

Introductory overview: Hydrate knowledge development

E. DENDY SLOAN*

Center for Hydrate Research, Colorado School of Mines, Golden, Colorado 80401, U.S.A.

ABSTRACT

An overview is provided for the remainder of the volume. After an initial motivation section with hydrate applications, the hydrate structures are exposed, by considering two formation heuristics. Second, the history of hydrate knowledge both within and without the pipeline is outlined, and examples are given of technology transfer between the two arenas. The hydrate experimental physics and chemistry are then presented on three levels: micro-, meso-, and macroscopic. Finally it is suggested that the state-of-the-art of hydrate thermodynamics is satisfactory for most engineering applications, because the prediction accuracy is close to the experimental accuracy. Hydrate kinetics, on the other hand, is presented as a major physico-chemical challenge for the future.

INTRODUCTION

Clathrate hydrates are ice-like substances, found when small guest molecules (between 0.35 and 0.9 nm) combine with water at low temperatures and high pressures. While there are many guest molecules in this size range, this volume principally concerns those guests in the size range between nitrogen and normal pentane, which includes the size of eight natural gas components (methane, ethane, propane, iso- and normal-butane, nitrogen, hydrogen sulfide, and carbon dioxide).

Furthermore, the major ultimate concern with natural gas clathrate guests is that of energy production—particularly the energy associated with natural gas. It has been suggested (Economides and Oligney 2000) that the welfare of societies is closely related to energy consumption. Because natural gas burns with less pollution than most other fuels, it will be the preferred fuel for this century, until we can economically produce hydrogen for fuel cells. Many believe we are “on a natural gas bridge to a hydrogen economy.”

For natural gas production, there are two areas of clathrate concern—hydrates inside the flowline and hydrates outside the flowline—and much of the knowledge in each area impacts the other. The solid clathrate compounds inside deepwater flowlines are the major obstruction concern—an order of magnitude more problematic than wax, the next largest obstruction concern. In one Gulf of Mexico flowline alone (Hare and Case 2003) each week over \$1 million of hydrate inhibitor is injected during startup. The worldwide flow assurance economics are substantial, and make this topic one of the largest technical concerns of 110 oil and gas companies (Welling and Associates 1999).

In situ hydrate formations in the Arctic and on continental margins offshore comprise an enormous unconventional natural gas resource. The U.S.’s in-place hydrated methane gas resource is estimated at 5665 Tm³. As a reference, the annual U.S. use of methane is 0.65 Tm³, with a U.S. recoverable conventional gas resource of 40 Tm³. Even though there are many uncertainties associated with the economic viability of this resource, its

overwhelming magnitude mandates that we consider ways to recover it. If only 1% production of methane from hydrates can be achieved, the nation’s energy future will be assured for almost a century (87 years) at the current level of usage.

A secondary concern of natural hydrates is that of climate effects. Because methane has 21 times the greenhouse gas effect of carbon dioxide, questions arise about whether the natural hydrates resources can dissociate and affect both ancient and modern climates. It is fair to say that there is a great deal of controversy in the community on this topic, as attested by several papers in this issue.

HYDRATE KNOWLEDGE EXPANSION

Due to motivators such as those given above, the hydrate knowledge base is expanding rapidly. For example, while there were only eight hydrate-related publications in the 19th century, the numbers in the 20th century grew exponentially, as shown in the semi-logarithmic plot of Figure 1. Each decade of the 20th century saw an increase of hydrate publications by an average factor of 2.5 beyond that of the previous decade, extrapolating to a staggering 7500 publications in the first decade of the 21st century!

As another way to consider the expansion of hydrate research, Table 1 presents the numbers of papers and authors at each of the past four triennial international hydrate conferences. Each of these conferences has a complete proceedings, to which any

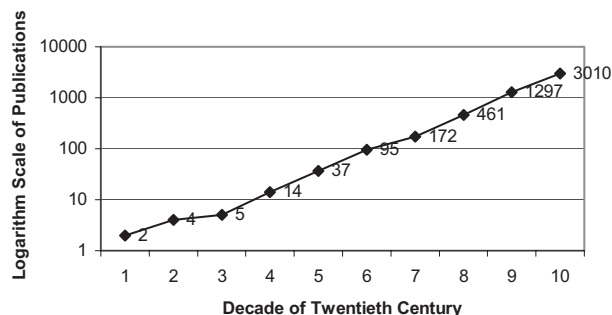


FIGURE 1. Hydrate-related publications in the 20th century by decade.

