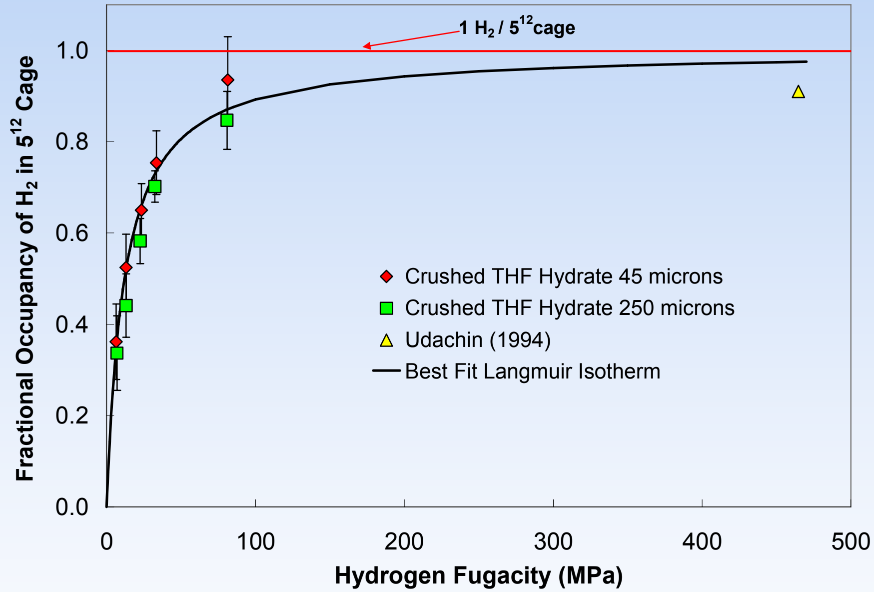


BINARY CLATHRATE HYDRATE RESULTS

Gas Release Measurements Confirms H_2 Storage in Hydrates

- 1 wt.% H_2 in binary hydrate THF/H_2

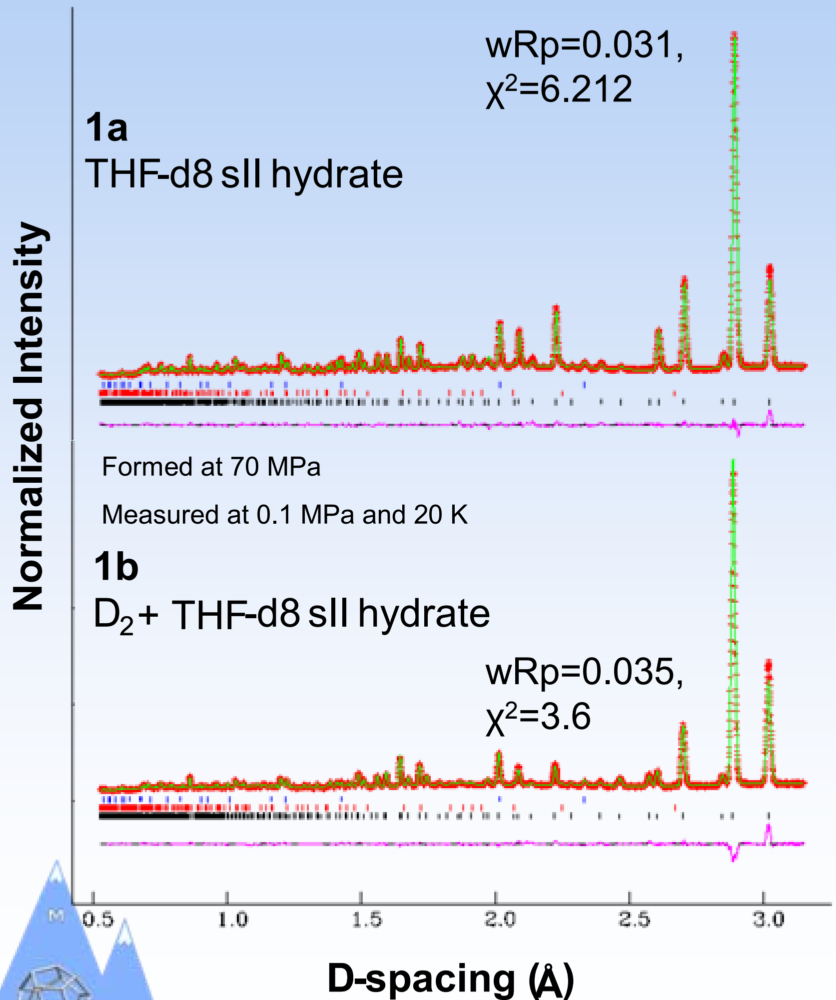




$$\theta_{H_{2Small}} = \frac{C_{H_{2small}} f_{H_2}}{1 + C_{H_{2small}} f_{H_2} + C_{THF_{small}} f_{THF}}$$

