

Reviews

Gas Hydrates: Review of Physical/Chemical Properties

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An overview is provided of time-independent physical/chemical properties as related to crystal structures. The following two points are illustrated in this review: (1) Physical and chemical properties of structure I (sI) and structure II (sII) hydrates are well-defined; measurements have begun on sH. Properties of sI and sII are determined by the molecular structures, described by three heuristics: (i) Mechanical properties approximate those of ice, perhaps because hydrates are 85 mol % water. Yet each volume of hydrate may contain as much as 180 volumes (STP) of the hydrate-forming species. (ii) Phase equilibrium is set by the size ratio of guest molecules within host cages, and three-phase (L_w -H-V) equilibrium pressure depends exponentially upon temperature. (iii) Heats of formation are set by the hydrogen-bonded crystals and are reasonably constant within a range of guest sizes. (2) Fundamental research challenges are (a) to routinely measure the hydrate phase (via diffraction, NMR, Raman, etc.), and (b) to formulate an acceptable model for hydrate formation kinetics. The reader may wish to investigate details of this review further, via references contained in several recent monographs.

Introduction

Gas clathrates (commonly called hydrates) are crystalline compounds which occur when water forms a cagelike structure around smaller guest molecules. While they are more commonly called hydrates, a careful distinction should be made between these non-stoichiometric clathrate hydrates of gas and other stoichiometric hydrate compounds which occur, for example, when water combines with various salts.

Gas hydrates of current interest are composed of water and the following eight molecules: methane, ethane, propane, isobutane, normal butane, nitrogen, carbon dioxide, and hydrogen sulfide. Yet other apolar components between the sizes of argon (0.35 nm) and ethylcyclohexane (0.9 nm) can form hydrates. Hydrate formation is a possibility where water exists in the vicinity of such molecules at temperatures above and below 273 K when the pressure is elevated.

Hydrate discovery is credited in 1810 to Sir Humphrey Davy. Due to their crystalline, nonflowing nature, hydrates first became of interest to the hydrocarbon industry in 1934, the time of their first observance⁴ blocking pipelines. Hydrates act to concentrate hydrocarbons: 1 m³ of hydrates may contain as much as 180

SCM (SCM = standard cubic meter) of gas. Makogon⁵ indicated that large natural reserves of hydrocarbons exist in hydrated form, both in deep oceans and in the permafrost. Evaluation of these reserves is highly uncertain, yet even the most conservative estimates concur that there is twice as much energy in hydrated form as in all other hydrocarbon sources combined. While one commercial example exists of gas recovery from hydrates, the problems of in situ hydrate dissemination in deepwater/permafrost environments will prevent their cost-effective recovery until the next millennium.

What are Hydrates: How Do Structures Relate to Properties?

Hydrates normally form in one of three repeating crystal structures shown in Figure 1. Structure I (sI), a body-centered cubic structure, forms with small natural gas molecules found in situ in deep oceans. Structure II (sII), a diamond lattice within a cubic framework, forms when natural gases or oils contain molecules larger than ethane but smaller than pentane. Structure II represents hydrates which commonly occur in hydrocarbon production and processing conditions, as well as in many cases of gas seeps from faults in ocean environments.

The newest hydrate structure H, named for the hexagonal framework, was discovered⁶ and shown⁷ by

(1) Sloan, E. D. *Clathrate Hydrates of Natural Gases*, 2nd ed.; Marcel Dekker: New York, 1998.

(2) Sloan, E. D., Happel, J., Hnatow, M. A., Eds. *(First) International Conference on Natural Gas Hydrates*. *Ann. N.Y. Acad. Sci.* **1994**, 715.

(3) Monfort, J. P., Ed. *Proceedings of the 2nd International Conference on Natural Gas Hydrates*; F. Foucaud, Secretariat, 18 Chemin de la Loge, 31078 Toulouse Cedex, France 2–6 June, 1996.

(4) Hammerschmidt, E. G. *Ind. Eng. Chem.* **1934**, 26, 851.

(5) Makogon, Y. F. *Gazov. Promst.* **1965**, 14.

(6) Ripmeester, J. A.; Tse, J. A.; Ratcliffe, C. I.; Powell, B. M. *Nature* **1987**, 325, 135.