* E-mail: esloan@mines.edu

TABLE 1. Five international triennial hydrate conferences

Date	Place/Sponsor	No. of papers	No. of authors
June 1993	New York/NYAS	61	130
June 1996	Toulouse/ENSIGC	87	195
July 1999	Salt Lake City/NYAS	104	258
May 2002	Yokohama/ Keio U.	204	500
June 13–16, 2005	Trondheim/Statoil	taus@statoil.com	

student of clathrate hydrates will wish to refer.

The topics of hydrate research in the four conferences can be divided into four applications: (1) energy resources, (2) pipeline blockage prevention and remediation, (3) environmental effects, and (4) hydrate-based technologies. Like the above conferences, this volume comprises a snapshot in time of hydrate state-of-the-art advances, with particular emphasis on the energy industry.

However, one of the first lessons of this introductory work is that hydrate chemical physics phenomena cross application boundaries. Examples are given below, in which funding for hydrates inside the pipeline has provided physics and chemistry explanations for hydrate applications outside the pipeline. It is clearly unhealthy to compartmentalize knowledge, when there is so much to be learned from other, more holistic perspectives.

HYDRATE STRUCTURES AND HEURISTICS OF FORMATION

What are hydrates?

Natural gas hydrates are solid crystalline compounds composed of molecules of natural gas trapped in cages of water molecules. Although hydrates look like ice and have a similar density, these compounds contain concentrated methane—1 m³ of hydrate contains as much as 163 m³ of methane at 1 atm and 273 K. The amount of energy in each unit of hydrates is much more than enough to support their own combustion, and provide additional energy.

Four conditions are required to form hydrates: (1) low temperature (commonly less than 300 K), (2) high pressure (greater than 38 bar hydrostatic pressure at 277 K), (3) a non-polar guest molecule smaller than 0.9 nm, such as methane, and (4) water.

In the laboratory, hydrates form in three common crystal structures, I, II, and H, shown in Figure 2, as a function of the guest gases. The unit cells of these crystals have dimensions of approximately 1 nm. Each structure is composed of hydrogen-bonded water cavities, with each containing at most one guest molecule such as methane, shown to the left in Figure 2. The basic building block of all three structures is the 5¹² cavity, so-called because it contains 12 pentagonal faces. Different combinations of these building blocks form all three common hydrate structures.

However, because the 5¹² cavities cannot fill space without

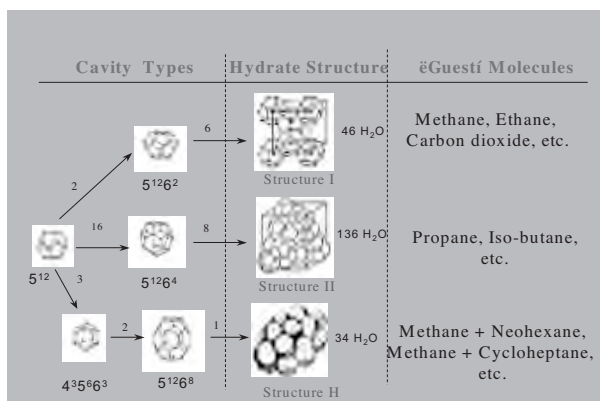


FIGURE 2. The three common gas hydrate structures and constituent cavities.

undue bond strain, relief is provided by other cavities containing hexagonal faces, for example two 5¹² cavities combine with six 5¹²6² cavities (with 12 pentagonal faces and 2 hexagonal faces) to compose the structure I (sI) unit crystal, most commonly found in nature.

There are two additional hydrate structures shown in Figure 2, sII and sH, but these are less commonly found in the natural environment with biogenic gas, and occur more regularly in artificial formations with thermogenic, larger hydrocarbons, (e.g., propane, isobutane, and other molecules smaller than 0.9 nm). The three crystal structure types are described in Table 2.

Although the cavities are never completely filled, when all cavities are filled with one molecule, each of the three crystal structure types has about the same composition: 82.61 mol% water and 17.39% guests for structure I, and 82.35% water and 17.64% guests for structures II and H. This concentration of hydrocarbon guests is remarkably high relative to other liquid or solid water compounds, and the proximity of the guest molecules in neighboring cavities provide the energy density of a compressed gas. When heat is applied (approximately 70% more than is required to melt ice) the guest methane molecules are released, producing both methane gas and water (or ice) with a negligible amount of methane dissolved.

Two heuristics of hydrate formation

The fit of the guest molecule within each cavity determines the hydrate stability pressure and temperature. Each hydrate crystal structure type empty of guests is unstable, and the expanded hydrogen-bonded water structure will collapse without the guest molecules to keep the cavities propped open.

