
1 Overview and Historical Perspective

Natural gas hydrates are crystalline solids composed of water and gas. The gas molecules (guests) are trapped in water cavities (host) that are composed of hydrogen-bonded water molecules. Typical natural gas molecules include methane, ethane, propane, and carbon dioxide.

Historically, the research efforts on natural gas hydrates can be classified into three landmark phases that cover the following periods:

- The first period, from their discovery in 1810 until the present, includes gas hydrates as a scientific curiosity in which gas and water are transformed into a solid.
- The second period, continuing from 1934 until the present, predominantly concerns man-made gas hydrates as a hindrance to the natural gas industry.
- The third period, from the mid-1960s until the present, began with the discovery that nature predated man's fabrication of hydrates by millions of years, *in situ* in both the deep oceans and permafrost regions as well as in extraterrestrial environments.

As a result, the present is a culmination of three periods, representing the most fascinating and productive time in the history of natural gas hydrates. During the first century after their discovery, the number of hydrate publications totaled approximately 40; in modern times, the number of hydrate publications, both in the technical and in the popular press, has increased dramatically with over 400 publications in 2005 alone. The semilogarithmic plot of [Figure 1.1](#) illustrates the exponential growth in the number of hydrate-related publications in the twentieth century. Table 1.1 lists reviews, chapters, and monographs on the subject of hydrates.

The purpose of this chapter is to review the three periods mentioned above, as an overview and historical perspective. The major concepts will be discussed briefly; detailed investigations are presented in the following chapters.

1.1 HYDRATES AS A LABORATORY CURIOSITY

In 1778, Joseph Priestley performed cold experiments in his Birmingham laboratory by leaving the window open before departing on winter evenings, returning the next morning to observe the result. He observed that vitriolic air (SO_2) would impregnate water and cause it to freeze and refreeze, whereas marine acid air (HCl)

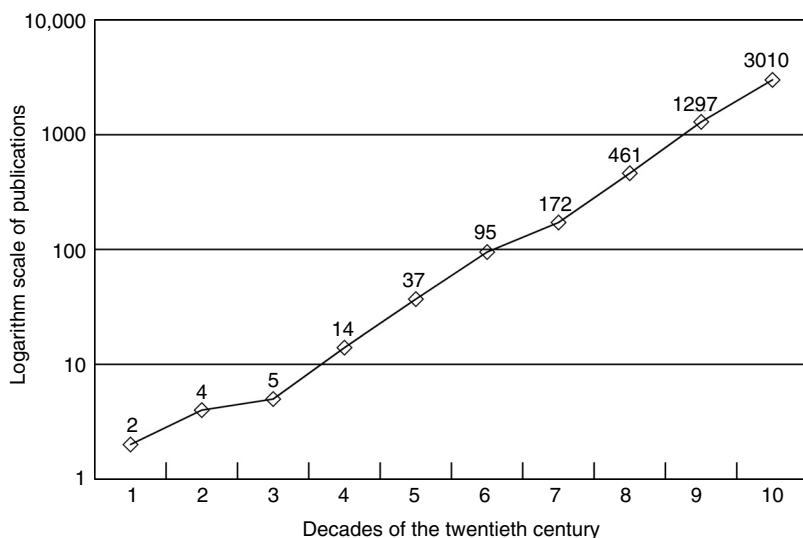


FIGURE 1.1 The growth of hydrate-related publications in the twentieth century by decade. (Reproduced from Sloan, E.D., *Am. Mineral.*, **89**, 1155 (2004). With permission from the Mineralogy Society of America.)

and fluor acid air (SiF_4) would not. With such experiments, Makogon and Gordejev (1992, unpublished data) suggest that Priestley might have discovered clathrate hydrates more than 30 years before Davy's discovery of clathrate hydrates.

