

SOME PHYSICAL AND THERMOPHYSICAL PROPERTIES OF CLATHRATE HYDRATES

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1. STRUCTURES OF HYDRATES WITH SMALL GUEST MOLECULES

Oxygen, nitrogen and air, like argon and krypton (1), are found to preferentially form gas hydrates of structure II, rather than structure I as previously expected for gas hydrates of small guest molecules. Lattice parameters from X-ray diffraction are given in the Table.

TABLE I. Hydrate Structures of Small Guest Molecules

<u>Guest</u>	<u>Diameter</u>	<u>Structure</u>	<u>a/Å at 100K</u>
Ar	3.83Å	II	17.07±0.04
Kr	4.04	II	17.08±0.08
O ₂	4.01	II	17.07±0.01*
N ₂	4.10	II	17.11±0.06
Air		II	17.24±0.06
CO	4.10	?	
CH ₄	4.58	I	11.77±0.01*
Xe	4.57	I	11.84±0.02

*Neutron diffraction of D₂O hydrate at 5K.

Laboratory-synthesized "air hydrate", like naturally-occurring air hydrate from the Greenland ice-cap, contains air which is enriched in oxygen and argon. The stable clathrate structure changes back to II for molecules of the size of SF₆ (5.9Å) and larger.

2. CARBON MONOXIDE HYDRATE

This hydrate, whose presence in comets has been suspected for some years, has been prepared for the first time and found to have a dissociation pressure of 128 bars at 0°C (figure 1).

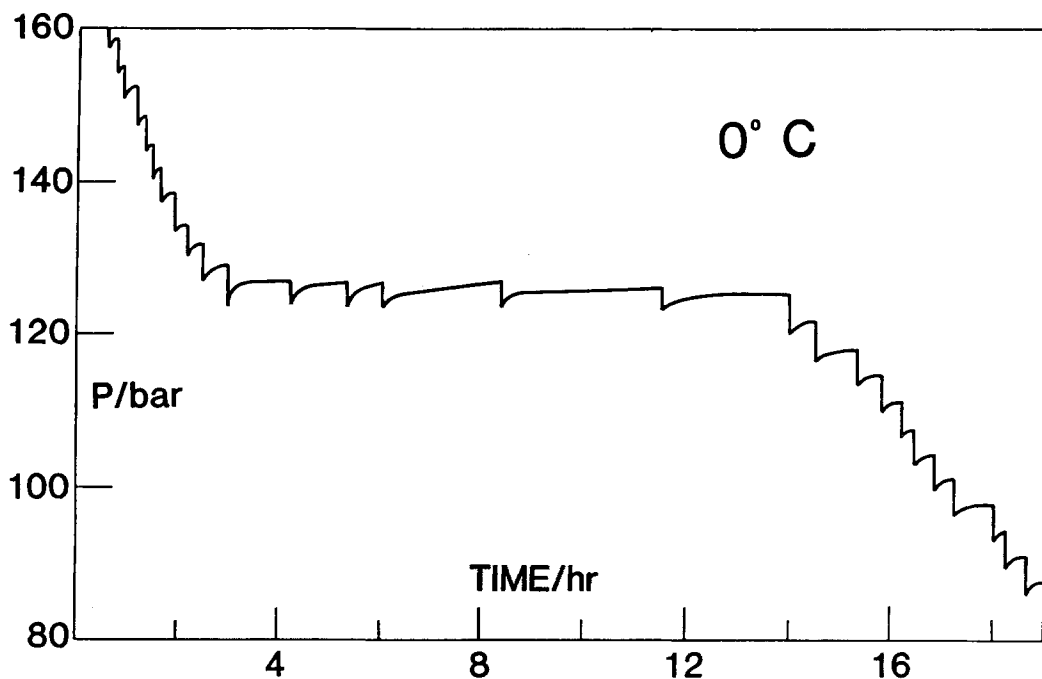


Fig. 1. The response of the pressure over a sample of CO hydrate to step-wise release of gas from the pressure vessel in which the hydrate was formed.

Dielectric absorption arising from reorientation of slightly dipolar CO molecules in the hydrate cages shows the barriers to reorientation to be extremely low (on average <0.5 kJ/mol) and widely distributed because of the frozen-in disorder of the orientations of the water molecules of the lattice. In solid CO itself the barrier is 6 kJ/mol.

3. THERMAL EXPANSIVITIES

Thermal expansivity measurements of ethylene oxide and tetrahydrofuran hydrates have been made by determining the temperature dependence of the spacings of several prominent lines in the powder X-ray diffraction patterns. These lines corresponded to Miller indices of 222, 123, 035 and 135 for ethylene oxide hydrate and 115+333, 135, and 066+228 for tetrahydrofuran hydrate. Expansivities at specific temperatures are given in Table II. These are seen to be much larger than for ice.

