

Gas Clathrates

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Clathrate ices form from water and non-stoichiometric amounts of small non-polar molecules (hence usually gaseous) under moderate pressure (typically of a few MPa) and at cold temperatures (typically close to 0 °C, but increased pressure raises the melting point). Every water molecule forms a vertex of four cages, which may, or may not, contain a small guest molecule. Their structures require a minimum amount of these small molecules to fit into and stabilize the cavities (usually one or none in each cavity) without forming any covalent or hydrogen bonds to the water molecules. Without these interstitial molecules the clathrate cavities, shown left, would collapse at positive pressures and they have been shown to dissipate, if surprisingly slowly, after the clathrate ice melts [897]. During formation and dissociation, the solid clathrates interact significantly with the structure of the neighboring aqueous solution [904]. The hydrogen bonding in the clathrate ices are oriented in an imperfectly disorderly manner obeying the 'ice rules' [1990].

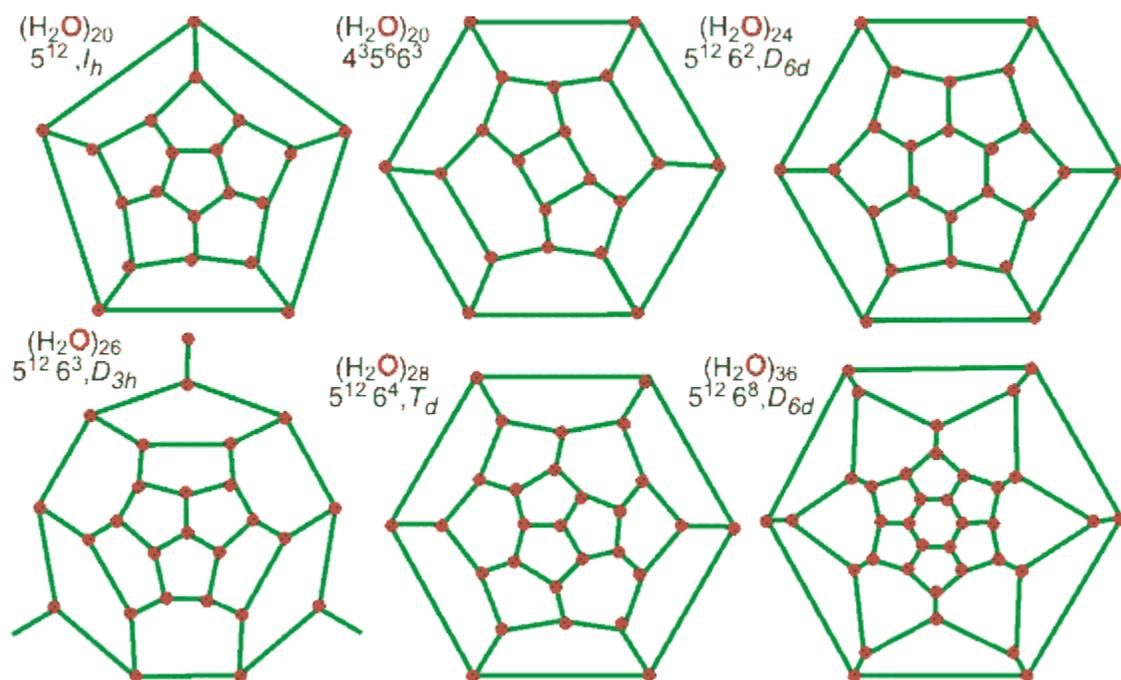
CS-I and CS-II are the most stable structures and no other hydrate structure with a single guest component has been found at an ambient condition (except for bromine clathrate) [1732]. It has been proposed that the HS-I_Q clathrate (maximum 0.175 guest/H₂O) structure may be an intermediate in the gas pressure transition of CS-I (maximum 0.174 guest/H₂O) to CS-II (maximum 0.176 guest/H₂O) [1870].