"It is water impregnated with vitriolic acid air that may be converted into ice, whereas water impregnated with fluor acid will not freeze . . . I had observed that with respect to marine acid air and alkaline air (NH_3) that they dissolve ice, and that water impregnated with them is incapable of freezing, at least in such a degrees of cold as I had exposed them to. The same I find, is the case with fluor acid air, but it is not so at all with vitriolic acid air, which, entirely contrary to my expectation, I find to be altogether difficult . . . But whereas water impregnated with fixed air discharges it when it is converted into ice, water impregnated with vitriolic acid air, and then frozen retains it as strongly as ever."

However, unlike Davy's experiments, Priestley's temperature (17°F) of the gas mixture was below the ice point, so there is no unequivocal evidence that the frozen system was hydrate. There is also no record of validation experiments by Priestley; consequently, Davy's independent discovery of chlorine hydrate is generally credited as the first observance.

Natural gas hydrates were first documented by Sir Humphrey Davy (1811), with these brief comments on chlorine (then called oxymuriatic gas) in the Bakerian lecture to the Royal Society in 1810.

"It is generally stated in chemical books, that oxymuriatic gas is capable of being condensed and crystallized at low temperature; I have found by several experiments that this is not the case. The solution of oxymuriatic gas in water freezes more

TABLE 1.1
Reviews, Chapters, and Monographs on Clathrate Hydrates

- 1927 Schroeder: *Die Geschichte der Gas Hydrate*
- 1946 Deaton and Frost: *Gas Hydrates and Relation to the Operation of Natural-Gas Pipelines*
- 1959 Katz et al.: "Water-Hydrocarbon Systems" in *Handbook of Natural Gas Engineering*
- 1967 Jeffrey and McMullan: "The Clathrate Hydrates" in *Progress in Inorganic Chemistry*
- 1973 Davidson: "Clathrate Hydrates" in *Water: A Comprehensive Treatise* Vol. 2
- 1974 Makogan: *Hydrates of Natural Gas*
- 1977 Berez and Balla-Achs: *Gas Hydrates*
- 1980 Kvenvolden and McMenamin: *Hydrates of Natural Gas: A Review of Their Geologic Occurrence*
- 1983 Cox, ed.: *Natural Gas Hydrates: Properties, Occurrence and Recovery*
- 1983 Lewin & Associates and Consultants: *Handbook of Gas Hydrate Properties and Occurrence*
- 1987 Krason and Ciesnik: *Geological Evolution and Analysis of Confirmed or Suspected Gas Hydrate Localities* (13 volumes)
- 1988 Holder et al.: "Phase Behavior in Systems Containing Clathrate Hydrates" *Rev. Chem. Eng.*
- 1990 Katz and Lee: "Gas Hydrates and Their Prevention" in *Natural Gas Engineering: Production and Storage*
- 1990 Sloan: *Clathrate Hydrates of Natural Gases*
- 1993 Englezos: "Clathrate Hydrates" *Ind. Eng. Chem. Res.*
- 1994 Sloan, Hoppel and Hnatow, eds.: *International Conference on Natural Gas Hydrates*, NY
- 1995 Kvenvolden, K.A.: *A Review of the Geochemistry of Methane in Natural Gas Hydrate*
- 1996 Monfort, ed.: *Second International Conference on Natural Gas Hydrates*, Toulouse
- 1997 Makogan: *Hydrates of Hydrocarbons*
- 1998 Henriot and Mienert, eds.: *Gas Hydrates: Relevance to World Margin Stability and Climate Change*
- 1998 Ginsburg and Soloviev: *Submarine Gas Hydrates*
- 2000 Holder and Bishnoi, eds.: *Third International Conference on Natural Gas Hydrates*, Salt Lake City
- 2000 Sloan: *Hydrate Engineering*
- 2000 Paull et al.: *Proc. Ocean Drilling Program, Science Results for Leg 164 (Blake Ridge)*
- 2001 Paull and Dillon, eds.: *Natural Gas Hydrates: Occurrence, Distribution and Detection*
- 2002 Mori, ed.: *Fourth International Conference on Natural Gas Hydrates*, Yokohama
- 2003 Kennett et al.: *Methane Hydrates in Quaternary Climate Change: The Clathrate Gun Hypothesis*
- 2003 Max, ed. *Natural Gas Hydrates in Oceanic and Permafrost Environments*
- 2004 Taylor and Kwan, eds.: *Advances in the Study of Gas Hydrates*
- 2004 Zhang and Lanoil, eds.: "Geomicrobiology and Biogeochemistry of Gas Hydrates and of Hydrocarbon Seeps" in *Chemical Geology*
- 2005 Austvik, ed.: *Fifth International Conference on Natural Gas Hydrates*, Trondheim
- 2005 Dallimore et al., eds.: "Report of the Mallik 5L International Field Experiment on Recovering *In Situ* Hydrates from Permafrost", *Geological Survey of Canada Report*.
- 2005 IODP: Preliminary Report Leg 311 (Northern Cascadia Margin)
- 2006 Johnson et al., eds.: *Economic Geology of Natural Gas Hydrates*
- 2006 Tréhu et al.: *Ocean Drilling Program Scientific Report Leg 204*

