Contents

Pref	ace			xix
Auth	ors			xxv
Cha	pter 1	Overvie	ew and Historical Perspective	1
1.1	Hydra	tes as a L	aboratory Curiosity	1
	1.1.1	Hydrate	s of Hydrocarbons Distinguished from Inorganic	
		Hydrate	s and Ice	5
	1.1.2	Method	s to Determine the Hydrate Composition	5
	1.1.3	Phase D	Diagrams Provide Hydrate Classification	6
1.2	Hydra	tes in the	Natural Gas Industry	9
	1.2.1	Initial E	Experiments on Natural Gas Hydrates	9
	1.2.2	Initial C	Correlation of Hydrate Phase Equilibria	11
	1.2.3	Hydrate	Crystal Structures and Hydrate Type Definitions	11
	1.2.4	Basis fo	or Current Thermodynamic Models	14
	1.2.5	Time-D	ependent Studies of Hydrates	16
	1.2.6	Work to	Enable Gas Production, Transport, and Processing	19
	1.2.7		s in Mass and Energy Storage and Separation	20
1.3	Hydra	ites as an	Energy Resource	22
	1.3.1	In Situ I	Hydrates	23
	1.3.2	Investig	ations Related to Hydrate Exploration and Recovery	26
1.4	Envire	onmental	Aspects of Hydrates	27
1.5	Safety	Aspects	of Hydrates	27
1.6	Relati	onship of	This Chapter to Those That Follow	28
Refe	erences		-	29
Cha	pter 2	Molecu	lar Structures and Similarities to Ice	45
2.1	Crysta	al Structu	res of Ice Ih and Natural Gas Hydrates	46
	2.1.1	Ice, Wat	ter, Hydrogen Bonds, and Clusters	46
		2.1.1.1	Ice and Bjerrum defects	46
		2.1.1.2	The water molecule	49
		2.1.1.3	Hydrogen bonds	49
		2.1.1.4	Hydrogen bonds cause unusual water, ice, and	
			hydrate properties	50
		2.1.1.5	Pentamers and hexamers	52

	2.1.2	Hydrate Crystalline Cavities and Structures	53
		2.1.2.1 The cavities in hydrates	53
		2.1.2.2 Hydrate crystal cells—structures I, II, and H	59
	2.1.3	Characteristics of Guest Molecules	72
		2.1.3.1 Chemical nature of guest molecules	72
		2.1.3.2 Geometry of the guest molecules	73
		2.1.3.3 Filling the hydrate cages	85
	2.1.4	Summary Statements for Hydrate Structure	91
2.2		arison of Properties of Hydrates and Ice	92
	2.2.1	Spectroscopic Implications	93
	2.2.2	Mechanical Properties	95
		2.2.2.1 Mechanical strength	95
		2.2.2.2 Elastic properties	96
	2.2.3	Thermal Properties	97
	2.2.0	2.2.3.1 Thermal conductivity of hydrates	97
		2.2.3.2 Thermal expansion of hydrates and ice	101
2.3	The W	/hat and the How of Hydrate Structures	102
			102
Kele	ichees	······································	102
Cha	pter 3	Hydrate Formation and Dissociation Processes	113
3.1	•	te Nucleation	116
5.1	3.1.1	Knowledge Base for Hydrate Nucleation	117
	5.1.1	3.1.1.1 Key properties of supercooled water	117
		3.1.1.2 Solubility of natural gases in water	119
		3.1.1.3 Nucleation theory for ice and hydrates	121
		3.1.1.4 Site of hydrate nucleation	129
	3.1.2	Conceptual Picture of Hydrate Nucleation at the Molecular	129
	5.1.2	Level	130
		3.1.2.1 Labile cluster nucleation hypothesis	130
		• -	131
		3.1.2.2 Nucleation at the interface hypothesis	134
	212	3.1.2.3 Local structuring nucleation hypothesis	
	3.1.3	Stochastic Nature of Heterogeneous Nucleation	138
	3.1.4	Correlations of the Nucleation Process	142
	215	3.1.4.1 Driving force of nucleation	143
	3.1.5	The "Memory Effect" Phenomenon	147
	3.1.6	State-of-the-Art for Hydrate Nucleation	149
3.2	Hydra	te Growth	150
	3.2.1	Conceptual Picture of Growth at the Molecular Level	150
		3.2.1.1 Crystal growth molecular concepts	150
		3.2.1.2 The boundary layer	152
	3.2.2	Hydrate Crystal Growth Processes	155
		3.2.2.1 Single crystal growth	155
		3.2.2.2 Hydrate film/shell growth at the water-hydrocarbon	
		interface	156
		3.2.2.3 Crystal growth with interfacial agitation	166

