SOME STRUCTURAL AND THERMODYNAMIC STUDIES OF CLATHRATE HYDRATES

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ABSTRACT. X-ray and neutron diffraction studies show argon and
krypton to preferentially form clathrate hydrates of structure II,
rather than structure I as previously assumed; methane and hydrogen
sulphide do form structure I. Re-examination of solid-solution
thermodynamic theory shows that structure II is basically the more
stable; structure I is generally formed only when the guest molecule
is in the size range that favours occupancy of the 14-hedral over the
12-hedral cages. For molecules too large to enter the 12-hedra the
relative stability of structure II is greatest at 0°C, in agreement
with the observed sequence of change of stability of cyclopropane
hydrate: I to II at −16° and II to I at 1.5°. Carbon dioxide
hydrate is observed to decompose on prolonged standing at 105K in
accord with the low-temperature instability predicted by Miller.

1. CRYSTALLOGRAPHIC STUDIES

Thirty years ago gas hydrates were shown by the X-ray studies of Mark
von Stackelberg [1] to consist of water clathrates of two distinct
cubic structures. Since then it has been assumed that structure I,
which contains 12- and 14-hedral cages in a hydrogen-bonded water
lattice, is preferentially formed by relatively small molecules, up
to about 5.7Å in largest dimension, while structure II, with 12- and
16-hedral cages, is formed by larger molecules, up to about 6.6Å in
size. Structure II hydrates have compositions close to $M \cdot 17H_2O$
because the guest molecules M occupy the large 16-hedra only
(Table I). Compositions of structure I hydrates are in the range
$M \cdot (6 \text{ to } 8) H_2O$ and depend particularly on the degree of occupancy of
the small 12-hedral cages. No exceptions to these general
observations have been found either among the hundred-odd simple gas
hydrates whose compositions have been estimated or among the sixty
gas hydrates whose structures are known from X-ray crystallography.
    The structures of the hydrates formed by very small guest
molecules have however never been reported, probably because these
hydrates exist near 0°C only under relatively high pressures. We

have performed X-ray and/or neutron diffraction studies of such
hydrates at low temperatures where they are stable at low pressure.
We find that **argon and krypton,** the two smallest molecules to
form gas hydrates, **preferentially form structure II,** while
methane and hydrogen sulfide form structure I (see Table II).
Oxygen, nitrogen and carbon monoxide are all rather smaller than
methane: the preferred structures of the hydrates formed by these
molecules remain to be determined.

Table I. The two principal clathrate hydrate structures

	Structure I	Structure II
Size of cubic unit cell/Å	12.0	17.2
Water molecules/unit cell	46	136
12-hedral cages/unit cell	2	16
14-hedral cages/unit cell	6	0
16-hedral cages/unit cell	0	8
Compositions (M = guest):		
All cages full	$M \cdot 5\frac{3}{4} H_2O$	$M \cdot 5\frac{2}{3} H_2O$
Only large cages full	$M \cdot 7\frac{2}{3} H_2O$	$M \cdot 17 H_2O$

Table II. Clathrate hydrates formed by small guest molecules

Guest	Host	Guest diameter	Method	Structure	Lattice parameter a
Ar	H_2O	3.83Å	X-ray	II	17.07 (100K)
Kr	H_2O	4.04	X-ray	II	17.08 (100K)
Kr	D_2O		X-ray	II	17.01 (100K)
Kr	D_2O		neutron	II	17.01 (5.7K)
CH_4	D_2O	4.36	neutron	I	11.77 (5.2K)
H_2S	H_2O	4.58	X-ray	I	11.96 (125K)

2. THE SOLID SOLUTION MODEL

In qualitative terms the preference for structure II shown by both
the largest and the smallest clathrate-hydrate-forming molecules is
due to presence in this structure of (1) the largest (16-hedral)
cavities and (2) the larger number of the smallest (12-hedral)
cavities. In more quantitative terms the stabilities of the two
structures relative to ice or liquid water may be expressed [2] as

$$\mu(I) - \mu^0(I) = \frac{kT}{23} \left[\ln(1-\theta_{12}) + 3\ln(1-\theta_{14}) \right] \tag{1}$$

$$\mu(II) - \mu^0(II) = \frac{kT}{17} \left[2\ln(1-\theta_{12}) + \ln(1-\theta_{16}) \right] \tag{2}$$