readily than pure water, but the pure gas dried by muriate of lime undergoes no change whatever at a temperature of 40 below 0° of Fahrenheit.”

Over the following one and one-quarter centuries, researchers in the field had two major goals, namely, (1) to identify all the compounds that formed hydrates and (2) to quantitatively describe the compounds by their compositions and physical properties. Table 1.2 provides a summary of the research over this period.

TABLE 1.2
Hydrates from 1810 to 1934

| Year | Event |
|------------|--|
| 1810 | Chlorine hydrate discovery by Sir Humphrey Davy |
| 1823 | Corroboration by Faraday—formula $\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ |
| 1882, 1883 | Ditte and Mauméné disputed the composition of chlorine hydrates |
| 1884 | Roozeboom confirmed the composition as $\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ |
| 1884 | LeChatelier showed that the Cl hydrate P – T curve changes slope at 273 K |
| 1828 | Bromine hydrates discovered by Löwig |
| 1876 | Br_2 hydrates corroborated by Alexeyeff as $(\text{Br}_2 \cdot 10\text{H}_2\text{O})$ |
| 1829 | SO_2 hydrates found by de la Rive as $\text{SO}_2 \cdot 7\text{H}_2\text{O}$ |
| 1848 | Pierre determined the formula of $\text{SO}_2 \cdot 11\text{H}_2\text{O}$ |
| 1855 | Schoenfield measured the formula as $\text{SO}_2 \cdot 14\text{H}_2\text{O}$ |
| 1884, 1885 | Roozeboom postulated upper/lower hydrate quadruple points using SO_2 as evidence; determined univariant dependence of P on T |
| 1856–1858 | CS_2 hydrate composition disputed by Berthelot (1856), Millon (1860), Duclaux (1867), Tanret (1878) |
| 1877, 1882 | Cailletet and Cailletet and Bordet first measured mixed gas hydrates from $\text{CO}_2 + \text{PH}_3$ and from $\text{H}_2\text{S} + \text{PH}_3$ |
| 1882 | de Forcrand suggested $\text{H}_2\text{S} \cdot (12\text{--}16)\text{H}_2\text{O}$ and measured 30 binary hydrates of H_2S with a second component such as CHCl_3 , CH_3Cl , $\text{C}_2\text{H}_5\text{Cl}$, $\text{C}_2\text{H}_5\text{Br}$, $\text{C}_2\text{H}_3\text{Cl}$. He indicated all compositions as $\text{G} \cdot 2\text{H}_2\text{S} \cdot 23\text{H}_2\text{O}$ |
| 1883 | Wroblewski measured carbon dioxide hydrates |
| 1885 | Chancel and Parmentier determined chloroform hydrates |
| 1888 | Villard obtained the temperature dependence of H_2S hydrates |
| 1888 | de Forcrand and Villard independently measured the temperature dependence of CH_3Cl hydrate |
| 1888 | Villard measured hydrates of CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , N_2O |
| 1890 | Villard measured hydrates of C_3H_8 and suggested that the temperature of the lower quadruple point is decreased by increasing the molecular mass of a guest; Villard suggested hydrates were regular crystals |
| 1896 | Villard measured hydrates of Ar, and proposed that N_2 and O_2 form hydrates; first to use heat of formation data to get the water/gas ratio |
| 1897 | deForcrand and Thomas sought double ($\text{w}/\text{H}_2\text{S}$ or H_2Se) hydrates; found mixed (other than H_2S_x) hydrates of numerous halohydrocarbons mixed with C_2H_2 , CO_2 , C_2H_6 |
| 1902 | de Forcrand first used Clausius–Clapeyron relation for ΔH and compositions; tabulated 15 hydrate conditions |
| 1919 | Scheffer and Meyer refined Clausius–Clapeyron technique |
| 1923, 1925 | de Forcrand measured hydrates of krypton and xenon |

