



Methane trapped inside 5<sup>12</sup> cage of hydrate

sl



Unit cell

### **Clathrate hydrates: From an energy perspective**



#### Figure 11

(*a*) A comparison of energies in conventional hydrocarbons and hydrates. The distribution of organic carbon in Earth reservoirs is shown in gigatons ( $10^{15}$  tons) of carbon. 1 gigaton = 38.84 trillion ft<sup>3</sup> (TCF). (*b*) A comparison of hydrated resources and the difficulty of recovery, which increases as production progresses to the silts and undeformed muds shown lower in the diagram. The estimated global amount of methane in gas hydrate deposits is 700,000 TCF; the U.S. annual natural gas use is ~23 TCF. Adapted from Reference 84 with permission from AAAS.

### **Applications of clathrate hydrates**



"Ice on fire" burning of methane hydrate



#### **Applications:**

- Storage of natural gases and hydrogen (H<sub>2</sub>).
- Separation of flue gases and desalination of seawater.
- ➢ Flow assurance in gas pipelines.
- Renewable energy source.

Koh, A.C. et al., Annu. Rev. Chem. Biomol. Eng., 2011, 2, 237–257

#### Gas hydrate plug recovered from a subsea pipeline

#### **Occurrence of clathrate hydrates**



Hester, K. C. et al., Annu. Rev. Mar. Sci., 2009, 1, 303–327

### **Brief history of clathrate hydrates**

1810 Chlorine hydrate discovered by Sir Humphrey Davy 1823 Corroboration by Faraday—formula Cl<sub>2</sub>·10H<sub>2</sub>O 1828 Bromine hydrates discovered by Löwig 1829 SO<sub>2</sub> hydrates found by de la Rive as SO<sub>2</sub>·7H<sub>2</sub>O 1848 Pierre determined the formula of SO<sub>2</sub>·11H<sub>2</sub>O 1855 Schoenfield measured the formula as SO<sub>2</sub>·14H<sub>2</sub>O 1856–1878 CS<sub>2</sub> hydrate composition disputed by Berthelot (1856), Millon (1860), Duclaux (1867), Tanret (1878) **1876** Br<sub>2</sub> hydrates corroborated by Alexeyeff as (Br<sub>2</sub>·10H<sub>2</sub>O) 1877, 1882 Cailletet and Cailletet and Bordet first measured mixed gas hydrates from CO<sub>2</sub> + PH<sub>3</sub> and from H<sub>2</sub>S + PH<sub>3</sub> 1882 de Forcrand suggested H<sub>2</sub>S·(12–16)H<sub>2</sub>O and measured 30 binary hydrates of H<sub>2</sub>S with a second component such as CHCl<sub>3</sub> ,CH<sub>3</sub>Cl, C<sub>2</sub>H<sub>5</sub>Cl, C<sub>2</sub>H<sub>5</sub>Br, C<sub>2</sub>H<sub>3</sub>Cl. He indicated all compositions as G·2H<sub>2</sub>S·23H<sub>2</sub>O 1882, 1883 Ditte and Mauméné disputed the composition of chlorine hydrates 1883 Wroblewski measured carbon dioxide hydrates **1884, 1885** Roozeboom postulated upper/lower hydrate guadruple points using SO<sub>2</sub> as evidence; determined univariant dependence of P on T 1884 Roozeboom confirmed the composition as Cl<sub>2</sub>·10H<sub>2</sub>O **1884** LeChatelier showed that the CI hydrate *P*–*T* curve changes slope at 273 K 1885 Chancel and Parmentier determined chloroform hydrates 1888 Villard obtained the temperature dependence of H<sub>2</sub>S hydrates 1888 de Forcrand and Villard independently measured the temperature dependence of CH<sub>3</sub>CI hydrate 1888 Villard measured hydrates of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, N<sub>2</sub>O 1890 Villard measured hydrates of C<sub>3</sub>H<sub>8</sub> and suggested that the temperature of the lower quadruple point is decreased by increasing the molecular mass of a guest; Villard suggested hydrates were regular crystals 1896 Villard measured hydrates of Ar, and proposed that N<sub>2</sub> and O<sub>2</sub> form hydrates; first to use heat of formation data to get the water/gas ratio 1897 deForcrand and Thomas sought double (w/H<sub>2</sub>S or H<sub>2</sub>Se) hydrates; found mixed (other than H<sub>2</sub>Sx) hydrates of numerous halohydrocarbons mixed with C<sub>2</sub>H<sub>2</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>