Strobel et al. J. Phys. Chem. B (Submitted)

High Resolution Neutron Diffraction Confirms Single Occupancy of 5^{12} Cages



<u>Guest Occupancies</u>

D_2 5^{12} (Spherical harmonics) – 1.003 ±.02

D_2 5^{12} (Single atom) – 0.998 ± 0.02

THF $5^{12}6^4$ - unity

Hester et al. Phys. Rev. Lett. (Submitted)

Manipulation of Cavity Occupancy

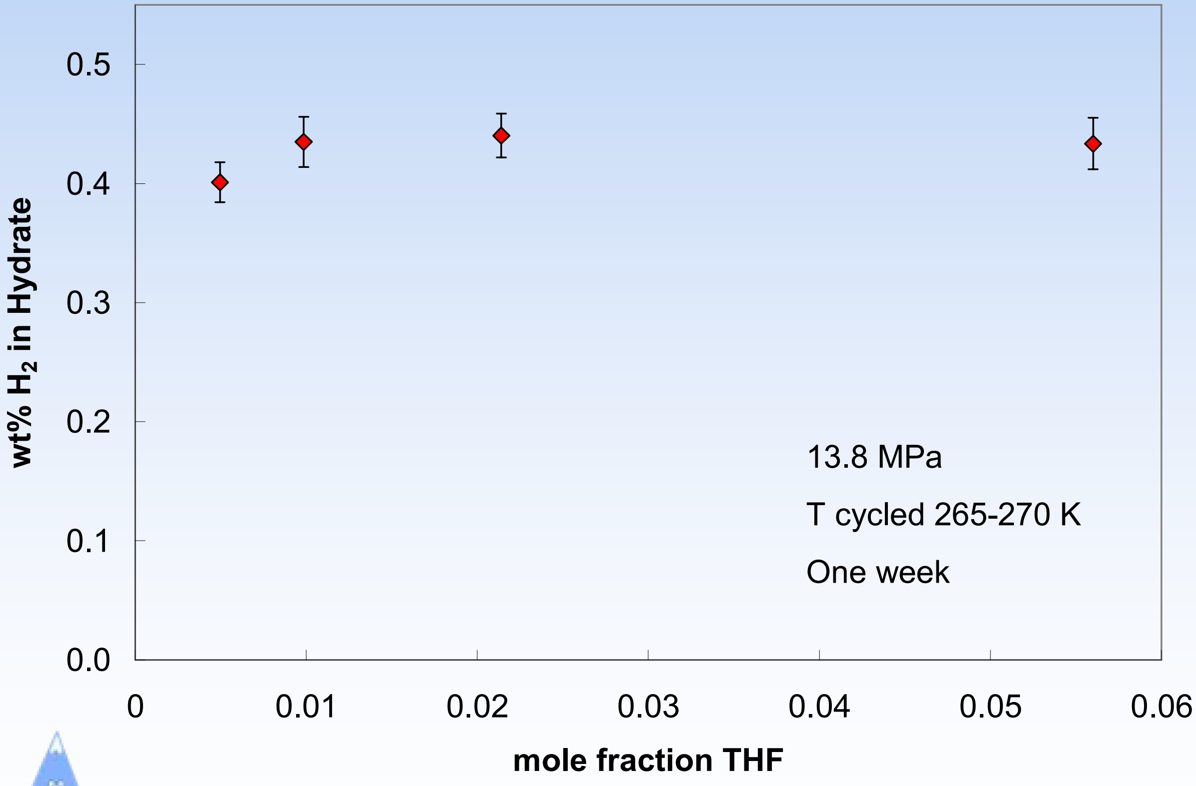
- Can H_2 storage be increased by decreasing concentration of THF?
- Can large cage THF occupancy be substituted for multiple H_2 molecules?

All large cages filled with THF

Some large cages filled with THF, balance filled with 4 H_2

H_2 Storage is Independent of xTHF

- Gas release measurements



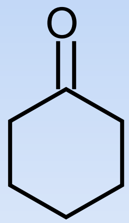
THF remains favorable guest in large cage

H_2 only occupies small cages

Strobel et al. J. Phys. Chem. B (Submitted)