In [Table 1.2](#), the following pattern was often repeated: (1) the discovery of a new hydrate was published by an investigator; (2) a second researcher disputed the composition proposed by the original investigator; and (3) a third (or more) investigator(s) refined the measurements made by the initial two investigators, and proposed slight extensions. As a typical example, in the case of chlorine hydrate after Davy's discovery in 1810, Faraday confirmed the hydrate (1823) but proposed that there were ten water molecules per molecule of chlorine. Then Ditte (1882), Mauméné (1883), and Roozeboom (1884) re-examined the ratio of water to chlorine.

The period from 1810 to 1900 is characterized by efforts of direct composition measurements with inorganic hydrate formers, especially bromine, inorganics containing sulfur, chlorine, and phosphorus, and carbon dioxide. Other notable work listed in [Table 1.2](#) was done by Cailletet and Bordet (1882), who first measured hydrates with mixtures of two components. Cailletet (1877) was also the first to measure a decrease in gas pressure when hydrates were formed in a closed chamber, using a precursor of an apparatus still in use at the Technical University of Delft, the Netherlands.

1.1.1 Hydrates of Hydrocarbons Distinguished from Inorganic Hydrates and Ice

Two French workers, Villard and de Forcrand, were the most prolific researchers of the period before 1934, with over four decades each of heroic effort. Villard (1888) first determined the existence of methane, ethane, and propane hydrates. de Forcrand (1902) tabulated equilibrium temperatures at 1 atm for 15 components, including those of natural gas, with the exception of iso-butane, first measured by von Stackelberg and Müller (1954).

The early period of hydrate research is marked by a tendency to set an integral number of water molecules per guest molecule, due to the existing knowledge of inorganic stoichiometric hydrates that differed substantially from clathrate hydrates. For example, Villard's Rule (1895) states that "all crystallize regularly and have the same constitution that can be expressed by the formula $M + 6H_2O$." Schroeder (1927) noted that Villard's Rule was followed by 15 of the 17 known gas hydrate formers. Today, we know that too many exceptions are required for Villard's Rule to be a useful heuristic. Molecules approximated by Villard's Rule are small guests that occupy both cavities of structures I or II (see [Chapter 2](#)).

It gradually became clear that the clathrate hydrates distinguished themselves by being both nonstoichiometric and crystalline; at the same time, they differed from normal hexagonal ice because they had no effect on polarized light.

1.1.2 Methods to Determine the Hydrate Composition

The work in [Table 1.2](#) illustrates one of the early research difficulties that is still present—namely, the direct measurement of the water to gas ratio in hydrates (hydration number, n = water molecules per guest). Whereas many solids

such as carbon dioxide precipitate in a relatively pure form, or a form of fixed composition, gas hydrate composition is variable with temperature, pressure, and the composition of associated fluid phases. Although the composition measurement of either the gas or the water phase is tractable (usually via chromatography), measurement of the hydrate composition is more challenging.

On a macroscopic basis, it is difficult to remove all excess water from the hydrate mass; this causes a substantial decrease in the accuracy of hydrate composition measurements. Hydrate formations often occlude water within the solid in a metastable configuration, thereby invalidating the composition obtained upon dissociation. Mixed guest compositions of the hydrate are also confounded by the concentration of heavy components in the hydrate phase. Unless the associated gas reservoir is large, preferential hydration may result in variable gas consumption and perhaps an inhomogeneous hydrate phase as discussed in [Chapter 6](#).