### **Brief history of clathrate hydrates**

**1902** de Forcrand first used Clausius–Clapeyron relation for H and compositions; tabulated 15 hydrate conditions

1919 Scheffer and Meyer refined Clausius–Clapeyron technique

**1923**, **1925** de Forcrand measured hydrates of krypton and xenon

1934 Hammerschmidt discovers hydrates as pipeline plugs; provides Hammerschmidt equation; discovers thermodynamic inhibitors

1941 Katz et al. begin K-values and gas gravity methods to predict hydrate mixtures

1946 Deaton and Frost present data summary on hydrates and their prevention

1949 von Stackelberg reports 20 years of diffraction data on hydrate crystals

**1949** Kobayashi begins a 50 year hydrate research effort with study of binary systems

1951 Claussen proposes, and von Stackelberg and Müller confirm sll unit crystal

1952 Claussen and Polglase, Müller and von Stackelberg, and Pauling and Marsh confirm sl unit crystal

**1954** von Stackelberg and Jahn measure sll hydrate formed from two sl guest molecules

the hydrates of xenon, chlorine, bromine, sulfur dioxide, hydrogen sulfide, methyl bromide, methyl iodide, ethyl chloride and chloroform. They reported that most of the crystals have a cubic unit cell with  $a_0$  equal to about 12.0 A. From single-crystal x-ray photographs of the hydrate of sulfur dioxide they decided on the space group  $O_h^3$ , and postulated a structure consisting of a framework of 48 oxygen atoms in a set of general positions x, y, z in the unit cell. With this structure each oxygen atom has neighboring oxygen atoms at a distance of about 2.4 A, and the framework has eight cavities in which the gas molecules could lie. The ideal formula would thus be M·6H<sub>2</sub>O. This structure is not acceptable because 1987 Ripmeester and coworkers discover new structure H (sH) hydrates

### **Brief history of clathrate hydrates**

1988 Danesh, Todd, and coworkers begin four phase experiments with hydrates

**1990**a,b Rodger studies relative stability using MD simulation

1991 Mehta obtains sH data, applied vdWP theory to CH<sub>4</sub> + large (>8 Å) guest(s)

1991 Behar et al. introduce water emulsification concept to control hydrate blockage

1991 Sloan proposes molecular mechanism with kinetic inhibition implications

1992 Kotkoskie et al. show that hydrates are controlled by drilling mud water activity

1996 Sum measures hydrate composition and hydration number using Raman spectroscopy

**1997** Kuhs et al. publish first report of double occupancy of nitrogen molecules in large cage of sll hydrate at high pressures, exceeding several hundred bar

**1997** Udachin et al. report first single crystal x-ray diffraction measurements of a sH gas hydrate

1997 Dyadin et al. discover a very high pressure phase of methane hydrate that is stable up to 600 MPa

1999 Dyadin et al. discover that H2 forms a clathrate hydrate at high pressures up to 1.5 GPa

**2004** Camargo et al. and BP/SINTEF introduce "cold flow" concept to prevent hydrate plug formation without the need of chemical additives

Sloan Jr, E. Dendy, and Carolyn Koh. Clathrate hydrates of natural gases. CRC press, 2007

#### **Classification of clathrate hydrates**



Warrier, P. et al., J. Chem. Phys. 2016, 145, 21705

#### Molecular evolution in the universe



#### Table 1.1 The history of the Universe according to the Standard Model

Time since $t = 0$	Temperature	Comments
10 <sup>-43</sup> s	10 <sup>32</sup> K	Gravity is now distinct from the three other forces: strong, weak nuclear and electromagnetic
10 <sup>-35</sup> s	10 <sup>27</sup> K	Inflation of the Universe - the strong force separates
10 <sup>-12</sup> s	10 <sup>15</sup> K	Weak and electromagnetic forces separate. Neutrons and protons are formed by photon-photon collisions
10 <sup>-2</sup> s	10 <sup>11</sup> K	Electrons and positrons are formed through collisions of photons
1 s	10 <sup>10</sup> K	The Universe becomes transparent to neutrinos
180 s	10 <sup>9</sup> K	Nucleosynthesis: hydrogen, deuterium, helium and some lithium
$3-7 \times 10^5$ s	3000 K	Light element atoms form, and the Universe is now transparent to radiation: cosmic background is emitted
10 <sup>9</sup> yr	20 K	Galaxies form
Present	2.726 K	Stars and galaxies