where $\mu^0(I)$ and $\mu^0(II)$ are the chemical potentials of water molecules in the empty hydrate lattices and θ_{12}, θ_{14} and θ_{16} the fractions of the cages which are occupied by guest molecules. The minimum cage occupancies necessary for hydrate stability relative to ice, say, correspond to values of

$$-\Delta\mu(I) = \mu(\text{ice}) - \mu^0(I) \text{ and } -\Delta\mu(II) = \mu(\text{ice}) - \mu^0(II)$$

which are respectively equal to the right sides of equations (1) and (2). Accurate values of $\Delta\mu$, the excess chemical potential of the empty hydrate lattice over ice, are not available but are almost certainly smaller for structure II than structure I, which is less ice-like in its hydrogen bonding [3]. This is also true of the excess enthalpy Δh, to be considered in section 3. For illustrative purposes we take $\Delta\mu(I) = 1262$ and $\Delta\mu(II) = 882$ J/mol at 0°C, as chosen by Parrish and Prausnitz [4] in their calculations of gas hydrate dissociation pressures, with the realization that these values are uncertain by as much as ±200 J/mol.

Ideally the energy of the absorption sites (cages) is independent of the number of sites already occupied and

$$\theta_i = C_i f/(1 + C_i f) \tag{3}$$

where f is the fugacity of the hydrate-forming gas and C_i the Langmuir constant for a cage of type i. In cases where most of the cages are occupied, $C_i f \gg 1$ and $1 - \theta_i$ is very nearly equal to $1/(C_i f)$.

In the event that all C_i are of similar magnitude, equations (1) and (2) and the above values of chemial potentials for equilibrium with ice at 0° lead to $(1 - \theta)(I)/(1 - \theta)(II) = 0.041/0.111 = f(II)/f(I)$ and structure II first becomes stable at a pressure of the hydrate-forming gas which is only about 40% the pressure at which structure I becomes stable. The assumption of reasonable values for the enthalpy difference between empty hydrate lattices and ice (see section 3) makes structure II relatively even more stable at lower temperatures: thus at −100° structure II is stable at a pressure only 20% of that required for structure I stability.

Structure II is thus more stable under all likely conditions when the guest species are small and C_{12}, C_{14} and C_{16} are approximately equal or, of course, when C_{12} is greater than C_{14} and C_{16}.

At the other extreme (large guest molecules) $C_{12} = 0$ or nearly so and $C_{16}f(II)/C_{14}f(I) = 10.4$ at 0°. Here structure II can be more stable than structure I only if the Langmuir constant for the 16-hedron is larger than that for the 14-hedron by more than a factor of ten, that is, only when the guest molecule is large enough (in general more than 5.8A in largest dimension) to enter the 14-hedron only with difficulty.

3. CYCLOPROPANE HYDRATES

It is instructive to consider the effect of temperature on the relative stabilities of the two structures for guest molecules which are too large to occupy the 12-hedral cages. Given a value of $\Delta\mu$ at 0°, and neglecting pressure effects which tend to be much the same for the two structures, one has

$$\frac{d(\Delta\mu/T)}{dT} = -\frac{\Delta h}{T^2} \tag{4}$$

where Δh is the excess enthalpy per water molecule of the empty hydrate lattice over that of ice if the temperature is below 0° or over that of liquid water above 0°. The former is small and positive for both structures, the latter is relatively large and negative. For concreteness we take [4] $\Delta h(I) = 1150$ J/mol and $\Delta h(II) =$ 807 J/mol below 0°. At a temperature of t° above 0°C one has

$$\Delta h(I) = -4853 - 38.1t + 0.070t^2 \tag{5}$$

$$\Delta h(II) = -5196 - 38.1t + 0.070t^2 \tag{6}$$

where the temperature-dependent terms arise from the variation of the heat of fusion of ice with temperature. Table III illustrates how the relative stability of the two structures changes over a small range of temperature between -20 and +10°.

Table III. Relative stability at different temperatures when $C_{12}=0$

	-20°	-10°	0°	5°	10°
$\Delta\mu(I)/J$ mol^{-1}	1254	1258	1262	1379	1501
$\Delta\mu(II)/J$ mol^{-1}	878	880	882	995	1116
$C_{16}f(II)/C_{14}f(I)$	12.5	11.2	10.4	15.5	23.9

It is clear that if structure II is barely the stabler form at 0° (because C_{16}/C_{14} slightly exceeds 10.4) it will lose its relative stability either (slowly) with decrease of temperature below 0° or (quite rapidly) with increase of temperature. It is unlikely that the **ratio** of the Langmuir constants will change with temperature sufficiently to prevent this consequence.