Villard (1896) proposed an indirect macroscopic method to determine hydration number, which uses the heat of formation, both above and below the ice point. In his review, Schroeder (1927) indicates that after 1900, researchers abandoned direct measurement of hydrate phase composition, preferring Villard's method (see [Section 4.6.2](#)) that relies on easier measurements of pressure and temperature. Miller and Strong (1946) provided another thermodynamic method to determine hydration number, discussed in [Section 4.6.2.2](#).

Circone et al. (2005) obtained hydration numbers from direct macroscopic measurements of the amount of gas released during dissociation. Their results were in close agreement with those obtained by Galloway et al. (1970) from measurements of gas uptake during synthesis and release during decomposition, and by Handa (1986e) from calorimetric measurements.

The advent of modern microscopic measurement tools and a means for bridging the microscopic and macroscopic domains (statistical thermodynamics) enable the direct determination of hydrate phase properties. The hydration number can be determined from single crystal or powder (using Rietveld refinement) x-ray and neutron diffraction. The hydration number can also be determined using Raman (Sum et al., 1997; Uchida et al., 1999) and NMR (Ripmeester and Ratcliffe, 1988) spectroscopy combined with statistical thermodynamics. Davidson et al. (1983) and Ripmeester and Ratcliffe (1988) first used NMR spectroscopy and Sum et al. (1997) first used Raman spectroscopy to determine the guest occupancies of each type of cage. Single crystal and powder x-ray and neutron diffraction (Udachin et al., 2002; Rawn et al., 2003) have also been applied to determine guest occupancies and hydrate composition. These methods are discussed in [Chapter 6](#).

1.1.3 Phase Diagrams Provide Hydrate Classification

Roozeboom (1884, 1885) generated the first pressure–temperature plot for SO₂ hydrate, similar to that in [Figure 1.2](#) for several components of natural gases. In the figure, H is used to denote hydrates, I for ice, V for vapor, and L_w and L_{HC} for aqueous and hydrocarbon liquid phases, respectively. For each component,

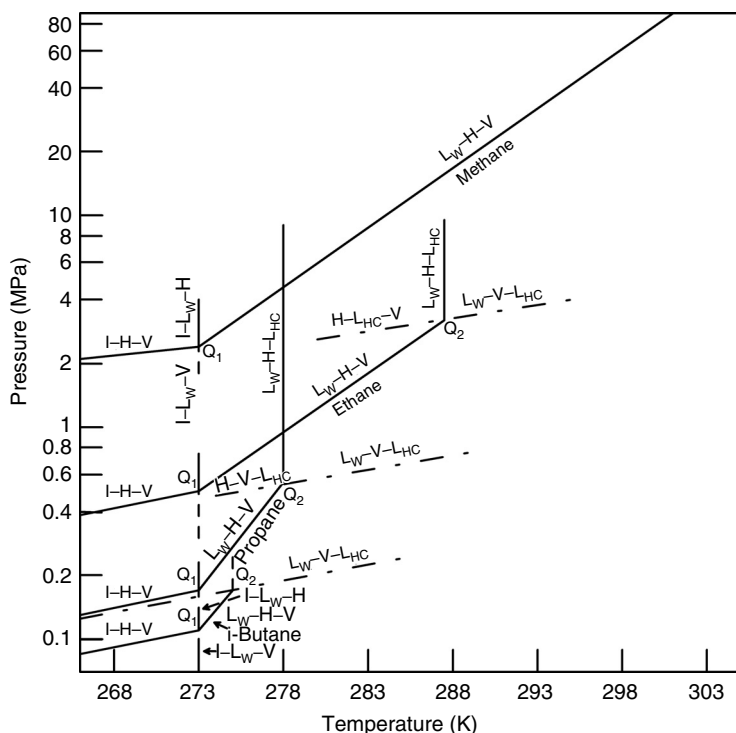


FIGURE 1.2 Phase diagrams for some simple natural gas hydrocarbons that form hydrates. Q_1 : lower quadruple point; Q_2 : upper quadruple point. (Modified from Katz, D.L., Cornell, D., Kobayashi, R., Poettmann, F.H., Vary, J.A., Elenbaas, J.R., Weinaug, C.F., *The Handbook of Natural Gas Engineering*, McGraw Hill Bk. Co. (1959). With permission.)