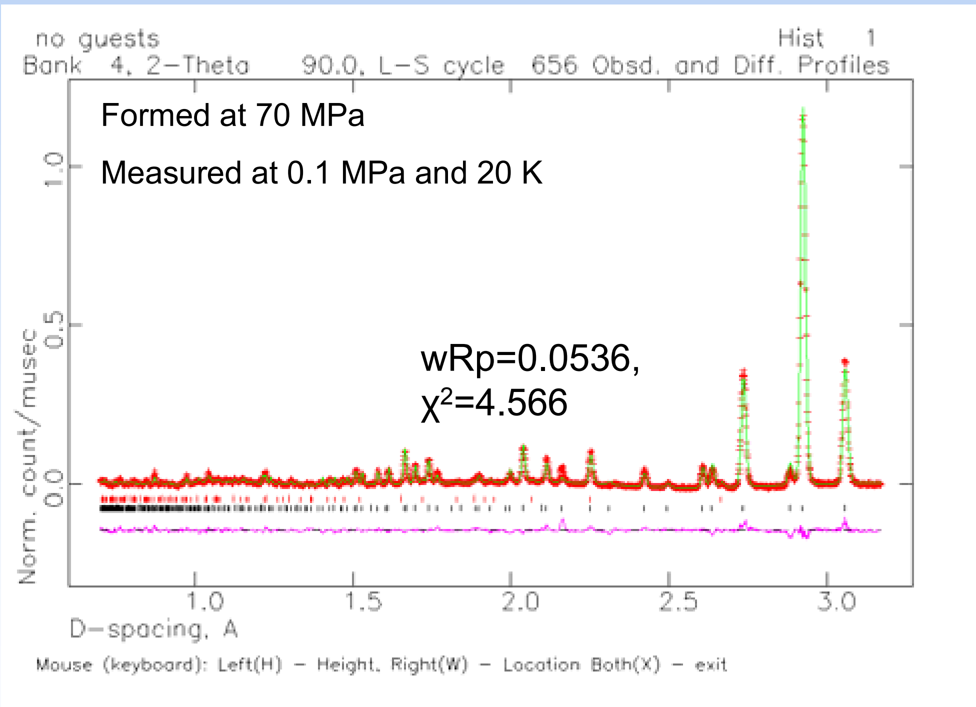
Cyclohexanone - Another Promoter Molecule

- No known pure CHone hydrate
  - Requires a second guest, *cf*. cyclohexane, benzene



- Neutron diffraction studies on the binary Cyclohexanone-H_2 hydrate
  - Confirm structure (sII or sH?)
  - Hydrogen occupancy

Neutron Diffraction Confirms CHone-H_2 sII hydrate Structure & Occupancy



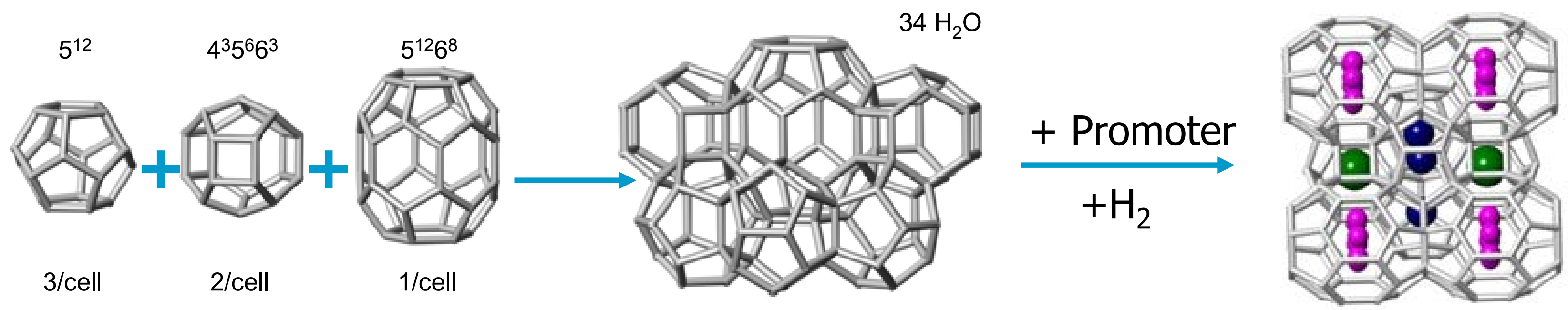
<u>Guest Occupancies</u>

D_2 5^{12} (Single atom) – 0.54

CHone $5^{12}6^4$ - unity

Implication of H_2 Stabilization Effect

- H_2 shown to stabilize sII lattice (otherwise unstable)
- Implication of hydrogen stabilizing other lattices that require a second guest, e.g. **sH**



