

GAS HYDRATE PHASE EQUILIBRIA AT THE MOLECULAR SCALE: RECENT ADVANCES AND FUTURE CHALLENGES

I. N. Tsimpanogiannis^{1,*}

¹ 6th km Harilaou-Thermi Rd, 57001 Thermi, Thessaloniki, GR,
Chemical Process & Energy Resources Institute (CPERI),
Centre for Research & Technology Hellas (CERTH)

* i.n.tsimpanogiannis@certh.gr

ABSTRACT

Three-dimensional cages/cavities formed by self-assembled water molecules can be stabilized by the inclusion of guest molecules that can fit within the cages (e.g., methane, carbon dioxide, nitrogen, hydrogen, etc.). The resulting ice-like, non-stoichiometric solid materials are known as “clathrate hydrates” or “gas hydrates” if the stabilizing guest is a gas.

The characteristic of gas hydrates to selectively incorporate in their solid structure particular guest molecules from a mixture, while excluding others, has attracted the attention of industry and are currently under consideration for a number of important industrial applications including gas mixture separation, storage and transportation of “energy carrier” gases (hydrogen, methane) or greenhouse gases (carbon dioxide), and water desalination. Hydrate-related issues are also encountered in “flow assurance” in oil/gas industry, as an ocean drilling hazard, as an environmental impact due to uncontrolled release of methane from oceanic hydrate sediments, and also hydrates are considered as a future energy source.

The process design of hydrate-related industrial applications requires the reliable knowledge of a number of thermodynamic, kinetic, transport and structural parameters. Such parameters can be obtained through (i) experimental measurements, (ii) estimation through theoretical/semi-theoretical methods at the continuum scale level. A third approach that is constantly gaining ground in recent years is that of molecular simulations, which is a direct result of the increase of computational power. Methods such as Monte Carlo (MC) and Molecular Dynamics (MD) increasingly prove their reliability by offering predictions of equal quality, while additionally possessing the intrinsic value of providing a more profound understanding of the related phenomena at a molecular level.

In the current study we provide a critical review of molecular level, hydrate-related studies with emphasis on the prediction of three-phase (hydrate – liquid water – vapor) equilibria conditions. While the primary emphasis of the study is providing a detailed discussion of advances associated with the “phase coexistence” methodology using MD simulations, other MC-based approaches are also included in the discussion. A historic perspective of the application of the methodology to hydrates is presented and success stories are discussed in detail. Finally, future challenges and tentative directions for research are presented.

KEYWORDS: molecular simulations, gas hydrates, phase equilibria