

Low-temperature Thermodynamic Study of the Empty Clathrate Hydrates

Fernando J.A.L. Cruz,^a Saman Alavi,^{b,c} José P.B. Mota^a

a) LAQV@Requimte, Dept. Chemistry, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal; b) National Research Council of Canada, Ottawa, Ontario, K1A 0R6, Canada; c) Dept. Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

Email: fj.cruz@fct.unl.pt

Clathrate hydrates (CHs) are naturally occurring guest-inclusion compounds, that can be found in the Earth permafrost regions and in deep-sea oil and gas pipelines where they act as clogging agents inhibiting the flow of industrially relevant fluids (oil, natural gas); commercial interest in CHs sparks from their ability to act as natural reservoirs for large volumes of CO₂, via injection into deep sea at depths of 3200 m, where hydrostatic pressure can reach 325 bar. Furthermore, the amount of CH₄ eventually trapped in natural methane CHs deposits, essentially in seafloor sediments, is expected to be quite significant (1–5×10¹⁵ m³).¹ Such inclusion compounds have also been observed in comets and outer planets, and their occurrence has been suggested in particular on Mars, Saturn, Uranus, and Neptune.² The empty structure of CHs is made up of approximately tetrahedrally arranged H₂O molecules, linked amongst themselves via strong hydrogen bonds, and giving rise to an ice-like crystalline solid exhibiting two or three distinct roughly symmetrical cages where guest molecules can be encapsulated. Here we focus on sl structures (**Figure 1**) because it is the most commonly occurring polymorph under natural environments where CH₄ is the principal species for hydrate formation.³

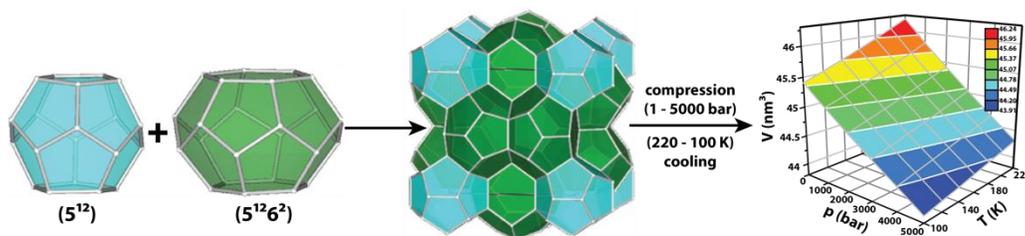


Figure 1: Pictorial representation of small (5^{12}) and large (5^{126^2}) cavities of a sl clathrate hydrate, containing 20 and 24 H₂O molecules, respectively, and complete p - V - T surface obtained from the calculations. Only the oxygen atoms in the polyhedral vertices are included. Note that the cavities obey Euler's convex polyhedra theorem: Face + Vertices = Edges + 2.

The thermodynamics of the metastable empty sl CHs are probed⁴ over broad temperature and pressure ranges ($100 \leq T/K \leq 220$, $1 \leq p/\text{bar} \leq 5000$), using large-scale molecular dynamics simulations and compared with available experimental data at 1 bar. The whole p - V - T surface is interpreted using the universal form of the Parsafar and Mason equation of state, with an accuracy of 99.7–99.9 %. Framework deformation brought about by applied temperature follows a parabolic law, and there is a critical temperature above which the isobaric thermal expansion becomes negative, 94.7 K (1 bar) and 166.2 K (5000 bar). Response to the applied (p , T) field is analysed in terms of an angular and length descriptors of a canonical tetrahedral structure, and observed to occur mainly by means of angular deformation for (p , T) > (2000 bar, 200 K). The length of the hydrogen bonds responsible for framework integrity is insensitive to the thermodynamic conditions and its average value is $\bar{r}_{(\text{O}-\text{H})} = 0.25$ nm.

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