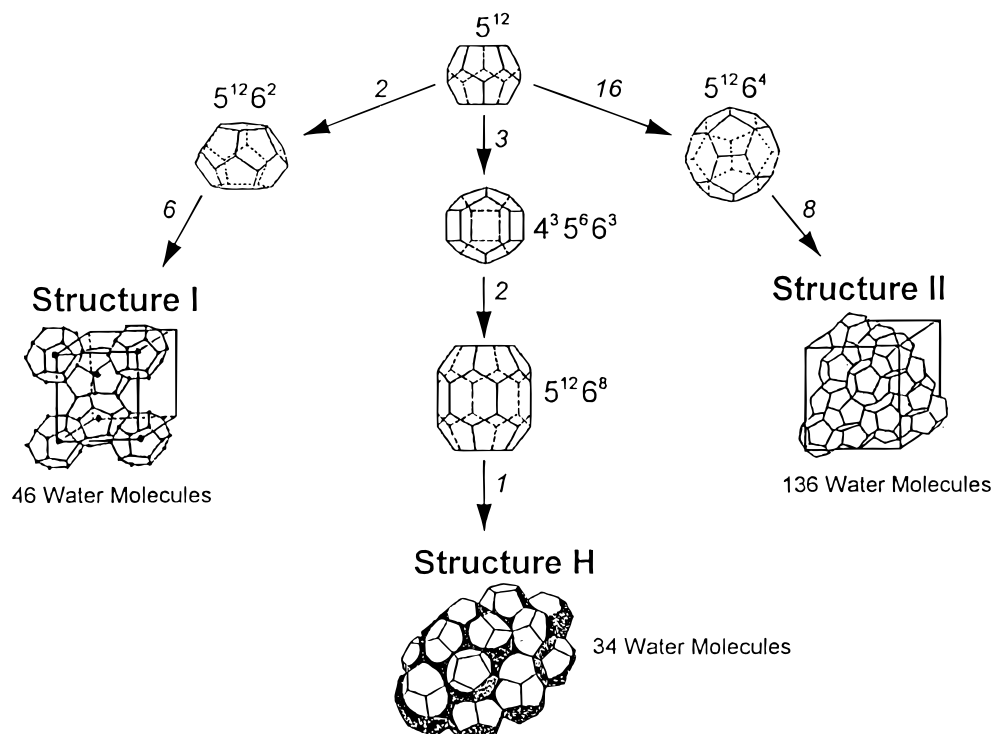


Figure 1. Three hydrate unit crystals and constituent cavities.

Table 1. Geometry of Cages in Three Hydrate Crystal Structures I, II, and H

cavity	I		II		H		
	small	large	small	large	small	medium	large
description	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$	5^{12}	$4^35^66^3$	$5^{12}6^8$
no. of cavities/unit cell	2	6	16	8	3	2	1
av cavity radius, Å	3.95	4.33	3.91	4.73	3.91 ^c	4.06 ^c	5.71 ^c
variation in radius, ^a %	3.4	14.4	5.5	1.73		not available	
coordination number ^b	20	24	20	28	20	20	36
no. of waters/unit cell	46		136		34		

^a Variation in distance of oxygen atoms from center of cage. ^b Number of oxygens at the periphery of each cavity. ^c Estimates of structure H cavities from geometric models.

Ripmeester et al. to have cavities large enough to contain molecules the size of common components of naphtha and gasoline. Initial physical properties, phase equilibrium data and models have been advanced,^{8–13} and one instance¹⁴ of in situ sH in the Gulf of Mexico has been found. Since information on structure H is in the fledgling stages, most of this review concerns sI and sII.

Hydrate Crystal Structures

Table 1 provides a hydrate structure summary for the three hydrate unit crystals (sI, sII, and sH) shown in Figure 1. The crystals structures are given with reference to the water skeleton, composed of a basic "building

block" cavity that has 12 faces with five sides per face, given the abbreviation 5^{12} . By linking the vertices of 5^{12} cavities one obtains sI; linking the faces of 5^{12} cavities results in sII; in sH a layer of linked 5^{12} cavities provides connections.