TABLE 2. Geometry of cages in the three hydrate crystal structures shown in Figure 1

Hydrate crystal structure	I (cubic)	II (cubic)	H (hexagonal)				
Lattice parameter, nm	$a = 1.2$	$a = 1.73$	$a = 1.226, c = 1.017$				
Space group	$Pm\bar{3}n$	$Fd\bar{3}m$	$P6/mmm$				
Cavity	Small	Large	Small	Large	Small	Medium	Large
Description	5 ¹²	5 ¹² 6 ²	5 ¹²	5 ¹² 6 ⁴	5 ¹²	4 ³ 5 ⁶ 3	5 ¹² 6 ⁸
Number of cavities/unit cell	2	6	16	8	3	2	1
Average cavity radius, Å	3.95	4.33	3.91	4.73	3.91 [†]	4.06 [†]	5.71 [†]
Coordination number*	20	24	20	28	20	20	36
Number of waters/unit cell	46	136	136	136	34	136	136

* Number of O atoms at the periphery of each cavity.

† Estimates of structure H cavities from geometric models.

Table 3 shows the size ratio of natural gas molecules within each of the four cavities of sI and sII. Note that a size ratio (guest molecule:cavity) of approximately 0.9 is necessary for stability of a simple (single guest) hydrate, given by the superscript “F”. When the size ratio exceeds unity, the molecule will not fit within the cavity and the structure will not form. When the ratio is significantly less than 0.9 the molecule cannot lend significant stability to the cavity.

Table 3 may be used to illustrate six points regarding the guest/cavity size ratio for hydrates formed of a *single* guest component in either sI or sII.

(1) The sizes of stabilizing guest molecules range between 0.35 and 0.75 nm, while only sizes between 0.41 and 0.71 nm are shown. Below 0.35 nm the molecules will not stabilize either structure and above 0.75 the molecules are too large for the sII cavities.

(2) Some molecules are too large to fit the smaller cavities of each structure (e.g., C₂H₆ fits in the 5¹²6² cavity in sI; C₃H₈ and i-C₄H₁₀ each fit the 5¹²6⁴ cavity in sII) in which case the structure forms with the smaller cavities vacant.

(3) Other molecules such as CH₄ and N₂ are small enough to enter both cavities (each with a script “F”) when hydrate forms with those single components.

(4) Because the fit of CH₄ is approximately the same in the 5¹² cavities of sI and sII, the structure is determined by the fit of the molecule in the large cavity (5¹²6²) of sI. However, below a certain size ratio (ca. 0.74) molecules such as nitrogen lend no stability to the large cage and the structure is determined by the fit in the 5¹² cavity and the fact that sII has more 5¹² cavities per unit volume.

(5) The largest molecules of a gas mixture usually determine the structure type. For example, because propane and i-butane are present in many thermogenic natural gases, they will cause sII to form. In such cases, methane will distribute in both cavities of sII and ethane is so large it can only enter the 5¹²6⁴ cavity of sII, with only minor occupancy fractions of the 5¹²6² cavity, except at high pressures.

(6) Molecules that are close to the size boundary separating the cavity sizes appear to exhibit the most non-stoichiometry, and the most susceptibility to changing cavities and crystals upon pressurization, due to their inability to fit securely within the cavity.

A second heuristic of hydrates is that their formation is a

TABLE 3. Ratios of molecular diameters to cavity diameters* for some molecules including natural gas hydrate formers

Molecule	Cavity type Guest diameter (Å)	(molecular diameter) / (cavity diameter)			
		Structure I		Structure II	
		5 ¹²	5 ¹² 6 ²	5 ¹²	5 ¹² 6 ⁴
N ₂	4.1	0.804	0.700	0.817 ^F	0.616 ^F
CH ₄	4.36	0.855 ^F	0.744 ^F	0.868	0.655
H ₂ S	4.58	0.898 ^F	0.782 ^F	0.912	0.687
CO ₂	5.12	1.00	0.834 ^F	1.02	0.769
C ₂ H ₆	5.5	1.08	0.939 ^F	1.10	0.826
C ₃ H ₈	6.28	1.23	1.07	1.25	0.943 ^F
i-C ₄ H ₁₀	6.5	1.27	1.11	1.29	0.976 ^F
n-C ₄ H ₁₀	7.1	1.39	1.21	1.41	1.07

Note: F indicates the cavity occupied by the single hydrate former.