Higher storage capacity

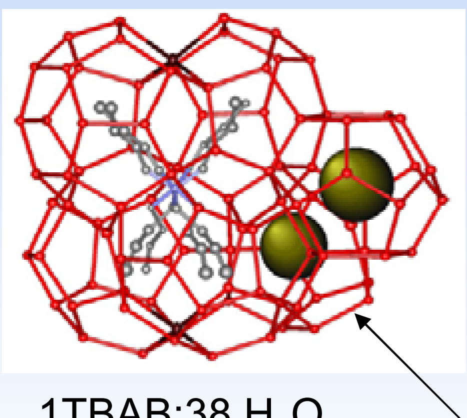
TBAB-H_2O Phase Diagram and Structure

TBAB-B semiclathrate – orthorhombic

4X.6Y.4Z

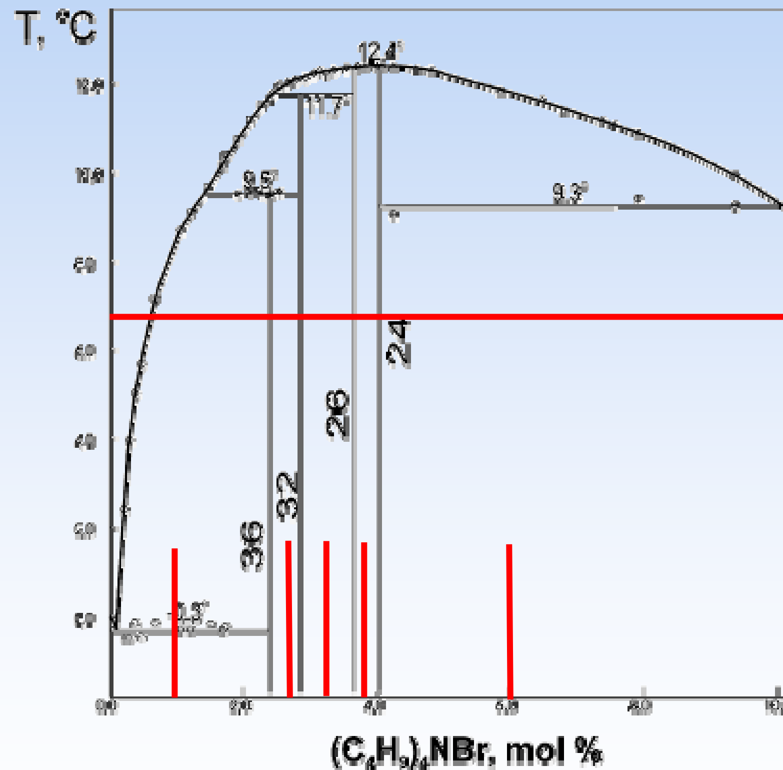
X=$5^{12}6^2$, Y=5^{12}, Z=$5^{12}6^3$

Tetra-n-butylammonium bromide



1TBAB:38 H_2O

Empty small cages available for H_2

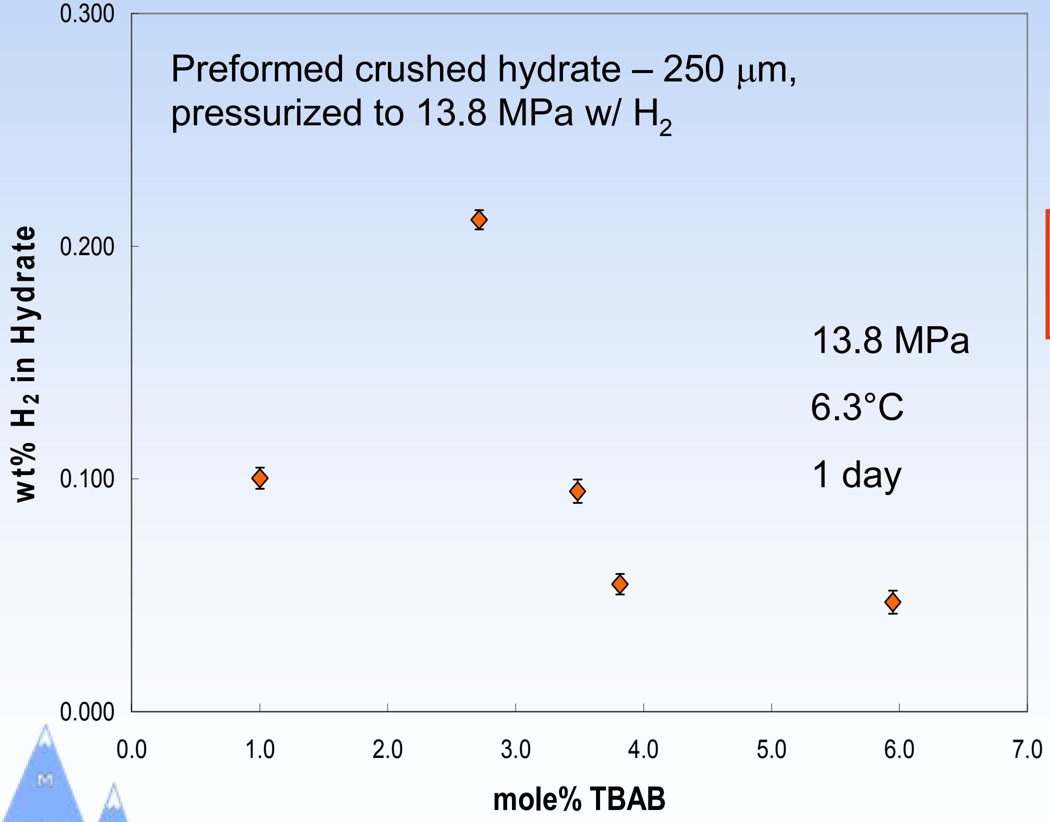


Shimada et al., Acta Cryst. (2005),C61, 65-66

Lipowski et al., J Supramol. Chem., (2002), 2, 435-439

The First Semiclathrate H_2 Hydrate Discovered

- Gas release measurements for different hydration numbers



H_2 storage is NOT limited to the classical hydrate structures

Wide variety of inclusion compounds for H_2 storage

Accomplishments

- H_2 hydrate pressure reduced by 2 orders of magnitude with THF
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Publications

- T.A. Strobel, C.J. Taylor, K.C. Hester, S.F. Dec, C.A. Koh, K.T. Miller, E.D. Sloan Jr. *Molecular Hydrogen Storage in Binary THF-H_2 Clathrate Hydrates*. **J. Phys. Chem. B.** *Accepted*
- K.C. Hester, T.A. Strobel, A. Huq, A.J. Schultz, E.D. Sloan, C.A. Koh. *Molecular Hydrogen Occupancy in Binary THF-H_2 Clathrate Hydrates by High Resolution Neutron Diffraction*. **Phys. Rev. Letters.** *Submitted*
- L.J. Rovetto, T.A. Strobel, C.A. Koh, E.D. Sloan Jr. *Is gas hydrate formation thermodynamically promoted by hydrotrope molecules?* **Fluid Phase Equilibria**. *Submitted*
- *Neutron diffraction studies of binary hydrates with H_2 and cyclohexanone. In preparation*
- *Hydrogen storage in semiclathrates with Tetra-n-butylammonium bromide. In preparation*

Future Work…

- High Pressure Raman facility
  - Pure H_2 Hydrate
    - Formation and dissociation mechanism
    - Occupancy dependence on pressure
  - Search for new promoters
    - sII and sH gas hydrates
    - Other structures
- Self Preservation Studies
  - Slow dissociation rates of hydrates outside the stability region