Interstices between the 5^{12} cavities are larger cavities which contain 12 pentagonal faces and either two, four, or eight hexagonal faces (denoted as $5^{12}6^2$ in sI, $5^{12}6^4$ in sII, or $5^{12}6^8$ in sH). In addition, sH has a cavity with square, pentagonal, and hexagonal faces ($4^35^66^3$). Figure 1 depicts the five cavities of sI, sII, and sH. In Figure 1 an oxygen atom is located at the vertex of each angle in the cavities; the lines represent hydrogen bonds with which one chemically bonded hydrogen connects to an oxygen on a neighbor water molecule.

Inside each cavity resides a maximum of one of the small guest molecules, typified by the eight guests associated with 46 water molecules in sI ($2[5^{12}] \cdot 6[5^{12}6^2] \cdot 46\text{H}_2\text{O}$), indicating two guests in the 5^{12} and 6 guests in the $5^{12}6^2$ cavities of sI. Similar formulas for sII and sH are $(16[5^{12}] \cdot 8[5^{12}6^4] \cdot 136\text{H}_2\text{O})$ and $(3[5^{12}] \cdot 2[4^35^66^3] \cdot 1[5^{12}6^8] \cdot 34\text{H}_2\text{O})$, respectively.

Structure I, a body-centered cubic structure, forms with natural gases containing molecules smaller than propane; consequently, sI hydrates are found in situ in

(7) Ripmeester, J. A. The Role of Heavier Hydrocarbons in Hydrate Formation. Presented at 1991 AIChE Spring Meeting, Houston, TX, April 10, 1991.

(8) Mehta, A. P.; Sloan, E. D. *J. Chem. Eng. Data* **1993**, *38*, 580.

(9) Mehta, A. P.; Sloan, E. D. *J. Chem. Eng. Data* **1994a**, *39*, 887.

(10) Mehta, A. P.; Sloan, E. D. *AIChE J.* **1994b**, *40*, 312.

(11) Mehta, A. P.; Sloan, E. D. *AIChE J.* **1996a**, *42*, 2036.

(12) Mehta, A. P.; Sloan, E. D. *Proc. 2nd Int. Conf. Natural Gas Hydrates* **1996b**, 1.

(13) Mehta, A. P.; Sloan, E. D. Structure H Hydrates: Implications for the Petroleum Industry. *Proc. 1996 Annu. Tech. Conf.* **1996c**, SPE 36742, 607.

(14) Sassen, R.; MacDonald, I. R. *Org. Geochem.* **1994**, *22*(6) 1029.

Table 2. Comparison of Properties of Ice and SI and SII Hydrates^a

property (measd and calcd)	ice	structure I	structure II
spectroscopic			
crystallographic unit cell			
space group	$P6_3/mmc$	$Pm3n$	$Fd3m$
no. H ₂ O molecules	4	46	136
lattice parameters at 273 K	$a = 4.52$ $c = 7.36$	12.0	17.3
dielectric constant at 273 K	94	~58	58
far-infrared spectrum	peak at 229 cm ⁻¹	peak at 229 cm ⁻¹ with others	
H ₂ O diffusion correl time (μ s)	220	240	25
H ₂ O diffusion activ energy (kJ/m)	58.1	50	50
mechanical property			
isothermal Young's modulus at 268 K (10 ⁹ Pa)	9.5	8.4 (est)	8.2 (est)
Poisson's ratio	0.33	~0.33	~0.33
bulk modulus (272 K)	8.8	5.6	NA
shear modulus (272 K)	3.9	2.4	NA
velocity ratio (comp/shear): 272 K	1.88	1.95	NA
thermodynamic property			
linear therm expt: 200 K (K ⁻¹)	56×10^{-6}	77×10^{-6}	52×10^{-6}
adiab bulk compress: 273 K (10 ⁻¹¹ Pa)	12	14 (est)	14 (est)
speed long sound: 273 K (km/s)	3.8	3.3	3.6
transport			
thermal conductivity: 263 K(W/(mK))	2.23	0.49 ± 0.02	0.51 ± 0.02

^a Modified from Davidson (1983) and from Ripmeester et al. (1994).

deep oceans with biogenic gases containing mostly methane, carbon dioxide, and hydrogen sulfide. Structure II, a diamond lattice within a cubic framework, forms when natural gases or oils contain molecules larger than ethane but smaller than pentane; sII represents hydrates from thermogenic gases. Finally, structure H hydrates must have a small occupant (like methane, nitrogen, or carbon dioxide) for the 5¹² and 4³5⁶3 cages but the molecules in the 5¹²6⁸ cage can be as large as 0.9 nm (e.g. ethylcyclohexane).