* Cavity radii from Table 2 minus 1.4 Å water radii.

surface phenomenon, when formed on an artificial time-scale. As shown in Figure 3, this is due to the fact that the amount of water and gas in hydrates is 82 and 18 mol%, respectively; such high concentrations are orders of magnitude greater than the solubility of gas in the bulk water (0.00084 mole fraction) or that of water in the bulk gas phase (0.001 mole fraction). As a consequence, while hydrates can form in small amounts in either bulk phase, they form primarily at interfaces, where sufficient host (water) and guest (gas) molecules are present for large amounts of solid formation.

HYDRATES IN THE LABORATORY AND FIELD

Interactions between the laboratory and the field

Before 1934, the date hydrates were found in pipelines, there were only 22 hydrate publications; yet these few were the foundation for building the remainder of hydrate science. However, since 1934, the number of hydrate publications has grown exponentially, as shown by the slope change at that date in Figure 1.

Hydrate research milestones driven principally by the motivation of flow assurance are shown in Table 4. This knowledge development followed the general pattern: (1) initial observation of phenomenon of pipeline plugging, (2) gathering of data to describe the phenomenon, (3) construction of macroscopic models for data interpolation/extrapolation, (4) development of thermodynamic phase diagrams, (5) determination of microscopic structure, and (6) generation of statistical mechanical models, connecting the microscopic and macroscopic domains.

Since 1934, the general research trend provided by the flow assurance vehicle has been from large to small phenomena, and from experiment to modeling, with statistical thermodynamics being the bridge to connect the macroscopic to the microscopic domains. In Figure 1 a second increase in slope of the number of publications is observed about 1965, the time of hydrate discovery in nature. The energy associated with natural hydrates provides a second major vehicle for research efforts over the

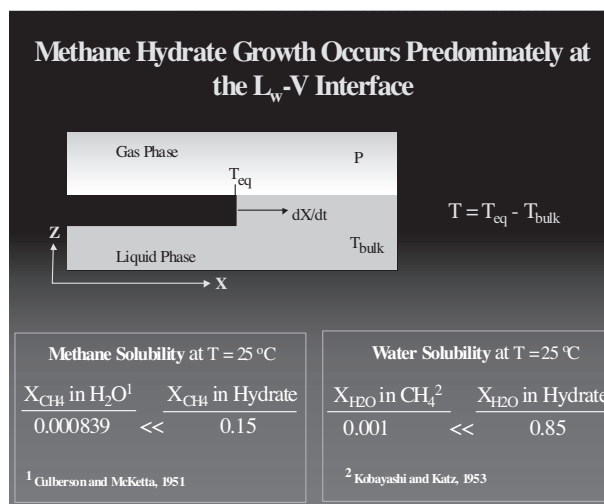


FIGURE 3. Comparison of bulk solubilities of CH₄ + H₂O to hydrate concentration.

TABLE 4. Hydrate research milestones driven by flow assurance

Date	Event	Principal work by
1934	Flowline discovery: Finding thermodynamic inhibitors	Hammerschmidt (1934)
1941–6	First systematic formation Pressure - Temperature data	Deaton and Frost (1946)
1942–5	Solid solution concept: macroscopic prediction methods	Katz (1945)
1949–51	Development of thermodynamic phase diagrams	Kobayashi and Katz (1949)
1946–51	X-ray diffraction data	von Stackelberg and Mueller (1951)
1951–2	sl and sll unit crystals established	Claussen (1951), Pauling and Marsh (1952)
1959	Statistical thermodynamics model	van der Waals and Platteeuw (1959)

last four decades.

Fortunately the research tools developed in the last seven decades of hydrate research for application inside the pipeline can be applied in parallel (rather than in sequential, historical development) to the phenomena of hydrates outside the pipeline. However, hydrates in nature is a substantially broader topic containing geological, geophysical, and geochemical concerns, in addition to the physical-chemical developments shown, for example, in Table 4. An abbreviated milestones summary for North America of hydrates outside the pipeline is presented in Table 5.

Because the author is not qualified to address the geo-research concerns of hydrates, a summary of them will be left to others, and many are included in this volume. Instead, the remainder of this article will concern an overview of the physical-chemical developments, with emphasis on the transfer of such technology between the two hydrate application domains—inside and outside the pipeline.

Macroscopic, mesoscopic, and microscopic experiments and modeling

Only an overview is presented here; readers interested in the details are referred to other manuscripts within this volume or to a recent summary (Sloan 2003) of the Fourth International Hydrate Conference. It is the purpose of these triennial conferences to provide summaries of the last three years, as well as forecasts of research to come during the three years before the next conference.