Acknowledgements

Ashfia Huq

Arthur Shultz

Jim Richardson

Questions? / Comments

Extra Slides

Overview

Timeline

- 9/1/05 - 8/31/08
- 20 % Complete

Budget

- Funding received 9/05
  - $ 250,000
- 3 years

Interactions /Collaborations

- Technical University of Delft
- Argonne National Laboratory
  - IPNS

Work and Facilities

Our Approach to Study H_2 Hydrates

Microscopic

- NMR
- Raman
  - 60,000 psi
- Neutron diffraction

Macroscopic

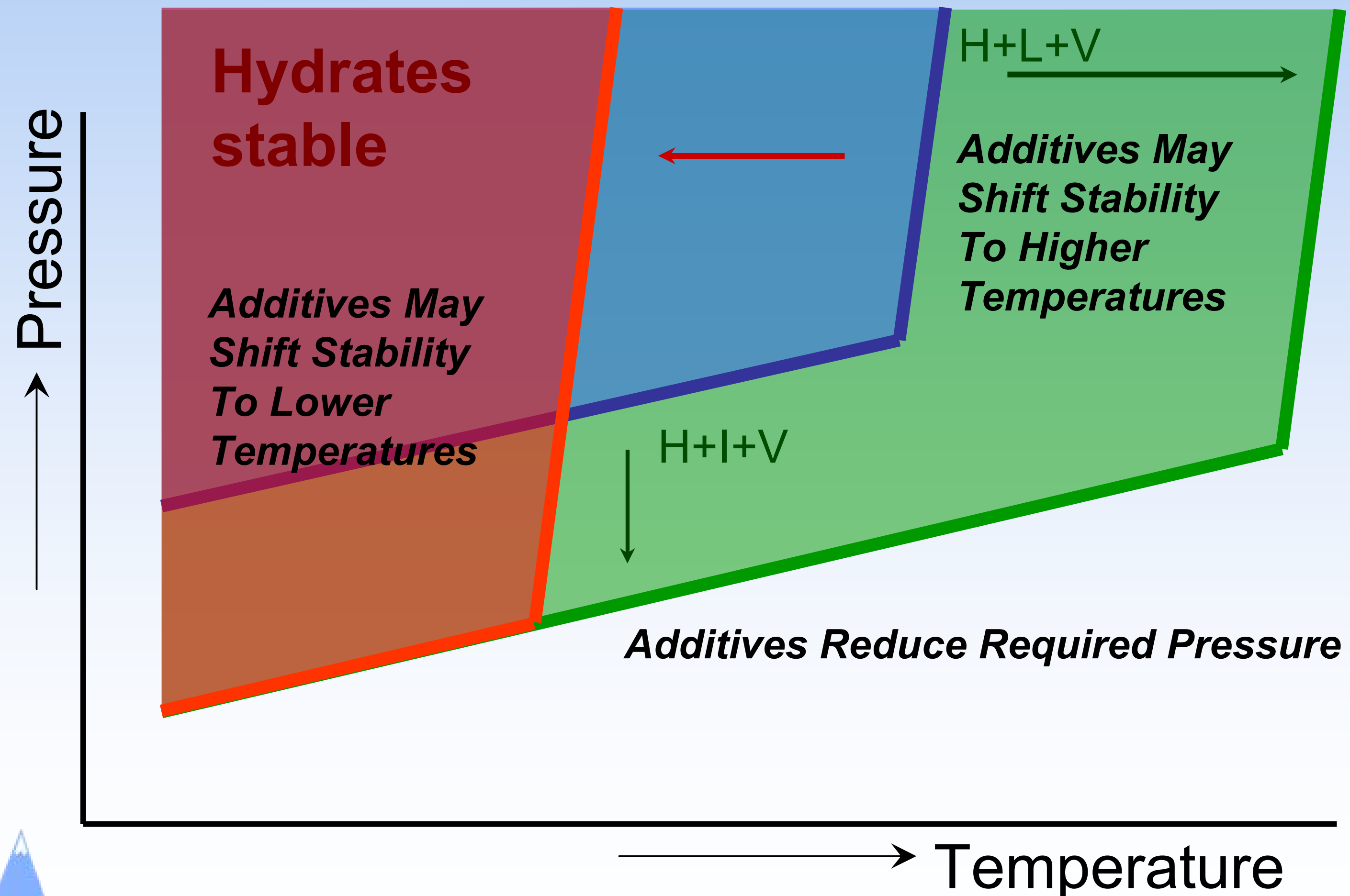