Time-Independent Properties from Hydrate Crystal Structures

Mechanical Properties of Hydrates. As may be calculated via Table 1, if all the cages of each structure are filled, all three hydrates have the amazing property of being approximately 85% (mol) water and 15% gas. The fact that the water content is so high suggests that the mechanical properties of the three hydrate structures should be similar to those of ice. This conclusion is true to a first approximation as shown in Table 2, with the exception of thermal conductivity and thermal expansivity.^{15,16} Many mechanical properties of sH have not been measured to date.

To date scientists and engineers have had only peripheral interest in hydrate mechanical properties. The phase transition that occurs at higher temperatures cause concern when structures are placed in the vicinity of hydrates. Details of hydrate mechanical properties are discussed in the literature.^{2,15}

Guest: Cavity Size Ratio: A Basis for Property Understanding. The hydrate cavity occupied is a function of the size ratio of the guest molecule within the cavity. To a first approximation, the concept of "a ball fitting within a ball" is a key to understanding many hydrate properties. Figure 2 (corrected from von Stackelberg¹⁷) may be used to illustrate five points

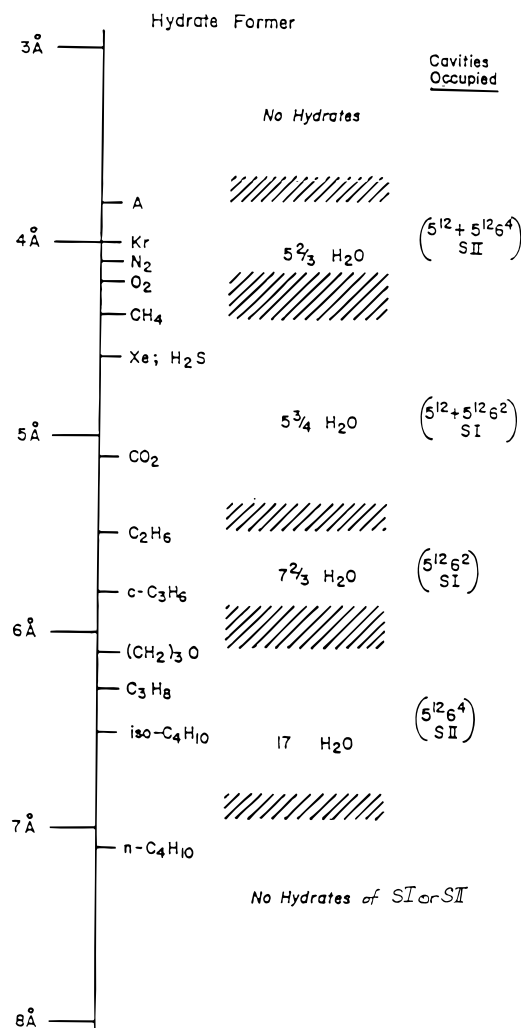


Figure 2. Relative sizes of hydrate guests and host cavities.

regarding the guest:cavity size ratio for hydrates formed of a *single* guest component in sI or sII.

1. The sizes of stabilizing guest molecules range between 0.35 and 0.75 nm. Below 0.35 nm, molecules will not stabilize sI and above 0.75 nm molecules will not stabilize sII.

(15) Davidson, D. W. In *Natural Gas Hydrates: Properties, Occurrence and Recovery*; Cox, J. L., Ed.; Butterworths: Boston, MA, 1983; p 1.

(16) Tse, J. S. (First) *International Conference on Natural Gas Hydrates*, Ann. N.Y. Acad. Sci. **1994**, 715, p 187.

(17) von Stackelberg, M. *Naturwissenschaften* **1949**, 36, 327, 359.