Temperature-dependent change in stability of this kind is admirably illustrated by the results of Hafemann and Miller [5] for the cyclopropane-water system. The more stable form of cyclopropane hydrate changes from type I to type II at -16° and back from type II to type I at 1.5°; corresponding changes occur at -23° and 5.5° for the cyclopropane deuteriohydrates. The general conclusion that among

molecules of this size range structure II is relatively more stable near $0°$ than at other temperatures is not dependent on the exactness of the thermodynamic parameters which have been assumed. It is also worth noting that the relative stabilities at low temperatures are opposite to what would have been expected for a molecule large enough to fit only with difficulty into the 14-hedron if thermal contraction of the lattice determined the behaviour.

4. STRUCTURE I HYDRATES

For guest molecules small enough that $C_{14} \approx C_{12}$ structure II is the more stable unless C_{16} approaches zero. We must therefore conclude that $C_{14} > C_{12}$ is a stability requirement for most type I hydrates. This contradicts much of the conventional wisdom about small guest molecules in which nearly equal occupancies of the 12-and 14-hedral cages are commonly found (e.g., references [2], [3] and [4]) from model calculations of dissociation pressures. Most of these calculations, in addition to erroneously taking argon and krypton hydrates as model type I structures for fixing molecular interaction parameters, appear to under-estimate the effective size of the water molecule.

Table IV. Equilibrium cage occupancy ratios of type I hydrates at $0°C$

Guest	Size/$\overset{o}{A}$	n	Measured θ_{12}/θ_{14} Cady[6]	Other	Calculated θ_{12}/θ_{14} Parrish[4]	Tse[10]
CH_4	4.36				0.90	0.95
H_2S	4.58	6.12	1.0		0.93	
Xe	4.58	6.48	0.67	0.77[7]	0.96	0.70
CO_2	5.12			0.12[8]	0.66	
NF_3	5.16			0.55[9]		
SO_2	5.27	7.24	0.26			
CF_4	5.35			0.0[11]		0.0
CH_3CH_3	5.54				0.0	
CH_3Cl	5.55	7.72	0.05			
Cl_2	5.59	7.50	0.14			
CH_3Br	5.79	7.83	0.01			
$CHClF_2$	5.88	7.84	0.005			

        Cady has recently determined [6] accurate compositions of a number of structure I hydrates (equilibrium values of **n** in $M \cdot nH_2$) from which values of the cage occupancy ratio θ_{12}/θ_{14} may

be estimated at the smallest gas pressure required for hydrate
stability at 0°C. These and some other estimates are given in Table
IV for guest molecules arranged in the order of increasing largest
diameter. Of the "measured" values given, only the value for xenon
hydrate, which is based on direct measurement [7] of the relative
intensities of Xe-129 NMR lines from xenon atoms in the small and
large cages, is free of any assumption. Cady's values of the
occupancy ratio assume $\Delta\mu(I) = 1108$ J/mol, as do the results for
carbon dioxide hydrate [8] and the new hydrate of nitrogen
trifluoride [9]. Values of 1262 and 1296 J/mol have been assumed in
the Parrish-Prausnitz [4] and Tse-Davidson [10] calculations,
respectively. However, the derived values of θ_{12}/θ_{14} are not greatly
dependent on the value assumed. The Parrish-Prausnitz treatment is
seen to exaggerate the occupancy of the small cages.

Only methane and hydrogen sulphide have similar occupancy
factors for the small and large cages and there is some indication
that even these molecules prefer 14- to 12-hedral cages. This is
certainly so for xenon where an occupancy ratio of 0.77 corresponds
to a value of C_{14} which is an order of magnitude larger than C_{12}.
The occupancy ratio roughly decreases with increasing molecular
diameter, which is only an approximate criterion of 12-hedron
encagability. Other structure I forming molecules which probably
occupy the small cages to a negligible extent and therefore have
compositions close to $M \cdot 7.85H_2O$ are CH_3SH (5.65Å), SO_2F_2 (5.67),
ClO_3F (5.68), $(CH_2)_2S$ (5.91), COS (5.97) and $(CH_2)_3O$ (6.1).