Table II. Linear Expansivities $d \ln a/d T$ ($\times 10^6$ K)

	100K	150K	200K	250K
Ice (average)	13	25	37	48
EO Hydrate (I)*	40	58	77	95
THF Hydrate (II)*	36	45	54	61
THF Hydrate**	28	42	52	62

*This work,

**Dilatometric results of Roberts et al. (1984) (2)

Compared to ice, the Grüneisen parameter is abnormally large for the clathrate hydrates at low temperatures. Molecular dynamics simulations using pair-wise additive intermolecular potentials show that the large anharmonicities in the forces acting between water molecules which are necessary to account for large expansivities occur because of the open structures of the lattices of clathrate structures and the presence of the guest molecules

4. CALORIMETRY OF CLATHRATE HYDRATES

Heat capacities above 90K and heats of dissociation of several of the most important gas hydrates have been measured with an automated Tian-Calvet heat flow calorimeter equipped for simultaneous measurement of the pressure. Hydrate compositions were determined by analysis of the decomposition products. The contribution of the water molecules to the heat capacity appears to be nearly the same as for the water molecules in ice.

The tabulated (table III) calorimetric values of the heats of dissociation of gas hydrate into ice and gas have been reduced to the standard state (0°C and 1 bar) by making use of small corrections based on heat capacities and compressibilities. These heats are in all cases more accurate than the heats which have been determined by application of the Clausius-Clapeyron equation to the temperature dependence of the dissociation pressures along the hydrate-ice-gas equilibrium line. The only previous data of comparable accuracy are the unpublished xenon hydrate dissociation pressure results of S.L. Miller at 16 temperatures between -28.5 and 0°C which give 25.32 ± 0.25 kJ/mol. This result is to be compared with the first entry in table III. The second entry refers to hydrate prepared under xenon pressure much higher than the three-phase equilibrium value. Combination of the two entries suggests that the heat of engagement of Xe depends on the degree of cage occupancy, at least for large cage occupancies.

Table III. Calorimetrically determined molar enthalpy changes for the dissociation of a hydrate into ice and gas at 273.15K and 1 bar

Hydrate	$\Delta H_m / \text{kJ mol}^{-1}$
Xe·6.29H ₂ O	25.43 ± 0.17
Xe·5.90H ₂ O	26.50 ± 0.17
Kr·6.10H ₂ O	19.54 ± 0.24
CH ₄ ·6.00H ₂ O	18.13 ± 0.27
C ₂ H ₆ ·7.67H ₂ O	25.70 ± 0.37
C ₃ H ₈ ·17.0H ₂ O	27.00 ± 0.33
i-C ₄ H ₁₀ ·17.0H ₂ O	31.07 ± 0.20

5. FREE ENERGY OF THE EMPTY STRUCTURE I LATTICE

The basic requirement for stability of a clathrate is that there be sufficient occupancy of the clathrate cages to reduce the free energy of the molecules making up the lattice to a value equal to or less than the free energy of the same molecules in the form (solid or liquid) stable in the absence of the guest species. In the case of gas hydrates of structure I, the minimum condition of stability is given by the ideal solution as

$$-\Delta\mu = kT [\ln(1-\theta_s) + 3 \ln(1-\theta_L)]/23$$

where $\Delta\mu$ is the chemical potential of the water molecules in the empty hydrate lattice relative to ice (or liquid water) and θ_s and θ_L are the degrees of occupancy of the small and large cages which just stabilize the hydrate. We have determined $\Delta\mu$ for Xe hydrate (3) the most ideal of structure I hydrates.

The equilibrium hydrate at 0°C was found to have the composition Xe·(6.286±0.030)H₂O. The ¹²⁹Xe proton-decoupled NMR spectrum gives two well-resolved peaks with relative areas which, allowing for the presence of three times as many large as small cages, give $\theta_s/\theta_L = 0.73\pm 0.02$. Together these results determine $\Delta\mu = 1297\pm 110$ J/mol. A nearly identical result was obtained from a recent study by Dharma-Wardhana et al. of type I cyclopropane hydrate with the assumption that cyclopropane is too large to occupy any of the small cages.

1. D.W. Davidson, Y.P. Handa, C.I. Ratcliffe, J.S. Tse, and B.M. Powell, *Nature* 311, 142 (1984).
2. R.B. Roberts, C. Andrikidis, R.J. Tarnish and G.K. White, *Proc. 10th Int. Cryogenic Eng. Conf.*, Helsinki, p. 409, Butterworth (1984).
3. D.W. Davidson, Y.P. Handa and J.A. Ripmeester, *J. Phys. Chem.* (in press).