
Contents

Preface	ix
Chapter 1. Neutron Scattering of Clathrate and Semiclathrate Hydrates	1
Arnaud DESMEDT, Laura BEDOURET, Jacques OLLIVIER and Claire PETUYA	
1.1. Introduction	1
1.2. Neutron scattering	2
1.2.1. A basic ideal scattering experiment	3
1.2.2. Neutron scattering theory	4
1.2.3. Correlation functions	6
1.2.4. Coherent and incoherent scattering	7
1.2.5. A simple example of scattering	11
1.3. Probing structural and dynamical properties of gas hydrates	14
1.3.1. Structures	15
1.3.2. Relaxation of guest molecules and water molecules	16
1.3.3. Excitations and vibrational density of states	19
1.4. Selected examples	22
1.4.1. Inhibition and formation mechanisms	22
1.4.2. Guest replacement in gas hydrates	29
1.4.3. Hydrogen: from its dynamics properties to its storage capabilities	33
1.4.4. Ionic clathrate hydrates and semiclathrates	41
1.5. Concluding remarks	47
1.6. Bibliography	49

Chapter 2. Spectroscopy of Gas Hydrates: From Fundamental Aspects to Chemical Engineering, Geophysical and Astrophysical Applications	63
Bertrand CHAZALLON, Jennifer A. NOBLE and Arnaud DESMEDT	
2.1. Introduction.	63
2.2. Vibrational spectrum	65
2.2.1. Intramolecular modes	66
2.2.2. Intermolecular modes	68
2.3. Applications to the investigation of formation mechanism.	72
2.3.1. Formation mechanism: nucleation and growth.	72
2.3.2. The Raman contribution.	74
2.3.3. Insights from IR spectroscopy	77
2.3.4. Formation mechanism: chemical engineering applications	81
2.4. NGHs: contribution of spectroscopy	84
2.5. Clathrate hydrates in astrophysical environments.	92
2.5.1. IR spectroscopy of astrophysical ices.	93
2.5.2. Interstellar ices.	94
2.5.3. Solar system ices.	96
2.5.4. Insights from laboratory spectroscopy	100
2.6. Concluding remarks	101
2.7. Bibliography	102
Chapter 3. High-Resolution Optical Microscopy of Gas Hydrates	113
Nelly HOBEIKA, Maria Lourdes MARTINEZ DE BAÑOS, Patrick BOURIAT, Daniel BROSETA and Ross BROWN	
3.1. Introduction.	113
3.2. Optical methods	114
3.2.1. Beyond bright-field modes in optical microscopy	114
3.2.2. Brewster angle microscopy	123
3.3. Selected examples	126
3.3.1. Hydrate halos growing on glass substrates	128
3.3.2. Hydrate crystallization in a guest-in-water emulsion	131
3.3.3. Adsorption of kinetic hydrate inhibitors	136
3.4. Concluding remarks	141
3.5. Acknowledgments	142
3.6. Bibliography	142

Chapter 4. Calorimetric Characterization of Clathrate and Semiclathrate Hydrates.	145
Didier DALMAZZONE, Luiz Paulo SALES SILVA, Anthony DELAHAYE and Laurence FOURNAISON	
4.1. Introduction.	145
4.2. DTA and differential scanning calorimetry	146
4.2.1. Principles of DTA and DSC.	146
4.2.2. Examples of pressure-controlled DTA and DSC devices for hydrate studies	147
4.2.3. Temperature calibration of DSC	152
4.3. Phase equilibrium determination in hydrate systems using pressure-controlled TDA and DSC.	153
4.3.1. Proper exploitation of DSC thermograms	153
4.4. Measuring the heat of dissociation and heat capacity of gas hydrates	158
4.4.1. Quantitative <i>in situ</i> hydrate formation	160
4.4.2. Indirect enthalpy measurement and gas content evaluation	162
4.4.3. Heat capacity measurement	163
4.5. Measuring the kinetics of hydrate formation	166
4.6. Conclusion	168
4.7. Bibliography	169
Chapter 5. Thermodynamic Modeling of Solid–Fluid Equilibria: From Pure Solid Phases to Gas Semiclathrate Hydrates.	177
Patrice PARICAUD	
5.1. Introduction.	177
5.2. Solid–fluid equilibrium between a fluid mixture and a pure solid phase	179
5.2.1. Solid–liquid equilibrium condition	179
5.2.2. SLE in the presence of electrolyte solutions	185
5.2.3. Solid–fluid equilibrium condition.	188
5.3. Solid–liquid equilibrium between a liquid mixture and a solid solution	189
5.4. SLE between a liquid mixture and a solid compound	192
5.4.1. Solid–liquid equilibrium with salt hydrates	192
5.4.2. Solid–liquid equilibrium with semiclathrate hydrates	199
5.5. Thermodynamic model for gas semiclathrate hydrates	202
5.5.1. Paricaud’s approach	203
5.5.2. The Eslamimanesh <i>et al.</i> model.	213

5.6. Conclusion	215
5.7. Bibliography	215
Chapter 6. Volume and Non-Equilibrium Crystallization of Clathrate Hydrates	227
Baptiste BOUILLOT and Jean-Michel HERRI	
6.1. Introduction.	227
6.2 Driving force and evidence for non-equilibrium gas hydrate crystallization	229
6.2.1. Driving force.	229
6.2.2. Cage occupancy from equilibrium thermodynamics.	233
6.3. Non-equilibrium hydrate formation?	235
6.3.1. Evidence from experimental studies	236
6.3.2. Clathrate hydrates in fluid inclusions	238
6.3.3. Evidence from molecular dynamics	239
6.3.4. Experimental and modeling issues	240
6.4. Modeling gas to hydrate transfer: equilibrium thermodynamics versus kinetics	241
6.5. Non-equilibrium flash calculations	242
6.5.1. Basics of flash calculations	242
6.5.2. Conventional flash approach for clathrate hydrates	243
6.5.3. Conclusions on standard flash approaches	248
6.5.4. Non-stoichiometric flash approaches	249
6.5.5. Discussion	255
6.6. A kinetic Langmuir based modeling approach	258
6.6.1. Introduction to the kinetic approach of mixed hydrates	258
6.6.2. Kinetic approach of enclathration.	267
6.7. Conclusion	274
6.8. Nomenclature.	274
6.8.1. Letters	274
6.8.2. Greek letters	275
6.8.3. Subscript	276
6.8.4. Superscript	276
6.9. Bibliography	276
List of Authors	283
Index	285