Characteristic properties of the clathrates				
Type	Lattice	Space group	Unit cell	Unit cell formula ^a
Clathrate I, CS-I	Cubic	<i>Pm3n</i>	a=1.203 nm	(S) ₂ ·(L) ₆ ·46H ₂ O
Clathrate II, CS-II	Face-centered cubic	<i>Fd3m</i>	a=1.731 nm	(S) ₁₆ (L+) ₈ ·136H ₂ O
Clathrate H, HS-III	Hexagonal	<i>P6/mmm</i>	a=1.23 nm c=1.02 nm	(S) ₅ (L++)·34H ₂ O
Clathrate TS-I, [1734]	Tetragonal	<i>P4₂/mnm</i>	a=2.318 nm c=1.215 nm	(L+) ₁₆₋₂₀ ·172H ₂ O
Clathrate HS-I _Q [1869]	Hexagonal	<i>P6/mmm</i>	a=1.1987 nm c=1.1509 nm	(L) ₇ ·40H ₂ O

Cavity	5 ¹²	5 ¹² 6 ²	5 ¹² 6 ³	5 ¹² 6 ⁴	5 ¹² 6 ⁸	4 ³ 5 ⁶ 6 ³
H ₂ O	20	24	26	28	36	20
Mean cavity radius, Å	3.95	4.33	4.53	4.73	5.71	4.06
free volume, Å ³	51	77	98	120	213	44

CS-I, /unit cell	2	6	-	-	-	-
CS-II, /unit cell	16	-	-	8	-	-
HS-III, /unit cell	3	-	-	-	1	2
TS-I, /unit cell	10	16	4	-	-	-
HS-I _Q , /unit cell	3	2	2	-	-	-
Guest molecules, for example; approximate radius, Å	Ar, O ₂ , N ₂ , CH ₄	CO ₂ , C ₂ H ₆	Br ₂	C ₃ H ₈ , (CH ₃) ₃ CH	(CH ₃) ₃ CC ₂ H ₅ , Xe	CH ₄
	1.8-2.2	1.8-2.7	~2.4	2.8-3.1	3.5-4.3	1.8

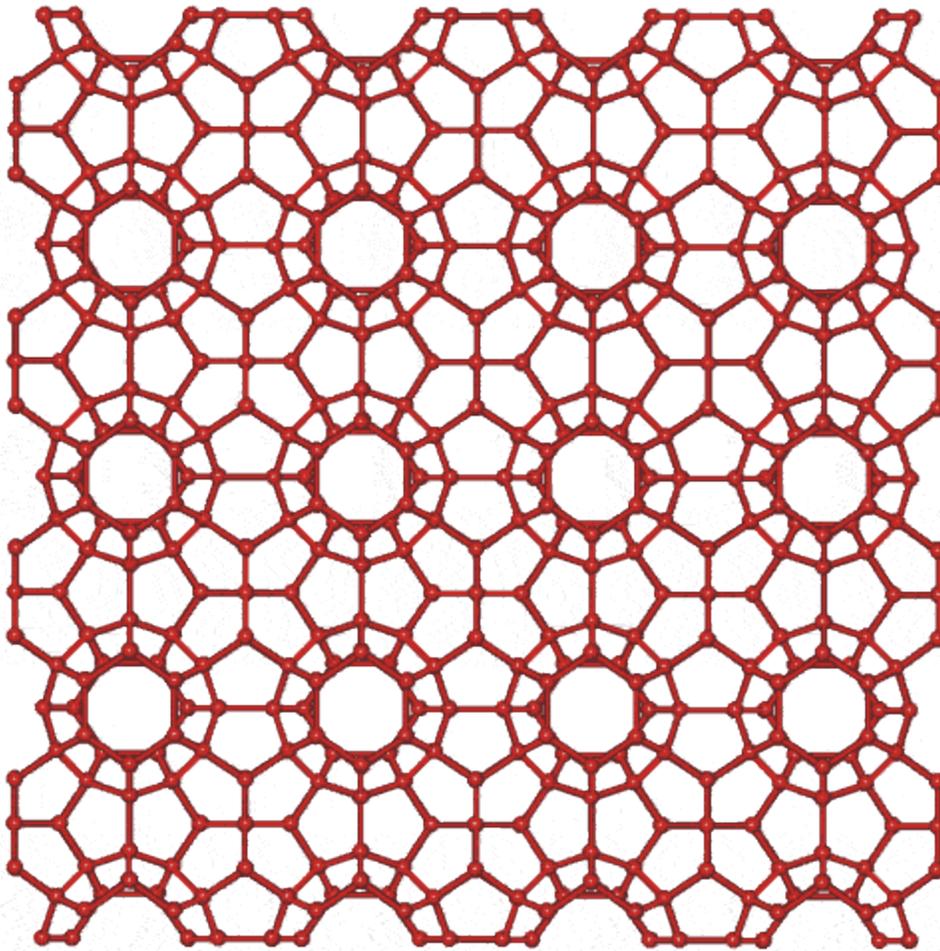
^a Not all cavities would normally be filled; S = small guest; L = large guest; L+ = larger guest; L++ = largest guest