		3.2.2.4 Growth of metastable phases	167
	3.2.3	Correlations of the Growth Process	168
		3.2.3.1 Growth kinetics-the Englezos-Bishnoi model	
		3.2.3.2 Mass transfer—the Skovborg–Rasmussen model	
		3.2.3.3 Heat transfer models	172
	3.2.4	State-of-the-Art for Hydrate Growth	176
3.3		te Dissociation	176
	3.3.1	Conceptual Picture of Hydrate Dissociation	176
	3.3.2	Correlations of Hydrate Dissociation	177
	3.3.3	Anomalous Self-Preservation	179
	3.3.4	State-of-the-Art for Hydrate Dissociation	180
3.4		ary	180
		·····	181
1.010	nemees.		101
Cha	pter 4	Estimation Techniques for Phase Equilibria of Natural Gas	
0	Prox 1	Hydrates	189
Intro	oduction	n	189
4.1		te Phase Diagrams for Water + Hydrocarbon Systems	196
	4.1.1	Pressure–Temperature Diagrams of the $CH_4 + H_2O$ (or	170
	7.1.1	$N_2 + H_2O$) System	197
	4.1.2	Systems (e.g., $H_2O + C_2H_6$, C_3H_8 , or i-C ₄ H ₁₀) with Upper	177
	4.1.2	Quadruple Points \dots	200
	4.1.3	Pressure–Temperature Diagrams for Multicomponent Natural	200
	4.1.5	Gas Systems	201
	4.1.4	Pressure–Temperature Diagrams for Systems with	201
	4.1.4	Inhibitors	202
	415		
	4.1.5	Temperature–Composition Diagrams for Methane + Water	
	4.1.6	Solubility of Gases Near Hydrate Formation Conditions	
4.0	4.1.7	Pressure-Temperature Diagrams for Structure H Systems	205
4.2		-Phase (L _W -H-V) Equilibrium Calculations	
	4.2.1	The Gas Gravity Method	
		4.2.1.1 Hydrate limits to gas expansion through a valve	
	4.2.2	The Distribution Coefficient (K_{vsi} -Value) Method	215
4.3		uple Points and Equilibrium of Three Condensed Phases	
		H-L _{HC})	
	4.3.1	The Location of the Quadruple Points	
	4.3.2	Condensed Three-Phase Equilibrium	
4.4			
	4.4.1	Hydrate Inhibition via Alcohols and Glycols	
	4.4.2	Hydrate Inhibition Using Salts	
4.5	Two-F	Phase Equilibrium: Hydrates with One Other Phase	
	4.5.1	Water Content of Vapor in Equilibrium with Hydrate	237
	4.5.2	Water Content of Liquid Hydrocarbon in Equilibrium with	
		Hydrates	239
	4.5.3	Methane Content of Water in Equilibrium with Hydrates	240

and the second

4.6	Hydra	te Enthalpy and Hydration Number from Phase	
	Equilibrium		
	4.6.1	The Clausius–Clapeyron Equation and Hydrate	
		Equilibrium	241
		4.6.1.1 Enthalpy of dissociation and cavity occupation	243
	4.6.2	Determination of the Hydration Number	
		4.6.2.1 Using the Clapeyron equation to obtain hydration	
		number	247
		4.6.2.2 Hydration numbers by the Miller and	
		Strong method	250
4.7	Summ	hary and Relationship to Chapters Which Follow	
Cha	pter 5	A Statistical Thermodynamic Approach to Hydrate Phase	
	-	Equilibria	257
Intro	duction	n and Overview	
5.1	Statist	tical Thermodynamics of Hydrate Equilibria	258
	5.1.1	Grand Canonical Partition Function for Water	
	5.1.2	The Chemical Potential of Water in Hydrates	
	5.1.3	The Langmuir Adsorption Analogy	
	5.1.4	Relating the Langmuir Constant to Cell Potential Parameters	
	5.1.5	Activity Coefficient for Water in the Hydrate	
	5.1.6	Defining the Hydrate Fugacity and Reference Parameters	
	5.1.7	The Gibbs Free Energy Method	
	5.1.8	Accuracy of CSMGem Compared to Commercial	
		Hydrate Programs	291
	5.1.9	Ab Initio Methods and the van der Waals and	
		Platteeuw Method	293
5.2	Applic	cation of the Method to Analyze Systems of	275
		ane + Ethane + Propane	296
		Pure Hydrate Phase Equilibria	
	5.2.2	Binary Hydrate Phase Equilibria	
	0.40.20	5.2.2.1 Methane + propane hydrates	
		5.2.2.1 Methane + propane hydrates	
		5.2.2.2 Internate + cinate hydrates	
		5.2.2.4 Ternary hydrate phase equilibria and industrial	502
		application	205
5.3	Comp	uter Simulation: Another Microscopic–Macroscopic Bridge	207
5.5	5.3.1		307
	5.5.1	Basic Techniques of Monte Carlo and Molecular Dynamics	308
		Simulation	
		5.3.1.1 Molecular dynamics	309
	520	5.3.1.2 Monte Carlo	
5 A	5.3.2	What Has Been Learned from Molecular Simulation?	311
5.4	-	er Summary and Relationship to Following Chapters	313
References			