For macroscopic measurements (on a scale of 0.1 to 10^3 m), researchers concerned with hydrates in the pipeline have constructed flow loops, flow wheels, and agitated smaller apparatuses. Such experiments are very costly, both financially and time-wise. For example, the capital expense of a flow loop may easily exceed a million dollars, with an equivalent annual amount for operating expense. Similarly, both the capital and operating expense of a smaller, agitated apparatus is approximately \$50 000 in 2003 dollars.

However, for a macroscopic hydrate experiment in nature, the expense is usually at least an order of magnitude larger than the most expensive macroscopic experiment inside a flow loop. The two most recent macroscopic hydrate experiments in nature are the Mallik 5L well in the Mackenzie Delta (Matsumoto 2002) and the ODP Leg 204 drilling off Hydrate Ridge in Oregon (Suess et al. 2002), for hydrates in the permafrost and ocean, respectively. While no cost data are available for the latter, the cost of the Mallik well experiment is estimated at \$17 million dollars. Both the Mallik 5L well and the Hydrate Ridge drilling will provide benchmarks for future large-scale experiments on hydrates in nature. Publications documenting both will become available in 2004.

TABLE 5. North America hydrate research milestones driven by hydrates in nature

Date	Event	Principal work by
1965	Natural hydrates first discovered in Russia	Makogon (1965)
1971	1st US paper on hydrates in nature	Katz (1971)
1980	First estimate of worldwide hydrates	Kvenvolden and McMenamin (1980)
1982	Recovery of Guatemalan Leg 67 Hydrate Core	Deep Sea Drilling Project
1982–92	DOE \$8 million hydrate research program	Malone
1997	Recommendation of 5 year DOE Program	PCAST*
1999	CH ₄ Hydrate Multi-Year R & D Plan	Allison and Tomer (1999)
2000	CH ₄ Hydrate R & D Act of 2000	US Congress
2002	Mallik 5L test well and Hydrate Ridge Leg 204	JNOC† and ODP‡

* President's Committee of Advisors on Science and Technology

† Japanese National Oil Corporation (Matsumoto 2002)

‡ Offshore Drilling Program (Suess et al. 2002)

The mesoscopic region (with dimensions of 0.1 to 10^{-7} m) provides a connecting partition between the macroscopic and the microscopic domains. Single-crystal growth experiments indicate which crystal faces appear and provide information on morphology and growth inhibition. The results from atomic force microscopy (AFM) and scanning electron microscopy (SEM) can provide useful insights into hydrate morphology. For example, using SEM groups in Menlo Park (Stern et al. 2002) and Göttingen (Doroteya et al. 2002) have observed porous hydrates, which appear to be related both to the amount of methane in the sample, and to hydrates kinetics/transport properties.

For microscopic scale hydrate work (10^{-7} to 10^{-10} m) three experimental techniques have proven most successful: X-ray and neutron diffraction, nuclear magnetic resonance (NMR) spectroscopy, and Raman spectroscopy. With these non-destructive techniques one can measure such things as hydrate structure, cage occupancy, and quantities that can only be modeled otherwise.

Until the evolution of these spectroscopic techniques, beginning with NMR measurements at the Canadian National Research Council, the above properties of the hydrate phase were only modeled, using the statistical mechanics approach of van der Waals and Platteeuw (1959), developed (see Table 4) in response to flow assurance concerns. Most modern thermodynamic models of hydrate are based upon the initial work of van der Waals and Platteeuw (1959), but even this excellent model relies upon fits of measurements such as fluid pressure and temperature. The spectroscopic techniques have been combined with techniques from other domains, such as Raman spectroscopy with macroscopic phase equilibria (Jager et al. 2002).

When hydrate phenomena themselves are too difficult or expensive to measure, it may be possible to simulate them on the computer, typically using molecular dynamics (MD) or Monte Carlo (MC) calculations. Such simulations are typically limited

by the computer to a few nanoseconds, and at most a few million particles. The result of this hardware limitation is that simulation of thermodynamic properties can be accurately done, but time-dependent phenomena such as nucleation and growth are still a challenge. Care must always be taken to ensure that the simulation is closely connected to physical reality.

Technology transfer between hydrates in flow assurance and hydrates in nature

The physics and chemistry of hydrates within and without the pipeline are very similar (if not identical). It may be interesting to ask whether the constant hydrate-funding vehicle of flow assurance can inform the more sporadically funded topic of hydrates outside the pipeline—or whether activities such as those in Table 4 relate to those in Table 5. Two examples are presented below to suggest an affirmative answer, but many others exist.