- Gas evolution
- Phase equilibria HP cell

Modeling

- In house model

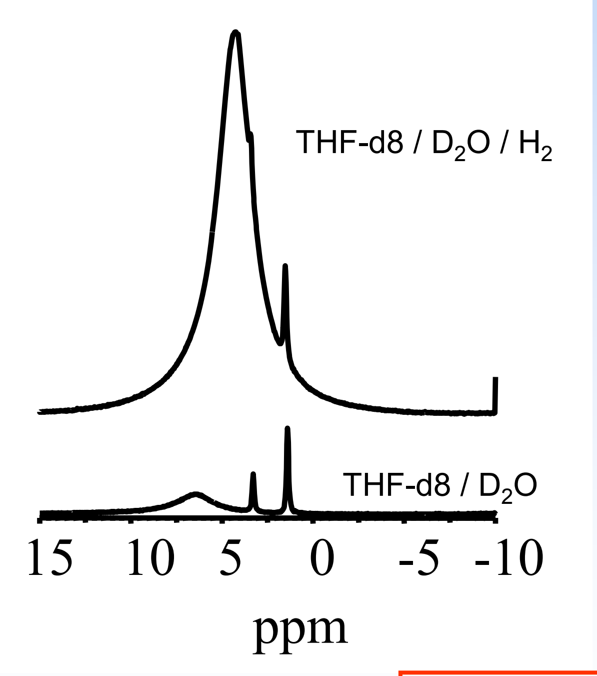
Stability of Gas Hydrates

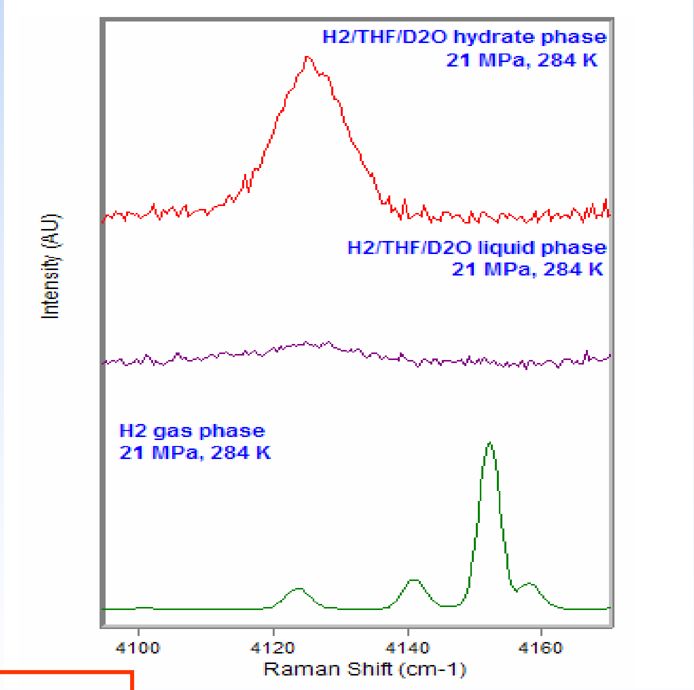
- Additives as Inhibitors or Promoters



Binary THF/H_2 Hydrate Confirmed Using Spectroscopy

- H_2 shown to occupy sII hydrate cages
  - ^1H MAS NMR Spectroscopy
  - Raman Spectroscopy





H_2 is enclathrated

Florusse, L. J. et al, *Science* **2004**, *306*, 469.

