

Clathrate Hydrates of Natural Gases

Third Edition

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Third Edition

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Preface

Since each reader has a unique perspective, it is worthwhile to provide a guide for reading and an apologia for this book. The goal of writing this book was for it to be of use in practice and in research.

The third edition conforms to the Library of Congress dictum that a minimum of 33% new material is required to determine a new edition, rather than a new printing. In particular, the third edition includes new information on

- New fundamental information on structure, kinetics, and prediction methods
- Industrial transition from time-independence to time-dependence
- New phase equilibrium data and kinetic models
- A new computer program CSMGem, for hydrate thermodynamic calculations
- A new program CSMPlug to predict safety/dissociation times for plug removal
- A description of the paradigm change in flow assurance to risk management
- Conceptual pictures in flow assurance of oil- and gas-dominated flowlines
- Concepts and case studies on low dosage hydrate inhibitor prevention
- The paradigm change from hydrate reservoir assessment to reservoir production
- Eight summary *in situ* conditions for hydrates in the permafrost and oceans
- New case studies summarizing Hydrate Ridge and Mallik 2002 test drillings

Our primary objective was to update the hydrate knowledge base over the last decade—an explosion of knowledge with more than 4000 hydrate-related publications. These unique compounds are more properly called clathrate hydrates to distinguish them from the stoichiometric hydrates commonly found in inorganic chemistry. A modern, increased understanding of these compounds can provide a fresh perspective on past theories and data. It was hoped that such an overview would yield new insights for both the readers and the authors, and that directions might be suggested for future research and practical applications.

A second objective was to provide a balance between hydrate experimental and theoretical perspectives. The monograph was intended as a single record of the majority of hydrocarbon thermodynamic data obtained since 1934, the time of discovery of hydrates in pipelines. The third edition, in particular, shows the transition away from thermodynamics to kinetics, as mankind learns to study more sophisticated, time-dependent phenomena.

Often the comparative availability and low cost of computing causes the elevation of theory and simulation over experiment. In the field of hydrates, however, the most significant advances in knowledge have been made by researchers who have performed painstaking experiments guided by intuition, theory, and recently, simulation. Experiments have provided the physical foundation and correction of theories. In almost every case, the most marked theoretical advances, such as those of van der Waals and Platteeuw (1959), were founded upon significant experimental advances, such as the determination of the hydrate crystal structures by von Stackelberg and coworkers, Claussen, Pauling, and Marsh in the preceding two decades.

The final objective was to provide a complementary vehicle for the accompanying Windows + PC compatible computer programs. The principal program on the CD, CSMGem, is a complete Gibbs Energy Minimization revision of the program completed in this laboratory in 2002. Normally, such programs, based on fairly complex statistical thermodynamics, cannot be written precisely from the literature without substantial time and effort. It is not necessary to understand the theory ([Chapter 5](#)) in order to use the computer program to perform several hydrate calculations; the reader should follow the directions and examples in the User's Guide ([Appendix A](#)) and the User's Manual on the CD in this volume's end chapters. However, without the computer program, the theory would remain sterile. At the same time, the book provides a more thorough exposition of the program's principles than can be normally displayed in single papers accompanying a program.

A second major computer program, CSMPlug, also has a User's Guide in [Appendix B](#) and a User's Manual on the CD. This program enables the user to evaluate hydrate plug safety concerns and dissociation times. The safety aspects of plug dissociation should be a major concern in every hydrate situation, which sometimes results in damage to equipment and health. Often the plug dissociation times are much longer than intuition suggests and a prediction can help prevent "ineffective solutions" which sometimes worsen the problem. The program can be used to predict nonpressurized dissociation on core recovery, in addition to plug dissociation in a depressurized flowline.

Readers of different backgrounds will wish to follow different paths through the chapters. Both the engineer and the researcher may wish to read [Chapter 1](#) that provides a historical overview of clathrate hydrates. One cannot deal with hydrates without some knowledge of the all-important crystal structures provided in [Chapter 2](#). [Chapter 3](#) on hydrate kinetics gives the current picture of hydrate time-dependence to supplement the time-independent phase equilibria in [Chapter 4](#), the last chapter that should be of common interest to both the engineer and the

researcher. A recommendation summary for the book chapters is given in the following table:

A Suggestion on How to Read This Book

Reader's background	Engineer	Researcher
Chapter title	Applicable sections	
Chapter 1: Historical Overview	All sections	All sections
Chapter 2: Structures	All sections	All sections
Chapter 3: Kinetics	3.1.6, 3.2	All sections
Chapter 4: Phase Equilibria	4.1, 4.2, 4.4, 4.6	As needed
Chapter 5: Statistical Thermodynamics	None	All sections
Chapter 6: Experimental Methods and Data	6.1, 6.2 as needed	6.1, 6.2
Chapter 7: Hydrates in Nature	As needed	All sections
Chapter 8: Production, Transportation, and Processing	As needed	As needed
Appendices—Users Guide & Examples for CSMGem and CSMPlug	All sections	All sections

The initial limitations of the book are still largely present in the third edition. First the book applies primarily to clathrate hydrates of components in natural gases. Although other hydrate formers (such as olefins, hydrogen, and components larger than 9 Å) are largely excluded, the principles of crystal structure, thermodynamics, and kinetics in [Chapters 2](#) through [5](#) will still apply.

Second, primarily due to language inability and literature access, the third edition has a Western Hemisphere perspective. Two translations (Schroeder, 1927 and Makogon, 1985) were made in preparation for the first edition manuscript. Discussions at length were held with Drs. Y.F. Makogon and Ginsburg, and with Professor Berecz and Ms. Balla-Achs, whose earlier hydrate monographs were initially published in Russian and in Hungarian. Yet as in all bi-author manuscripts, this book is the limited product of two individuals' perspectives, which were shaped by past workers and present colleagues.

Dr. John Ripmeester and his colleagues at the Steacie Institute of NRC Canada have led the world in hydrate science for the last several decades, and they have been gracious hosts to help CSM visitors learn. Drs. K.A. Kvenvolden and T.S. Collett of the U.S. Geological Survey and Scott Dallimore of the Canadian Geological Survey, have been generous with their publications and discussions regarding *in situ* hydrates. Our academic colleagues: Professor R.J. Bishnoi and colleagues Professors M. Pooladi-Darvish and M. Clarke (University of Calgary), Professor M. Adewumi (Penn State University), Professor P. Clancy (Cornell University), Dr. S.F. Dec (Colorado School of Mines), Professor K.D.M. Harris (Cardiff University), Professor J.-M. Herri (St. Etienne School of Mines), Professor W. Kuhs (University of Göttingen), Professor K.E. Gubbins (North Carolina State University), Professor K. Marsh (University of Canterbury), Professor

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The intrinsic joy of learning about clathrate hydrates has in itself been a pleasure that we hope will be communicated through these pages to younger workers. The

survival of a research area, like that of a civilization, depends on whether the young see learning as a worthwhile goal. Noting that these pages doubtless contain several mistakes, the authors invoke the acute observation of Francis Bacon¹: “Truth emerges more readily from error than from confusion.”

The third edition is dedicated to her parents, Ann and Paul, and husband Ian by CAK, and to his wife Marjorie by EDS.

E. Dendy Sloan, Jr.
Carolyn A. Koh
Golden, Colorado

¹ “Novum Organum,” Vol. VIII, *The Works of Francis Bacon* (J. Spedding, R.L. Ellis, and D.D. Heath, eds.) New York, p. 210 (1969).

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