the hydrate region is to the left of the three phase lines (I-H-V), (L_w -H-V), (L_w -H-LHC); to the right, phases exist for liquid water or ice and the guest component as vapor or liquid.

In Figure 1.2, the intersection of the above three phase lines defines both a lower hydrate quadruple point Q_1 (I- L_w -H-V) and an upper quadruple point Q_2 (L_w -H-V-LHC). These quadruple points are unique for each hydrate former, providing a quantitative classification for hydrate components of natural gas.

Each quadruple point occurs at the intersection of four three-phase lines (Figure 1.2). The lower quadruple point is marked by the transition of L_w to I, so that with decreasing temperature, Q_1 denotes where hydrate formation ceases from vapor and liquid water, and where hydrate formation occurs from vapor and ice. Early researchers took Q_2 (approximately the point of intersection of line L_w -H-V with the vapor pressure of the hydrate guest) to represent an upper temperature limit for hydrate formation from that component. Since the vapor pressure at the critical temperature can be too low to allow such an intersection, some natural gas components such as methane and nitrogen have no upper quadruple point, Q_2 , and

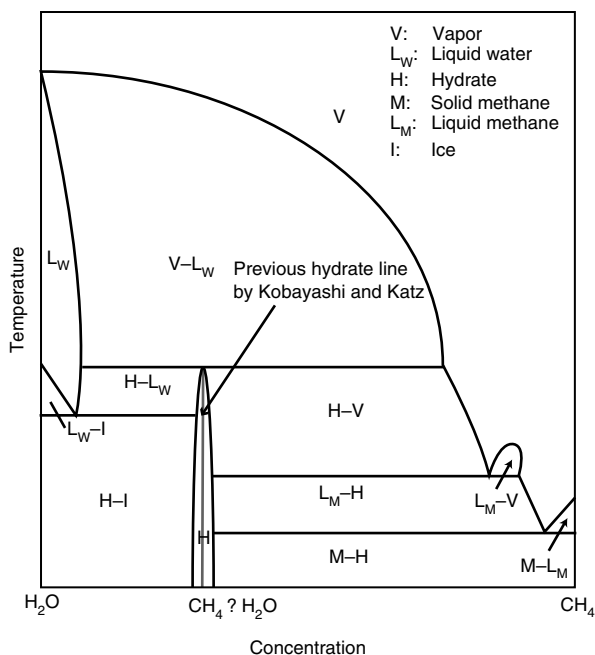


FIGURE 1.3 Proposed $\text{CH}_4\text{-H}_2\text{O}$ T - x phase diagram with the solid solution range ($P \approx 5$ MPa). Regions expanded for ease of viewing. (Reproduced from Huo, Z., Hester, K.E., Sloan, E.D., Miller, K.T., *AIChE J.*, **49**, 1300 (2003). With permission.)

consequently they have no upper temperature limit for hydrate formation. Phase diagrams are discussed in detail in [Chapter 4](#).

The isobaric methane–water phase diagram was produced by Kobayashi and Katz in 1949 (Figure 1.3). This classical phase diagram represents the hydrate composition as a vertical constant composition line. This assumes that the hydrate is stoichiometric and that cage occupancy is independent of temperature or system composition. Reassessment of this phase diagram was initiated by the authors' laboratory in 2002 (Huo et al., 2002, 2003). We revisited the largely overlooked work by Glew and Rath (1966). Glew and Rath (1966) found from density measurements of sl ethylene oxide that nonstoichiometry (with the minimum occupancy of the small cages varying from 19% to 40%) can occur depending on the solution composition. This work validated the earlier statistical thermodynamic calculations showing nonstoichiometry in clathrate hydrates (van der Waals and Platteuw, 1959).