Example 1. Hydrate detection and melting in cores. Figure 4 shows an infrared image of a hydrate undergoing depressurization in a pipeline on a Statoil platform in the North Sea. Because the pipeline is depressurized, the hydrate equilibrium temperature is far less than that of the surroundings, causing a cooling within the hydrated portion of the surroundings. Figure 4 shows that this cooling results in an infrared signal from hydrate blockages similar to those detected by energy companies for heat leaks from houses.

On September 28, 1999 the above picture was discussed at a Core Barrel Development Meeting of the Joint Oceanographic Institute at the Technical University of Berlin. The result was that an infrared device was developed for locating hydrates in core barrels and in recovered hydrate samples. The forthcoming Hydrate Ridge Leg 204 report from Trehu et al. (2003) contains infrared images used to locate hydrates in recovered samples.

As a second example of hydrate melting in cores, consider the two pictures of hydrate cores melting in pipelines, and recovered hydrate/sediment cores melting in Figures 5a and b; both cores melt radially. In Figure 5a we see evidence of radial melting in a hydrate plug at 1, 2, and 3 hours. In Figure 5b, a longitudinal view is given of melting in a recovered core liner, leaving a “soupy” sediment residue where the hydrate has melted, but a non-melted center core of higher mechanical integrity.

It is possible to apply a thermal conduction analysis for two moving boundaries (a double Stefan problem) to model the dissociation of both core types in Figures 5a and 5b, if the thermal diffusivities of hydrates and sediments are available. Such measurements have recently been obtained by Kumar et al. (2003) and the model results presented. Using this model and the gas evolution rate, the original amount of hydrate in the core



FIGURE 4. Infrared picture of hydrate plug formation in Statoil topsides pipeline.

can be determined.

Example 2. Differences in hydrates within and without the pipeline, represented on the phase diagram. Using X-ray diffraction and Raman spectroscopy Huo et al. (2003) determined the new methane + water isobaric phase diagram shown in Figure 6. Of particular interest is the former vertical hydrate line, which has been replaced with an area in the new diagram. To the left of this area, in the region marked “H-L_w” to indicate hydrates formed from methane dissolved in water (as sometimes explains formation in the ocean) the hydrates would have slightly lower methane contents. To the right of the hydrate area, in the region marked “H-V” for hydrates formed with excess gas (as always occurs in pipelines or in laboratory samples) the hydrate would contain slightly more methane than at the same temperature and pressure, but formed from a lower amount of methane in the feed.

This new phase diagram suggests that methane estimates in natural hydrates are likely to be high by as much as 4% when based on laboratory hydrate concentrations. This small concentration difference, when multiplied by the huge amount of energy in ocean hydrates, is sufficient to satisfy the current U.S. energy requirements for six centuries.

The above two examples demonstrate that hydrates in the pipeline (or laboratory) are neither exactly alike or unlike those in nature. Yet the results seem to point to the need for discriminating the similarities and differences between the two sample types, and to the danger of knowledge compartmentalization.

THE CURRENT STATE-OF-THE-ART AND THE FUTURE

A survey of the accuracy of hydrate phase equilibria prediction programs was recently made by Ballard and Sloan (2002). Five different prediction programs were tested against all of the published hydrate data (1685 points) in the following six

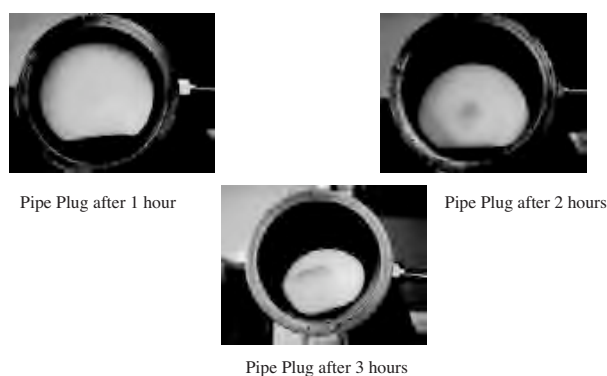


FIGURE 5. (a) Hydrate plug in pipeline dissociating at 1, 2, and 3 hours. (b) Hydrate melting in DSDP leg 67 sediment core (courtesy Paull 2001). Note that the center of the core has structural integrity, while the outer periphery has melted, similar to the hydrate in the pipeline in a.