The connectivity maps for the clathrate cages are shown right.

Some clathrate hydrates can form, at atmospheric pressure, at the interface between a liquid of suitable guest molecules and water (for example, $\text{CH}_3\text{CCl}_2\text{F}$ in clathrate CS-II hydrate [408]). At low pressures (*e.g.* atmospheric) most clathrate hydrates decompose to release the guest molecules, except at low temperatures (for example, < 270 K) where they may remain in a metastable state, for several hours. At very high pressures, clathrate hydrates show complex phase behavior, often giving filled hexagonal ice [1144] with the smaller guest molecules/atoms, then at higher pressures they break down to give high density ice and a solid phase formed by the guest molecules (for example, see [898]). Gas hydrates have been recently reviewed [395]. Water itself cannot be contained in the cavities of solid clathrates [1114].

The relative content of the cavities can be determined by techniques such as Raman spectroscopy or NMR as the different cavities present differing environments. [Back to Top ▲]



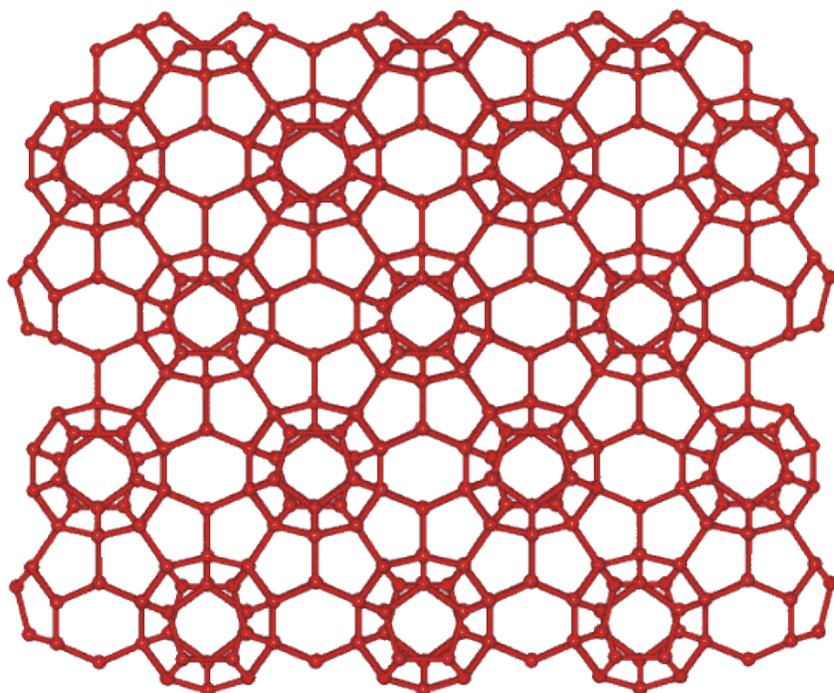
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CS-I clathrate