Cha	pter 6	Experimental Methods and Measurements of Hydrate	
		Properties	319
6.1	-	imental Apparatuses and Methods for Macroscopic	
		irements	320
	6.1.1	J	
		Kinetics	
		6.1.1.1 Principles of equilibrium apparatus development	
		6.1.1.2 Apparatuses for use above the ice point	
		6.1.1.3 Apparatus for use below the ice point	
		6.1.1.4 Apparatuses for two-phase equilibria	
		6.1.1.5 Flow loops for hydrate formation kinetics	
	6.1.2	Methods for Measurement of Thermal Properties	
		6.1.2.1 Heat capacity and heat of dissociation methods	
		6.1.2.2 Methods for thermal conductivity measurements	
6.2		arements of the Hydrate Phase	
	6.2.1	Mesoscopic Measurements of the Hydrate Phase	
	6.2.2	Molecular-Level Measurements of the Hydrate Phase	
		6.2.2.1 Diffraction methods	
		6.2.2.2 Spectroscopic methods	350
6.3		or Natural Gas Hydrate Phase Equilibria and	
		al Properties	
	6.3.1	Phase Equilibria Data	
		6.3.1.1 Equilibria of simple natural gas components	
		6.3.1.2 Equilibria of binary guest mixtures	
		6.3.1.3 Equilibria of ternary guest mixtures	
		6.3.1.4 Equilibria of multicomponent guest mixtures	
		6.3.1.5 Equilibria with inhibitors	
	6.3.2	Thermal Property Data	
	~	6.3.2.1 Heat capacity and heat of dissociation	
6.4		ary and Relationship to Chapters that Follow	
Refe	rences		523
Cha	pter 7	Hydrates in the Earth	537
Intro	duction	and Overview	537
7.1		aradigm Is Changing from Assessment of Amount to	
		ction of Gas	539
	7.1.1	Extent of the Occurrence of In Situ Gas Hydrates	
7.2	Sedim	ents with Hydrates Typically Have Low Contents of	
		nic Methane	550
	7.2.1	Generation of Gases for Hydrate Formation	551
	7.2.2	The SMI, the Hydrate Upper Boundary, and the SMI	
		Rule-of-Ten	555
	7.2.3	Mechanisms for Generation of Hydrates	557
		7.2.3.1 Hydrate formation in the two-phase region	558
		7.2.3.2 Models for <i>in situ</i> hydrate formation	560