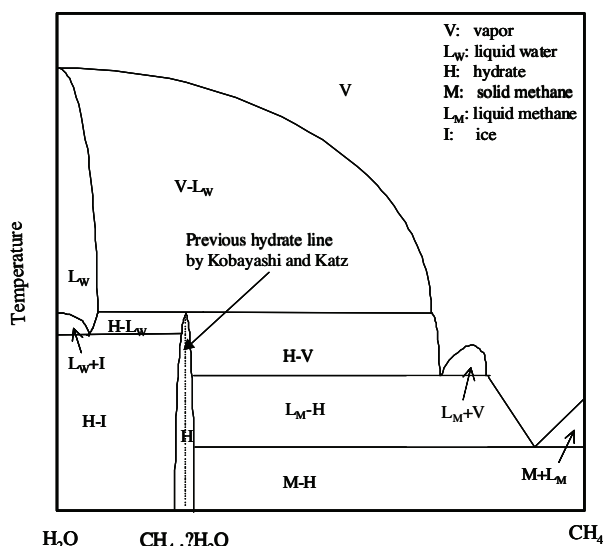


FIGURE 6. The phase diagram of $\text{CH}_4 + \text{H}_2\text{O}$. Note that the non-stoichiometric hydrate region replaces the previously proposed vertical line for stoichiometric hydrate concentration.

categories: (1) single guest (simple) hydrates, (2) binary guest hydrates, (3) ternary guest hydrates, (4) natural gas mixed hydrates, (5) black oil and gas condensate hydrates, and (6) structure H hydrate formers.

A summary of the absolute hydrate formation temperature error in all five prediction methods is given for the above six categories in Figure 7. The average absolute errors in temperature for the five common prediction programs varied between 0.40 and 0.66 K. These measures of prediction errors approximate the errors of the experiments, and are acceptable for engineering purposes. Thus it may not be practical to attempt to improve predictions for incipient hydrate formation temperature and pressure. This may be a unique position in the prediction ability of phase equilibria by statistical mechanics.

Hydrate kinetics pose the largest challenge to future understanding, which now rests on a comparatively sound thermodynamic foundation. We know very little about a kinetic mechanism founded on hydrate measurements. Due to the difficult, stochastic nature of nucleation, experiments have dealt with the deterministic growth process. Kinetic measurements are also gravitating from macroscopic to microscopic scales. More hydrate phase measurements are required at each of the micro-, meso-, and macroscopic levels to provide a needed breakthrough - a unifying hydrates kinetics mechanism.

Several ideas come from a study of hydrate knowledge development: (1) hydrates are a largely untapped future methane resource, which may affect important societal issues such as energy and climate; (2) hydrate publications are increasing at an exponential rate, by an average factor of 2.5 each decade, with an extrapolation to two publications per day in the current decade; (3) hydrate structure and formation can be understood in terms of two heuristics: (a) the fit of the guest within each cage, and (b) the formation at the vapor-liquid interface; (4) knowledge development has been driven by applications, and the steadiest, longest-term hydrate application is that of flow assurance, which

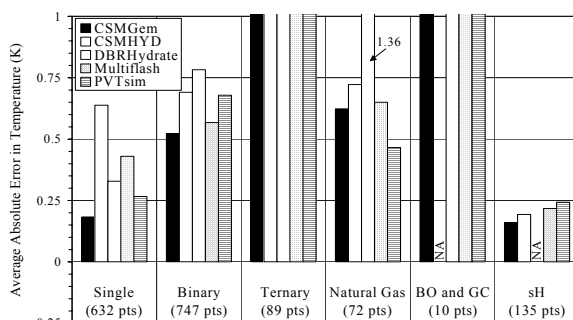


FIGURE 7. Absolute temperature errors of prediction for 1685 data points by five common programs.

has about twice the tenure of the application of hydrates in nature; (5) hydrate physics and chemistry phenomena determined by flow assurance can inform phenomena for hydrates in nature applications, and vice versa; (6) the state-of-the-art for hydrate thermodynamic predictions is satisfactory. Substantial progress is still to be made in the area of hydrate kinetics.