Shown opposite is the cubic clathrate CS-I network formed by small non-polar (gaseous) molecules, such as CH_4 and CO_2 , in aqueous solution (for example, $(\text{CO}_2)_{8-y} \cdot 46\text{H}_2\text{O}$) under pressure and at low but not necessarily (normally) freezing temperatures (only the oxygen atoms of water are shown.). The included molecules randomly occupy many of the cavities dependent on their size. Linear tetrakaidecahedral ($5^{12}6^2$) cavities form three orthogonal axes holding a dodecahedral cavity wherever they cross (ratio 6:2 respectively per unit cell); each dodecahedral cavity sitting (in a body-centered cubic arrangement) within a cube formed by six tetrakaidecahedral ($5^{12}6^2$) cavities. These ($5^{12}6^2$) cavities join at their hexagonal faces to form columns, going away from the viewer in the figure.

About 6.4 trillion (that is, 6.4×10^{12}) tons of methane lies at the bottom of the oceans in the form of its clathrate hydrate [899]. Each kilogram of fully occupied hydrate (actually only about 96% occupancy is found) holds about 187 liters of methane (at atmospheric pressure). [[Back to Top](#) ▲]

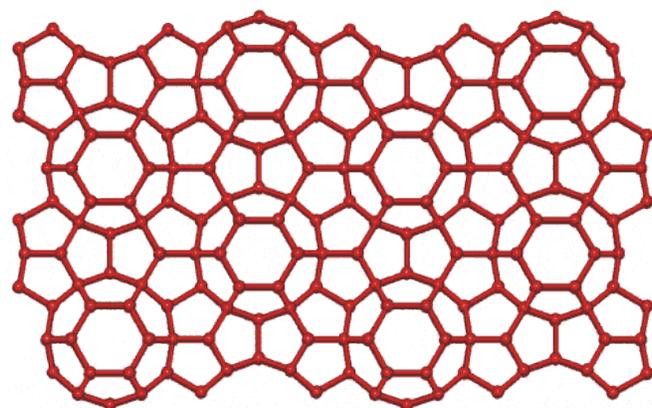
CS-II clathrate



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Opposite is shown the CS-II hydrate structure (cubic crystals containing sixteen 5^{12} cavities, eight larger $5^{12}6^4$ cavities and 136 H_2O molecules per unit cell, and containing larger molecules such as 2-methylpropane in the larger cavities only). The tetrahedral $5^{12}6^4$ cavities form an open tetrahedral network, with their centers arranged reminiscent to the cubic ice structure and separated by groups of three 5^{12} cavities. The large proportion of 5^{12} cavities is thought responsible for the similarities in the Raman spectra to gas saturated water [831].

Rather surprisingly the CS-II clathrate forms with molecular hydrogen (H_2), four molecules sitting in the large cages and one [1257b] or two [1257a] in the small cages, that is, $(2\text{H}_2)_{16} \cdot (4\text{H}_2)_8 \cdot 136\text{H}_2\text{O}$. [1257a]. [[Back to Top](#) ▲]



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HS-III clathrate

Opposite is shown the HS-III hydrate structure. It has hexagonal crystals containing three 5^{12} cavities, two small $4^3 5^6 6^3$ cavities, one large $5^{12} 6^8$ cavity and 34 H₂O molecules per unit cell, and containing even larger molecules such as 2,2-dimethylbutane in the larger cavities only). Each $5^{12} 6^8$ barrel-shaped cavity is surrounded by six $4^3 5^6 6^3$ cavities around its central ring of 6 hexagons. These ($5^{12} 6^8$) cavities join at their top and bottom hexagonal faces to form columns, going away from the viewer in the figure. [[Back to Top](#) ▲]

Other structures

Many other tiled three-dimensional structures are possible (see in JavaView) and other clathrate structures are being discovered; some related to the Frank-Kasper (FK) structures [1733].

Source:<http://www1.lsbu.ac.uk/water/clathrat2.html>