Astrochemistry : Astronomy to Astrobiology; Andrew M. Shaw, Wiley

#### **Big Bang Theory**

Table 1.2	Relative cosmi	c abundances	of the elements
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Element	Relative abundance	Element	Relative abundance
Н	1	S	$1.6 \times 10^{-5}$
He	0.085	Р	$3.2 \times 10^{-7}$
Li	$1.5 \times 10^{-9}$	Mg	$3.5 \times 10^{-5}$
С	$3.7 \times 10^{-3}$	Na	$1.7 \times 10^{-6}$
Ν	$1.2 \times 10^{-3}$	Κ	$1.1 \times 10^{-7}$
0	$6.7 \times 10^{-3}$	Si	$3.6 \times 10^{-6}$

Majority of the universe is made of H and He produced during the Big Bang although some He has been made subsequently.



http://supernovacondensate.net/2009/06/30/the-astronomers-periodic-table/

#### Molecules and ions detected in the interstellar medium (ISM)

	$H_2^{c,d}$	CF <sup>+</sup>	SiCN	$C_4H^-$	CH <sub>3</sub> NH <sub>2</sub>
	AlF	$C_3^{e,f}$	AlNC	HC <sub>2</sub> NC	c-C <sub>2</sub> H <sub>4</sub> O
	AlCl	$C_2H$	SiNC	HCOOH	$H_2CCHOH$
	$C_2^{d,e}$	C <sub>2</sub> O	HCP	H <sub>2</sub> CNH	$CH_2CHCN$
	CH <sup>e</sup>	$C_2S$	c-C <sub>3</sub> H	$H_2C_2O$	CH <sub>3</sub> C <sub>3</sub> N
	CH <sup>+e</sup>	$\mathrm{CH_2}^{\mathrm{d,f}}$	l-C₃H	H <sub>2</sub> NCN	HC(O)OCH <sub>3</sub>
	$CN^e$	HCN <sup>f,g</sup>	$C_3N$	HNC <sub>3</sub>	CH₃COOH
	$\rm CO^{c,d,f}$	HCO	C <sub>3</sub> O	SiH <sub>4</sub>	$C_7H$
	$CO^+$	HCO <sup>+</sup>	C <sub>3</sub> S	$H_2COH^+$	$H_2C_6$
	СР	HCS <sup>+</sup>	$C_2H_2^c$	HC <sub>3</sub> N	$CH_2OHCHO$
	SiC	HOC <sup>+</sup>	NH <sub>3</sub>	C₅H	CH <sub>2</sub> CCHCN
	HCl <sup>d</sup>	H <sub>2</sub> O	HCCN	$l-H_2C_4$	$CH_3C_4H$
	KCl	$H_2S$	HCNH <sup>+</sup>	$C_2H_4$	CH <sub>3</sub> CH <sub>2</sub> CN
	NH <sup>e</sup>	HNC	HNCO	CH <sub>3</sub> CN	$(CH_3)_2O$
	NO	HNO	HNCS	CH3NC	$CH_3CH_2OH$
	NS	MgCN	HOCO <sup>+</sup>	CH <sub>3</sub> OH	$HC_7N$
	NaCl	MgNC	$H_2CO$	CH₃SH	$CH_3C(O)NH_2$
209 molecules	$OH^{d,f}$	$N_2H^+$	$H_2CN$	HC <sub>3</sub> NH <sup>+</sup>	$C_8H$
ac on lan 2010	PN	N <sub>2</sub> O	$H_2CS$	HC <sub>2</sub> CHO	$C_8H^-$
	SO	NaCN	$H_3O^+$	NH <sub>2</sub> CHO	$CH_3C_5N$
https://zeus.ph	SO <sup>+</sup>	OCS	c-SiC <sub>3</sub>	$C_5N$	$(CH_3)_2CO$
1.uni-	SiN	SO <sub>2</sub>	CH <sub>3</sub> <sup>c</sup>	<i>l</i> -HC <sub>4</sub> N	$(CH_2OH)_2$
kooln do /cdmc/	SiO	c-SiC <sub>2</sub>	C5	c-H <sub>2</sub> C <sub>3</sub> O	CH <sub>3</sub> CH <sub>2</sub> CHO
KUelli.ue/cullis/	SiS	$CO_2^c$	$C_4H$	$C_6H$	HC <sub>9</sub> N
molecules	CS	NH2 <sup>c</sup>	$l-C_3H_2$	$C_6H^-$	$CH_3C_6H$
	$\mathrm{HF}^{\mathrm{c,f}}$	$H_3^{+c}$	$c-C_3H_2$	$CH_3C_2H$	HC <sub>11</sub> N
	SH	$H_2D^+$	$H_2CCN$	HC5N	
	$O_2^{g}$	$HD_2^+$	$CH_4$	CH₃CHO	