REFERENCES CITED

- Allison, E. and Tomer, B. (1999) National Methane Hydrate Multi-Year R & D Program Plan. United States Department of Energy, Washington, D.C.
- Ballard, A. and Sloan, E.D. (2002) The Next Generation of Hydrate Prediction: An Overview, 307 p. Proceedings of the Fourth International Hydrate Conference, Yokohama, Japan (May 19–23, 2002).
- Claussen, W.F. (1951) Suggested structures of water in inert gas hydrates. *Journal of Chemical Physics*, 19, 259 (erratum 662).
- Deaton, W.M. and Frost, E.M. (1946) Gas Hydrates and Their Relation to the Operation of Natural-Gas Pipelines. U.S. Department of the Interior, Washington, D.C.
- Doroteya, K.S., Hansen, T., Salamatin, A.N., and Kuhs, W.F. (2002) Kinetic diffraction experiments on the formation of porous gas hydrates, 537 p. Proceedings of the Fourth International Hydrate Conference, Yokohama, Japan (May 19–23, 2002).
- Economides, M. and Oligney, R. (2000) The Color of Oil, p. 10–12. Round Oak Publishing Co., Katy, Texas.
- Hammerschmidt, E.G. (1934) Formation of gas hydrates in natural gas transmission lines. *Industrial Engineering Chemistry*, 26, 851.
- Hare, S. and Case, R. (2003) Canyon Express commissioning and start-up experience. Offshore Technology Conference Proceedings, OTC 15097, Houston, Texas, May 2003. Society of Petroleum Engineers, Richardson, TX.
- Huo, Z., Hester, K., Miller, K.T., and Sloan, E.D. (2003) Methane Hydrate Non-Stoichiometry and Phase Diagram. *AIChE Journal*, 49, 1300.
- Jager, M.D., Peters, C.J., and Sloan, E.D. (2002) Experimental determination of methane hydrate stability in methanol and electrolyte solutions. *Fluid Phase Equilibria*, 193, 17.
- Katz, D.L. (1945) Prediction of conditions for hydrate formation in natural gases. *Transactions AIME*, 160, 140.
- (1971) Depths to which frozen gas fields (gas hydrates) may be expected. *Journal of Petroleum Technology*, 419–423.
- Kobayashi, R. and Katz, D.L. (1949) Methane hydrate at high pressure. *Journal of Petroleum Technology*, 3, 66.
- Kumar, P., Turner, D.J., and Sloan, E.D. (2004) Thermal diffusivity measurement of methane hydrate and hydrate-sediment mixtures. *Journal of Geophysical Research*, in press.
- Kvenvolden, K.A. and McMenamin, M.A. (1980) Hydrates of Natural Gas: A Review of Their Geologic Occurrence. U.S. Geological Survey Circular 825, Washington, D.C.
- Makogon, Y.F. (1965) Hydrate formation in the gas-bearing beds under permafrost conditions. *Gazovaya Promyshlennost*, 5, 14.
- Matsumoto, R. (2002) Comparisons of marine and permafrost gas hydrates: Examples from the Nankai Trough and Mackenzie Delta, 1 p. Proceedings of the Fourth International Hydrate Conference, Yokohama, Japan (May 19–23, 2002).
- Pauling, L. and Marsh, R.E. (1952) The Structure of Chlorine Hydrate. Proceedings of the National Academy of Science, 38, 112.
- Paull, C.K. (2001) Personal Communication of DSDP Leg 67 Core Photograph, Yokohama, Japan, October 25, 2001.

- President's Committee of Advisors on Science and Technology (PCAST) (1997) Report to the President on Federal Energy Research and Development for the Challenges of the Twenty-First Century, Washington, D.C.
- Sloan, E.D. (2003) Clathrate hydrates measurements: Microscopic, mesoscopic, and macroscopic. *Journal of Chemical Thermodynamics*, 35, 41–53.
- Stern, L.A., Circone, S., Kirby, S., and Durham, W.B. (2002) New insights into the phenomenon of anomalous or "self" preservation of gas hydrates. Proceedings of the Fourth International Hydrate Conference, 673 p. Yokohama, Japan (May 19–23, 2002).
- Suess, E., Bohrmann, G., Rickert, D., Kuhs, W.F., Torres, M.E., Trehu, A., and Linke, P. (2002) Properties and fabric of near-surface methane hydrates at Hydrate Ridge, Cascadia Margin, 740 p. Proceedings of the Fourth International Hydrate Conference, Yokohama, Japan (May 19–23, 2002).
- Trehu, A.M. and the Leg 204 Shipboard Party (2003) Three-dimensional distribution of gas hydrate beneath southern hydrate ridge: Constraints from ODP Leg 204. Proceedings of Offshore Drilling Project, Scientific Results, 204, Washington, D.C.
- van der Waals, J.H. and Platteeuw, J.C. (1959) Clathrate solutions. *Advances in Chemical Physics*, 2, 1.
- von Stackelberg, M. and Mueller, H.R. (1951) On the structure of gas hydrates. *Journal of Chemical Physics*, 19, 319.
- Welling and Associates (1999) Survey cited by Macintosh, N., Offshore, October 2000, p. 21.

MANUSCRIPT RECEIVED OCTOBER 14, 2003

MANUSCRIPT ACCEPTED MAY 21, 2004

MANUSCRIPT HANDLED BY BRYAN CHAKOUMAKOS