Scientific Impact

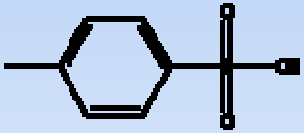
⇨ Discrepancy on cage occupancy

Mao, W. L.; ***Science*** **2002**, *297*, p 2247 **5.0 wt %**	Raman observations and phase volume ratio	~2k bar 234 K	Pure H_2 Hydrate	2 H_2/small 4 H_2/large cage
Patchkovskii, S. et al, **PNAS** **2003**, 100, p 14645	*DFT calculations*	2k bar 250 K	Pure H_2 Hydrate	2 H_2/small cage 3.96 H_2/ large cage
Lokshin, K. A. et al, **Phys. Rev. Lett**, **2004**, p 125503 **3.8 wt %**	Neutron scattering	2k bar 180 K	Pure H_2 Hydrate	1 H_2/small 2- 4 H_2/large cage
Sluiter, M.H., et.at. **Materials Transactions**, **2004**, pp 1452	*AB initio* calculations		Pure H_2 Hydrate	2 H_2/small 4 H_2/large cage
Alavi, S., et.al. **J.Chem.Phys**, **2005**, 123, p 024507	Molecular dynamic calculations	2.5k bar 100 K	Pure H_2 Hydrate	1 H_2/small 4 H_2/large cage
Alavi, S., et.al. **J.Chem.Phys**, **2005**, 124, p 014704	Molecular dynamic calculations	120 bar 273 K	THF/H2 Hydrate	Similar Energy for 1 or 2 H_2/small
Lee,H. and Ripmeester, J. et.al, **Nature**, **2005**, 434, p 743 **> 4 wt %**	Raman, NMR, gas evolution	120 bar 270 K	THF/H2 Hydrate	2 H_2/small Decreased THF -> 4 H_2 in some large cages

Hydrotropes and Gas Hydrates

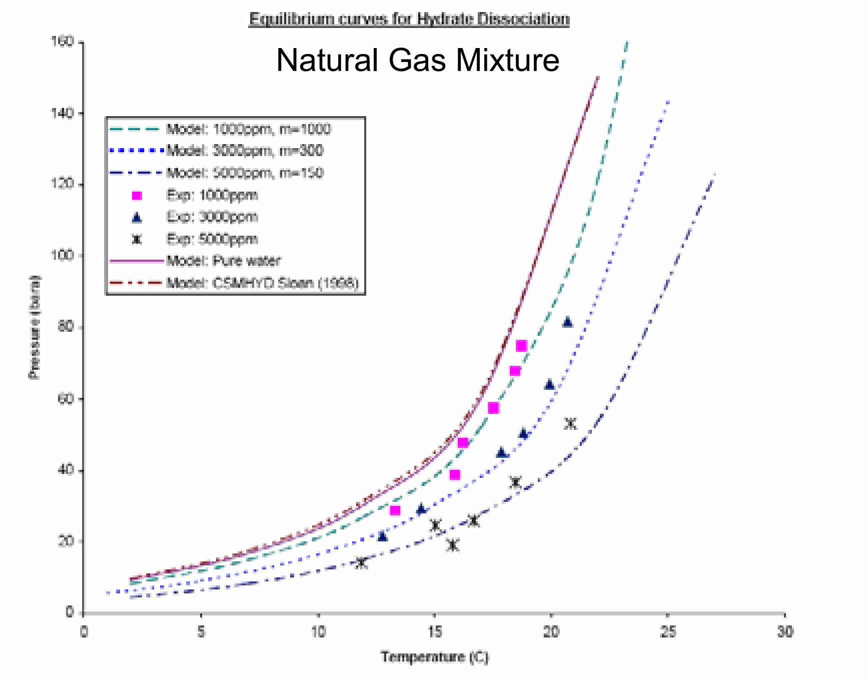
- ⇨ Reported to promote hydrate equilibrium

P-TSA (para-Toluene Sulfonic Acid)



$$\frac{\Delta\mu_w^{\ L}}{RT} = \frac{\Delta\mu_w^{\ 0}}{RT} - \int_{T_0}^{T} \frac{\Delta H_w}{RT^2} dT + \int_0^P \frac{\Delta V_w}{RT} dP - \ln(a_w)$$