Table 3. Ratios of Molecular Diameters to Cavity Diameters^a for Some Molecules Including Natural Gas Hydrate Formers

molecule	guest dia (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>i</i> -C ₄ H ₁₀	6.5	1.27	1.11	1.29	0.976 ^F
<i>n</i> -C ₄ H ₁₀	7.1	1.39	1.21	1.41	1.07

^aCavity radii from Table 2 minus 1.4 Å water radii. F indicates the cavity occupied by the simple hydrate former.

2. Some molecules are too large to fit the smaller cavities of each structure (e.g. C₂H₆ fits in the 5¹²6² of sI; or *i*-C₄H₁₀ fits the 5¹²6⁴ of sII).

3. Other molecules such as CH₄ and N₂ are small enough to enter both cavities (labeled as either 5¹²+5¹²6² in sI or 5¹²+5¹²6⁴ in sII) when hydrate is formed of those single components.

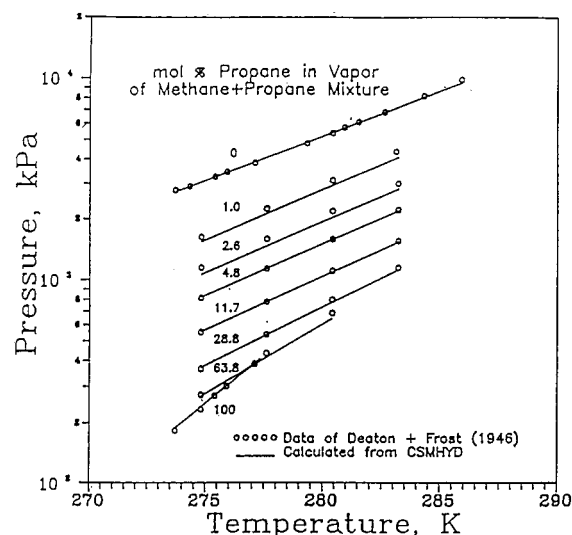
4. The largest molecules of a gas mixture usually determines the structure formed. For example, because propane and isobutane are present in many thermogenic natural gases, they will cause sII to form. In such cases, methane will distribute in both cavities of sII and ethane will enter only the 5¹²6⁴ cavity of sII.

5. Molecules which are very close to the hatched lines separating the cavity sizes appear to exhibit the most nonstoichiometry, due to their inability to fit securely within the cavity.

Table 3 shows the size ratio of several common 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 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.

Consider ethane, which forms in the 5¹²6² cavity in sI, because ethane is too large for the small 5¹² cavities in either structure and too small to give much stability to the large 5¹²6⁴ cavity in sII. Similarly, propane is too large to fit any cavity except the 5¹²6⁴ cavity in sII, so that gases of pure propane form sII hydrates from free water. On the other hand, methane's size is sufficient to lend stability to the 5¹² cavity in either sI or sII, with a preference for sI, because CH₄ lends slightly higher stability to the 5¹²6² cavity in sI than the 5¹²6⁴ cavity in sII.

Phase Equilibrium Properties. In Figure 3 pressure is plotted against temperature with gas composition as a parameter, for methane + propane mixtures. Consider a gas of any given composition (marked 0–100% propane) on a line in Figure 3. At conditions to the right of the line, a gas of that composition will exist in equilibrium with liquid water. As the temperature is reduced (or as the pressure is increased) hydrates form from gas and liquid water at the line, so three phases (liquid water + hydrates + gas) will be in equilibrium. With further reduction of temperature (or

**Figure 3.** Three-phase (L_w–H–V) equilibria of methane + propane mixtures.

increase in pressure), the fluid phase which is not in excess (gas in ocean environments) will be exhausted, so that to the left of the line the hydrate will exist with the excess phase (water).

All of the conditions given in Figure 3 are for temperatures above 273 K, and pressures along the lines vary exponentially with temperature. Put explicitly, hydrate stability at the three-phase (L_w–H–V) condition is always much more sensitive to temperature than to pressure. Figure 3 also illustrates the dramatic effect of gas composition on hydrate stability; as any amount of propane is added to methane the structure changes (sI → sII) to a hydrate with much wider stability conditions. Note that a 50% decrease in pressure is needed to form sII hydrates, when as little as 1% propane is in the gas phase.

