Gas Hydrates 1

Series Editor
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Fundamentals, Characterization and Modeling

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Cover image: DIC image of cyclopentane hydrate formed on a water drop (with diameter in the mm range) on hydrophilic glass, showing a faceted crust over the water, surrounded by a fine-grained halo, on the substrate under the guest phase (see Chapter 3). Pixel coloring by intensity (dark to light shades) highlights the delicate beauty of hydrate crystals revealed by high resolution microscopy.

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Preface

Clathrate hydrates are crystalline inclusion compounds resulting from the hydrogen bonding of water (host) molecules enclosing relatively small (guest) molecules, such as hydrogen, noble gases, carbon dioxide, hydrogen sulfide, methane and other low-molecular-weight hydrocarbons. They form and remain stable at low temperatures – often well below ambient temperature – and high pressures – ranging from a few bar to hundreds of bar, depending on the guest molecule. Long considered either an academic curiosity or a nuisance for oil and gas producers confronted with pipeline blockage, they are now being investigated for applications as diverse as hydrogen or methane storage, gas separation, cold storage and transport, water treatment, etc. The ubiquitous presence of natural gas hydrates not only in the permafrost, but also in deep marine sediments, has been identified, and their role in past and present environmental changes and other geohazards, as well as their potential as an energy source, are under intense scrutiny.

These perspectives are motivating an ever-increasing research effort in the area of gas hydrates, which addresses both fundamental issues and applications. Gas hydrates exhibit fascinating yet poorly understood phenomena. Perhaps the most fascinating feature exhibited by gas hydrates is *self-preservation,* or the existence of long-lived metastable states in some conditions far from stable thermodynamic equilibrium. Strong departures from equilibrium are also noted in gas hydrate compositions, depending on their formation and kinetic pathways. A proper understanding of these two effects could serve in developing gas storage and selective molecular-capture processes. The *memory effect*, or the ability of gas hydrates to reform rapidly in an aqueous solution where gas hydrates have been freshly melted, is another puzzling phenomenon. Gas hydrates are likely to be soon exploited for storing gas (guest) molecules or for separating or capturing some of them selectively; yet, the occupancy rates of the different hydrate crystal cavities by

the various guest molecules are not fully understood. Very little is known as well on hydrate formation and their stability in the extreme conditions (e.g. low or high pressures) such as on extraterrestrial bodies like comets and planets. How hydrates interact with substrates is a topic of prime interest for understanding not only the behavior of hydrates in sediments, but also why some mesoporous particles act as hydrate promoters. Nucleation and growth processes are still unsettled issues, together with the mechanisms by which additives (co-guest molecules, surfactants, polymers, particles, etc.) promote or inhibit hydrate formation. Depending on the application, these additives are needed to either accelerate or slow down the crystallization process; but their selection is still carried out on a very empirical basis. This book gathers contributions from scientists who actively work in complementary areas of gas hydrate research. They have been meeting and exchanging views regularly over the past few years at a national (French) level, and recently at a European level, within the COST Action MIGRATE (Marine gas hydrate – an indigenous resource of natural gas for Europe). This book is somehow the written expression of those meetings and exchanges. It is divided into two volumes: the first (and present) volume is devoted to the fundamentals, characterization and modeling of gas hydrates, whereas the second volume will focus on gas hydrates in their natural environment and for industrial applications.

The present volume starts with an extensive presentation of the experimental tools capable of probing small spatial and temporal scales: neutron scattering (Chapter 1), spectroscopy (Chapter 2) and optical microscopy (Chapter 3). In addition to providing fundamental insights into structural and dynamical properties, these tools have allowed considerable progress in the understanding of the molecular and mesoscopic mechanisms governing hydrate formation and growth. Moving to larger scales, the calorimetric tools used to measure heat and related thermodynamic properties are described in Chapter 4. Chapter 5 provides a comprehensive view of the thermodynamic modelling of solid-fluid equilibria, from pure solid phases to gas semiclathrate hydrates. Finally, Chapter 6 presents a novel approach coupling thermodynamics and kinetics to describe the non-equilibrium effects occurring during hydrate formation, with a focus on the evolution of the composition of the hydrate phase. Most of these chapters extend their scope to semi-clathrates, in which gas or small molecules still occupy the crystal cavities, but the cavities themselves consist of water and organic species, such as quaternary ammonium salts, strong acids or bases. These semiclathrates hold great promise from a practical point of view, because the temperature and pressure conditions of their formation and stability are closer to the ambient than their hydrate counterparts.

Volume 2 addresses geoscience issues and potential industrial applications. It deals with marine gas hydrates through a multidisciplinary lens, integrating both

field studies and laboratory work and analyses, with a focus on the instrumentations and methods used to investigate the dynamics of natural deposits. This is followed by the description of the geochemical models used for investigating the temporal and spatial behavior of hydrate deposits. Finally, potential industrial applications of clathrate and semiclathrate hydrates are also presented in that volume.

To conclude, we would like to warmly thank all the contributors to the present volume for taking the time to write concise and clear introductions to their fields.

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