Independent evidence of low occupancy of the small cages by
such molecules as CO_2, C_2D_6, CD_3Cl, and CD_3Br is provided by C-13 and
deuteron NMR lineshapes which show no appreciable contributions from
molecules in the nearly spherical 12-hedra. For geometric reasons
there is a close correlation between lowness of occupancy of the
small cage and preference for orientations within the ellipsoidal
large cage in which the long axis of the guest molecule lies close to
the equatorial plane. (See companion paper "^2H and ^{13}C study of
guest molecule orientation in clathrate hydrates".)

5. LOWER CRITICAL TEMPERATURES

The question of the possible presence of a critical temperature below
which a gas hydrate ceases to be thermodynamically stable is
important to speculation regarding the occurrence of gas hydrates in
the colder reaches of the solar system. It has been suggested that
such a quadruple point may exist for carbon dioxide hydrate.

Extrapolation to low temperatures of the CO_2 hydrate
dissociation pressure curve measured above 152K by Miller and Smythe
[12] suggested to those workers that it should intersect the vapour
pressure curve of solid CO_2 at about 121K. Below this temperature
the hydrate should be unstable relative to solid CO_2 and ice. The
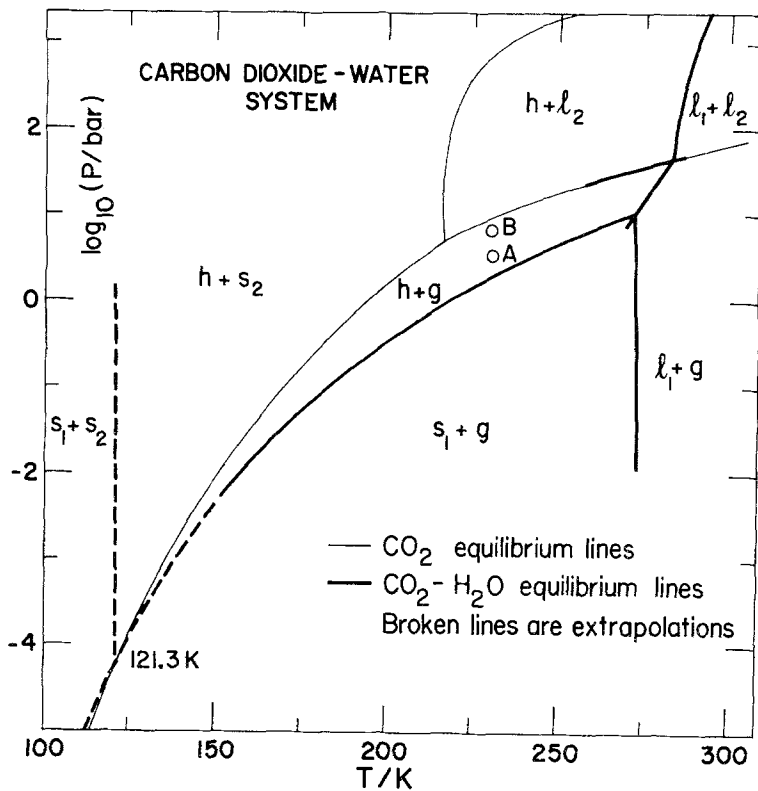phase diagram of the carbon dioxide-water system is shown in
Figure 1.

Figure 1. Phase equilibria in the carbon dioxide-water system. S_1 is ice, S_2 solid CO_2, l_1 and l_2 liquid water and CO_2, h hydrate and g gas. CO_2 hydrate data are from references [12] through [16].

Since equilibration is likely to be very slow at temperatures where the CO_2 vapour pressure is 100 microbars or less, an experiment was performed to test the long-time stability of the hydrate at low temperatures. CO_2 hydrate was prepared by rolling ice for two days in a vessel containing stainless steel rods (to ensure that the ice and hydrate were finely powdered) at a final temperature of 230.4K and a pressure of CO_2 gas of 3.6 bars (point A of Fig. 1). The vessel was then placed in a cryostat and held at about 105K for eleven weeks. When the temperature was allowed to warm to 230.4K over six hours the pressure rose to 6.8 bars (point B); after 90 hours the pressure had returned to the original 3.6 bars. Clearly a considerable fraction (at least half) of the original hydrate had decomposed at 105K and reformed at 230K.

6. REFERENCES

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