Any discussion of hydrate dissociation would be incomplete without indicating that hydrates provide the most industrially useful instance of statistical thermodynamics prediction of phase equilibria. The van der Waals and Platteeuw model¹⁸ was formulated after the determination of the crystal structures shown in Figure 1. With the model, one may predict the three-phase pressure or temperature of hydrate formation by knowing the gas composition. For further discussion of these details the reader is referred to Sloan¹ (Chapter 5).

Heat of Dissociation. The heat of dissociation (ΔH_d) is defined as the enthalpy change to dissociate the hydrate phase to a vapor and aqueous liquid, with values given at temperatures just above the ice point. For sI and sII, to a fair engineering approximation ($\pm 10\%$) it has been shown¹⁹ that ΔH_d is a function of the number of crystal hydrogen bonds (loosely taken as hydration number). However, the value of ΔH_d is relatively constant for molecules which occupy the same cavity, within a wide range of components sizes. Enthalpies of dissociation may be determined via the univariant slopes of phase equilibrium lines ($\ln P$ vs $1/T$) in the previous paragraphs, using the Clausius–Clapeyron relation [$\Delta H_d = -zR d(\ln P)/d(1/T)$].

(18) van der Waals, J. H.; Platteeuw, J. C. *Adv. Chem. Phys.* **1959**, 2, 1.

(19) Sloan, E. D.; Fleyfel, F. *Fluid Phase Equilib.* **1992**, 76, 123.

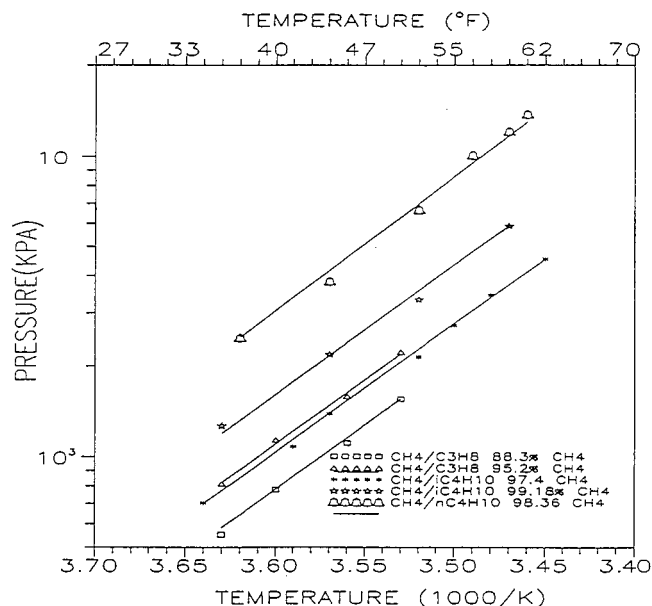


Figure 4. Three-phase equilibria of methane + (propane and two butanes).

As one illustration, simple hydrates of C_3H_8 or $i-C_4H_{10}$ have similar ΔH_d of 129 and 133 kJ/mol (measurements by Handa²⁰) because they both occupy the $5^{12}6^4$ cavity, although their size:cavity ratios are somewhat different (0.943 and 0.976). As a second illustration, Figure 3 shows that mixtures of $CH_4 + C_3H_8$ have a value of $\Delta H_d = 79$ kJ/mol over a wide range of composition. In such mixtures, C_3H_8 occupies most of the $5^{12}6^4$ cavities while CH_4 occupies a small number of $5^{12}6^4$ and many 5^{12} . In fact, most natural gases (which form sII) have similar values of ΔH_d . Figure 4 shows similar line slopes (and thus ΔH_d values) for binary mixtures of methane when the large guest is changed from C_3H_8 , to $i-C_4H_{10}$, to $n-C_4H_{10}$. Similarly, over a wide range of composition for mixtures of methane and ethane, ΔH_d values are similar (74 kJ/mol) for components entering both cavities of sI. Identical arguments may be used to explain similar calculated¹³ ΔH_d values of $79.5 \pm 7\%$ kJ/mol for sH mixtures of methane with seventeen larger components.