Increase water activity through self aggregation



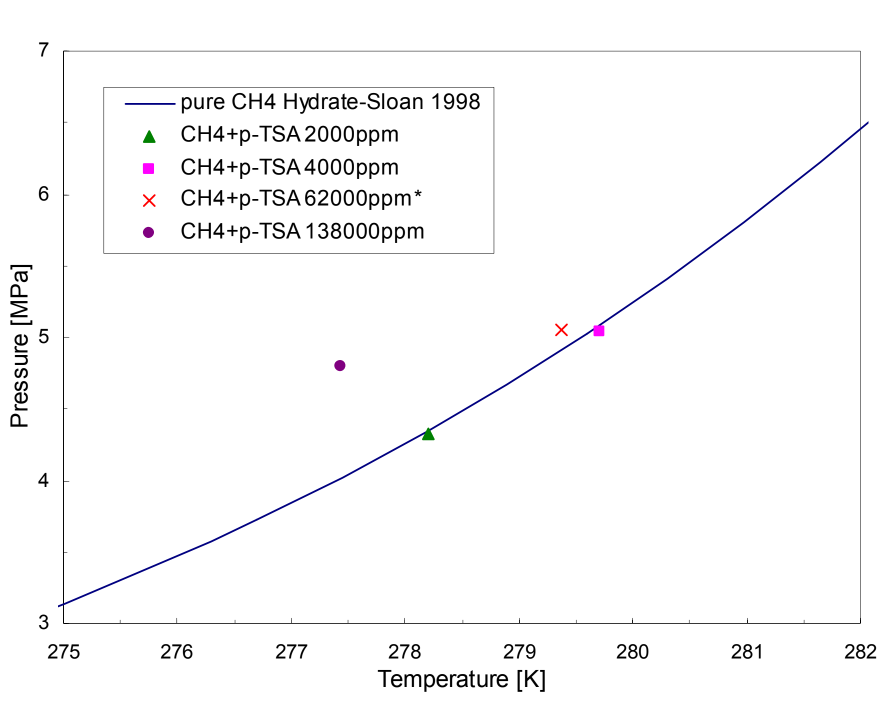
Gnanendran et al., FPE, (2004), 221, 175-187

Apply to pure H_2 hydrate

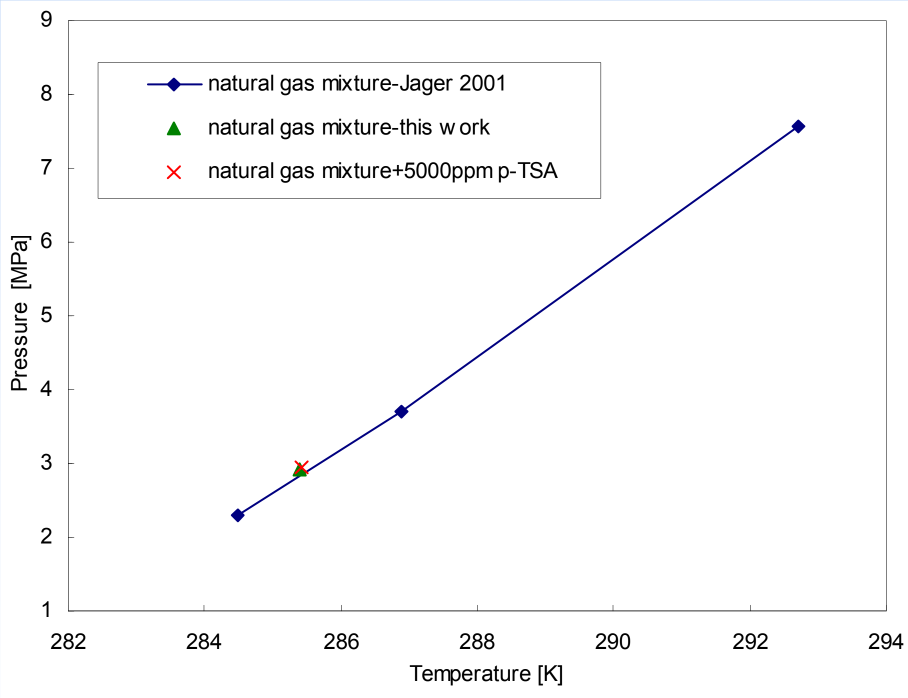
Reduce formation pressure w/o compromising storage ?

Hydrotropes Do Not Promote Gas Hydrate Formation

Methane



Natural gas mixture



No thermodynamic promotion with hydrotropes

No feasibility for H_2 hydrate

Rovetto et al. Fluid Phase Eq. (Submitted)