Snow, T.P. et al., Annu. Rev. Anal. Chem., 2008, 1, 229

# Ice chemistry



#### Instrumentation





#### **Experimental method**







#### **Clathrate hydrate at low pressure**

#### **P** = 10<sup>-6</sup> torr



Here, CO<sub>2</sub> hydrate was used as a local sensitive probe for the formation of methanol hydrate

 $H_2O:CH_3OH:CO_2 = 100:50:1$ 

Blake, D. et al., Science, **1991**, 254, 5031, 548-551

#### **Clathrate hydrate at low pressure**

**Table I.** Electron diffraction results for type II clathrate  $CH_3OH$  hydrate (space group Fd3m); h, k, and l are crystallographic indices and a is a cubic unit cell dimension.

h, k, l	Calc.* d-value	Irel†	Irel‡	2:1 ice slow warm to 130 K	2:1 ice rapid warm to 130 K	20:1 ice rapid warm to 130 K
(111)	9.399	70	(w)			
(220)	5.756	8	(w)			
(311)	4.909	23	(w)			
(222)	4.697	75				
(400)	4.070	70	(w)	3.96 (w)	3.96 (s)	3.96 (m)
(331)	3.735	60	(w)	3.74 (s)		3.74 (s)
(001)	000		()	3.61 (w)\$	3.57 (m)\$	3.61 (w)\$
				0.01 ()0		3.52 (w)
(422)	3.323	60	(vs)	3.40 (s)	3.39 (m)	3.39 (w)
(122)	0.020		()		3.27 (w)	
(333) + (511)	3.133	100	(m)	3.07 (m)	3.04 (m)	3.07 (w)
(000) (011)	0.200		()	()	2.98 (w)	( )
(440)	2.878	37	(m)		2.83 (w)	2.91 (vw)
(531)	2.752	87	(vw)	2.73 (vw)	2.74 (m)	2.73 (w)
(442)	2.713	•••	()			( )
(620)	2.574	17				
(533)	2.483	17			2.38 (m)	
(622)	2.454	-				
(444)	2.350					
(551) + (711)	2.280	6		2.30 (m)	2.28 (w)	2.31 (s)
(642)	2.176	•			2.19 (m)	
(553) + (731)	2.119	14		2.08 (m)	2.07 (m)	2.11 (m)
(800)	2.035			1.97 (w)	1.98 (m)	1.96 (m)

Blake, D. et al., Science, 1991, 254, 5031, 548-551



	5 <sup>12</sup> cage	5 <sup>12</sup> 6 <sup>2</sup> cage	5 <sup>12</sup> 6 <sup>4</sup> cage
CH4 Clathrate hydrate			
Experimental shift	8.0 cm <sup>-1</sup>	5	o @J
Computation- al shift	9.3 cm <sup>-1</sup>	-9.2 cm <sup>-1</sup>	-9.1 cm <sup>-1</sup>
CO2 Clathrate hydrate	A Contraction		
Experimental shift	-36.0 cm <sup>-1</sup>	-	o
Computation al shift	-86.0 cm <sup>-1</sup>	-16.6 cm <sup>-1</sup>	15.8 cm <sup>-1</sup>