Challenges for Future Research

A review of the literature suggests that there are two imminent challenges for future research. First, we must characterize the hydrate phase both in the laboratory and in the field. Second, we must characterize the kinetics of hydrate formation and dissociation.

Measurements of the Hydrate Phase. For the hydrate phase there are two measurement techniques: diffraction and spectroscopic. Neutron diffraction (typified by Tse¹⁶) can detect water atoms and guest molecules, while X-ray diffraction detects oxygen positions. Recently, Stern et al.²¹ have been remarkably successful at converting 97% of ice to water (as analyzed by X-ray diffraction), by raising the temperature of small ice grains above the solidus while under high pressure.

Two types of spectroscopy are useful with hydrates: (1) nuclear magnetic resonance (NMR) with cross polarization (CP) and magic-angle spinning (MAS), and (2) Raman spectroscopy. Virtually all NMR hydrate work to date comes from the Canadian National Research Council. The first comprehensive review of NMR studies of clathrates was written by Davidson and Ripmeester²² and a thorough update has been written by Ripmeester and Ratcliffe.²³ Of NMR hydrate compounds Xe has obtained prominence due to its large (ca. 100 ppm) chemical shift.

Recently, Sum et al.²⁴ have shown that Raman spectroscopy can be used to determine the fraction of filled cages in hydrates, and the fraction of various components in the cages. Since Raman appears to be both more versatile and less resource intensive, it holds substantial promise for the future, both in thermodynamic and kinetic measurements at the molecular level. It may be possible to combine microscopic of the hydrate phase with macroscopic measurements of the fluid phases (e.g. using fiber optics with Raman spectroscopy in a phase equilibria cell.)

Measurements of Hydrate Kinetics. Most hydrate kinetics research has come from the laboratory of Bishnoi, notably the work of Englezos et al.^{25,26} They modeled kinetics of methane and ethane hydrate after nucleation, for periods up to 100 min. A subsequent model by Skovborg and Rasmussen²⁷ assumed that the crystal growth was rate-controlled by mass transfer of gas to the liquid phase, allowing them to ignore both hydrate kinetics and diffusion to the hydrate phase.

However, even with the above excellent beginnings, hydrate kinetics still pose substantial challenges to hydrate researchers, particularly in the quantification and separation of hydrate kinetics from mass and heat transfer. For example, no model of hydrate nucleation can acceptably fit all the data of a single experimenter; no universal nucleation model is available. As another example, all models of hydrate growth kinetics are apparatus-dependent. While the growth model may be a satisfactory fit for the apparatus in which the data were generated, the model will not fit data generated in other apparatuses. Determining time-dependent hydrate behavior is one of the most significant challenges for research.

Conclusions

This review indicates how properties such as phase equilibria and heat of dissociation relate to hydrate crystal structures. While many time-independent properties of sI and sII hydrates are determined, those for newer structures (e.g., sH) are just beginning to be

(20) Handa, Y. P. *J. Chem. Thermodyn.* **1986**, *18*, 891.

(21) Stern, L. A.; Kirby, S. H.; Durham, W. B. *Science* **1996**, *273*, 1843.

(22) Davidson, D. W.; Ripmeester, J. A. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNichol, D. D., Eds.; Academic Press: New York, 1984; Vol. 3, Chapter 3.

(23) Ripmeester, J. A.; Ratcliffe, C. I. *Solid State NMR Studies of Inclusion Compounds*; Report C1181-89S; National Research Council of Canada, 1989.

(24) Sum, A. K.; Burruss, R. C.; Sloan, E. D. *J. Phys. Chem. B* **1997**, *101*, 7371.

(25) Englezos, P.; Kalogerakis, N.; Dholabhai, P.; Bishnoi, P. *Chem. Eng. Sci.* **1987a**, *42*(11), 2647.

(26) Englezos, P.; Kalogerakis, N.; Dholabhai, P.; Bishnoi, P. *Chem. Eng. Sci.* **1987b**, *42*(11), 2659.

(27) Skovborg, P.; Rasmussen, P. *Chem. Eng. Sci.* **1994**, *49*, 1131.

explored. The time-dependent characteristics of all three hydrate structures are largely unspecified and kinetic models to date appear to be apparatus-depend-

ent. Common measurement of the hydrate phase constitutes a current challenge.

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