X-ray diffraction and Raman studies were performed to re-evaluate the relation between hydrate and overall composition (Huo et al., 2002, 2003). A modified methane–water phase diagram was proposed to include a small solid solution range of around 3% (Figure 1.3). [A solid solution is a solid-state solution of one or more solutes (guests) in a solvent (host framework). Generally, the crystal structure (of the clathrate hydrate) remains homogeneous and unchanged when substituting/

adding solutes (varying guest occupancies) to the solvent (host framework).] The solid solution range is represented by a parabolic hydrate region (attributed to incomplete filling of small cages of sI hydrate) in the isobaric methane–water phase diagram, which replaces the vertical stoichiometric hydrate line of Kobayashi and Katz (1949).

1.2 HYDRATES IN THE NATURAL GAS INDUSTRY

In the mid-1930s Hammerschmidt studied the 1927 hydrate review of Schroeder (D.L. Katz, Personal Communication, November 14, 1983) to determine that natural gas hydrates were blocking gas transmission lines, frequently at temperatures above the ice point. This discovery was pivotal in causing a more pragmatic interest in gas hydrates and shortly thereafter led to the regulation of the water content in natural gas pipelines.

The detection of hydrates in pipelines is a milestone marking both the importance of hydrates to industry and the beginning of the modern research era. As a complement to the history prior to 1934 in [Table 1.2](#), hydrate studies in more recent times are indicated in [Table 1.3](#). The key scientific developments and applications to the natural gas industry are listed in [Table 1.3](#). With this listing as an abstract, an introduction to modern research is provided in the next few pages, with more details and literature references in later chapters.

1.2.1 Initial Experiments on Natural Gas Hydrates

After Hammerschmidt's initial discovery, the American Gas Association commissioned a thorough study of hydrates at the U.S. Bureau of Mines. In an effort spanning World War II, Deaton and Frost (1946) experimentally investigated the formation of hydrates from pure components of methane, ethane, and propane, as well as their mixtures with heavier components in both simulated and real natural gases.

Predictive method results are still compared to the Deaton and Frost data. It should be remembered, however, that while this study was both painstaking and at the state-of-the-art, the data were of somewhat limited accuracy, particularly the measurements of gas composition. As will be seen in [Chapters 4](#) and [5](#), small inaccuracies in gas composition can dramatically affect hydrate formation temperatures and pressures. For example, Deaton and Frost were unable to distinguish between normal butane and iso-butane using a Podbielniak distillation column, and so used the sum of the two component mole fractions. Accurate composition measurement techniques such as chromatography did not come into common usage until early in the 1960s.

Many workers including Hammerschmidt (1939), Deaton and Frost (1946), Bond and Russell (1949), Kobayashi et al. (1951), and Woolfolk (1952) investigated the effects of inhibitors on hydrates. In particular, many chloride salts such as those of calcium, sodium, and potassium, were considered along with methanol and monoethylene glycol. Methanol gradually became one of the