7.3	Sedim	ent Lithology and Fluid Flow Are Major Controls or	1 Hydrate	
	Depos	ition		566
7.4	Remo	te Methods Enable an Estimation of the Extent of a H	Iydrated	
		voir		566
	7.4.1	The Hydrate Pressure–Temperature Stability Envelo	ope	567
	7.4.2	Seismic Velocity Techniques and Bottom Simulatin		
		Reflections		571
	7.4.3	Methane Solubility Further Limits the Hydrate Occ		575
7.5	Drillin	ng Logs and/Coring Provide Improved Assessments of		
		ted Gas Amounts		576
	7.5.1	Open Hole Well Logs		577
		Evidence of Hydrates in Cores		
		Combining Laboratory and Field Experiments		582
7.6		te Reservoir Models Indicate Key Variables for Meth		
	•	ction		583
7.7		Hydrated Gas Production Trends Are from the Pern		
		cean		587
7.8		tes Play a Part in Climate Change and Geohazards		589
	•	Case Study 1: Leg 164 in the Blake-Bahama Ridge		
		Assessment)		592
		7.8.1.1 Site 994		594
		7.8.1.2 Site 995		597
		7.8.1.3 Site 997		598
		7.8.1.4 Common features		
	7.8.2	Case Study 2: Hydrate Ridge (Hydrate Assessment)		599
		7.8.2.1 Near surface hydrates: the chemosynthetic	·	
		community and chemoherms		601
		7.8.2.2 Deeper hydrates at Southern Hydrate Ridg		
		characterization and assessment		604
		7.8.2.3 Logs and remote sensing		
		7.8.2.4 Coring and direct evidence		
		7.8.2.5 The lessons of Hydrate Ridge		
	7.8.3	Case Study 3: Messoyakha (Hydrate Production		
		in Permafrost)		609
	7.8.4	Case Study 4: Mallik 2002 (Hydrate Production		
		in Permafrost)		616
		7.8.4.1 Background of the Mallik 2002 well		
		7.8.4.2 Overview of the Mallik 2002 well		
		7.8.4.3 Well logs in Mallik 2002		620
		7.8.4.4 Pressure stimulation tests in the 5L-38 we		620
		7.8.4.5 The Thermal stimulation test in Mallik 5L		621
		7.8.4.6 Modeling gas production from hydrates		625
7.9	Summ	ary		628
		·····		629

		Hydrates in Production, Processing, and Transportation	643
		1	
8.1	How I	Do Hydrate Plugs Form in Industrial Equipment?	644
	8.1.1	Case Study 1: Hydrate Prevention in a Deepwater	
		Gas Pipeline	645
	8.1.2	Case Study 2: Hydrates Prevention via Combination	
		of Methods	647
		8.1.2.1 Burying the pipeline	
		8.1.2.2 Line burial with wellhead heat addition	
		8.1.2.3 Burial, heat addition, and insulation	
		8.1.2.4 Methanol addition alternative	
	8.1.3	Case Study 3: Hydrate Formation via Expansion through	
		Valves or Restrictions	651
	8.1.4	Conceptual Overview: Hydrate Plug Formation in	
		Oil-Dominated Systems	653
	8.1.5	Conceptual Overview: Hydrate Formation in Gas-Dominated	
		Systems	654
8.2	How A	Are Hydrate Plug Formations Prevented?	
0.2	8.2.1	Case Study 4: Thermodynamic Inhibition Canyon Express	000
	0.2.1	and Ormen Lange Flowlines	656
	822	Case Study 5: Under-Inhibition by Methanol in a Gas Line	
		Kinetic Hydrate Inhibition	
	0.2.5	8.2.3.1 Antiagglomerant means of preventing	057
		hydrate plugs	662
	871	Case Study 6: AAs are a Major Hydrate Plug	002
	0.2.4	Prevention Tool	669
8.3	Ham I	s a Hydrate Plug Dissociated?	
0.5		Case Study 7: Gulf of Mexico Plug Removal in	009
	0.3.1		675
04	G . C . A	Gas Export Line	
8.4		and Hydrate Plug Removal.	070
	8.4.1	Case Study 8: Hydrate Plug Incident Resulting in	(77
0 7		Loss of Life	
8.5		ations to Gas Transport and Storage	
8.6		ary of Hydrates in Flow Assurance and Transportation	
Refe	rences		679
			60. .
		CSMGem Example Problems	
		oduction	
A.2		mple Problems	
A.3		ing up the Natural Gas Example	
A.4		pient Hydrate Formation Conditions	
A.5		ting a 2-Phase VLE Curve	688
A.6		ing Hydrate Inhibitor	
A.7	Add	ing Hydrate Inhibitor Solutions	690

A.8	Expansion Across a Valve	690
A.9	Expansion Across a Valve Solutions	691
A.10	Real Life Situation	691
Appen	dix B CSMPlug Example Problems	693
B.1	Introduction	693
B.2	Example Problem for One-Sided Dissociation	693
B.3	1SD Solutions	694
B.4	Example Problem for Two-Sided Dissociation	695
B.5	2SD Solution	697
B.6	Example Problem for Safety Simulator	697
B.7	Safety Simulator Solutions	698
B.8	Example Problem for Electrical Heating	699
B.9	Electrical Heating Solutions	
Index.		703