TABLE 1.3
Milestones in Hydrate Studies since 1934

| | |
|---------|--|
| 1934 | Hammerschmidt discovers hydrates as pipeline plugs; provides Hammerschmidt equation; discovers thermodynamic inhibitors |
| 1941 | Katz et al. begin K -values and gas gravity methods to predict hydrate mixtures |
| 1946 | Deaton and Frost present data summary on hydrates and their prevention |
| 1949 | von Stackelberg reports 20 years of diffraction data on hydrate crystals |
| 1949 | Kobayashi begins a 50 year hydrate research effort with study of binary systems |
| 1951 | Claussen proposes, and von Stackelberg and Müller confirm sII unit crystal |
| 1952 | Claussen and Polglase, Müller and von Stackelberg, and Pauling and Marsh confirm sI unit crystal |
| 1954 | von Stackelberg and Jahn measure sII hydrate formed from two sI guest molecules |
| 1959 | van der Waals and Platteeuw (vdWP) propose statistical theory based on structure |
| 1960 | Robinson begins 30 year hydrate research effort with study of paraffin/olefin hydrates |
| 1963 | McKoy and Sinanoglu apply Kihara potential to vdWP theory |
| 1963 | Davidson makes first dielectric measurements |
| 1965 | Kobayashi and coworkers apply vdWP theory to mixtures |
| 1966 | Davidson makes first broadband NMR measurements of hydrates |
| 1972 | Parrish and Prausnitz apply vdWP theory to natural gases |
| 1975 | Sloan begins measurements of two-phase hydrate equilibria |
| 1976 | Ng begins with three- and four-phase study of liquid hydrocarbons |
| 1976 | Holder et al. begin work with study of sI and sII coexistence and hydrates in earth |
| 1979 | Bishnoi and coworkers begin kinetic study with simulations of well blowouts |
| 1980 | Ripmeester and Davidson make first pulsed NMR measurements |
| 1982 | Tse and coworkers begin molecular dynamic (MD) simulation of hydrates |
| 1984 | Davidson et al. confirm Holder's suggestion that small, simple guests form sII |
| 1984 | Handa begins study of calorimetry and phase equilibria |
| 1985 | John and Holder determine effect of higher order coordination shells in vdWP theory |
| 1986 | Englezos begins study of kinetics of methane, ethane dissociation |
| 1987 | Ripmeester and coworkers discover new structure H (sH) hydrates |
| 1988 | Danesh, Todd, and coworkers begin four phase experiments with hydrates |
| 1990a,b | Rodger studies relative stability using MD simulation |
| 1991 | Mehta obtains sH data, applied vdWP theory to CH_4 + large ($> 8 \text{ \AA}$) guest(s) |
| 1991 | Behar et al. introduce water emulsification concept to control hydrate blockage |
| 1991 | Sloan proposes molecular mechanism with kinetic inhibition implications |
| 1992 | Kotkoskie et al. show that hydrates are controlled by drilling mud water activity |
| 1996 | Sum measures hydrate composition and hydration number using Raman spectroscopy |
| 1997 | Kuhs et al. publish first report of double occupancy of nitrogen molecules in large cage of sII hydrate at high pressures, exceeding several hundred bar |
| 1997 | Udachin et al. report first single crystal x-ray diffraction measurements of a sH gas hydrate |
| 1997 | Dyadin et al. discover a very high pressure phase of methane hydrate that is stable up to 600 MPa |
| 1999 | Dyadin et al. discover that H_2 forms a clathrate hydrate at high pressures up to 1.5 GPa |
| 2004 | Camargo et al. and BP/SINTEF introduce "cold flow" concept to prevent hydrate plug formation without the need of chemical additives |

most popular inhibitors, due to its ability to concentrate in free water traps after being vaporized into the upstream gas. Effects of thermodynamic inhibitors such as methanol are quantified in [Chapters 4, 5, 6, and 8](#).

1.2.2 Initial Correlation of Hydrate Phase Equilibria

When Hammerschmidt (1934) identified hydrates in pipelines, he published a correlation summary of over 100 hydrate formation data points. Shortly afterward, Professor D.L. Katz and his students at the University of Michigan began an experimental study. Because it was impractical to measure hydrate formation conditions for every gas composition, Katz determined two correlative methods.

The initial predictive method by Wilcox et al. (1941) was based on distribution coefficients (sometimes called K_{vsi} values) for hydrates on a water-free basis. With a substantial degree of intuition, Katz determined that hydrates were solid solutions that might be treated similar to an ideal liquid solution. Establishment of the K_{vsi} value (defined as the component mole fraction ratio in the gas to the hydrate phase) for each of a number of components enabled the user to determine the pressure and temperature of hydrate formation from mixtures. These K_{vsi} value charts were generated in advance of the determination of hydrate crystal structure. The method is discussed in detail in Section 4.2.2.

The second (and simplest available) method, generated by Professor Katz (1945) and students in a graduate class, is presented in [Figure 1.4](#). The plot enabled the user to estimate a hydrate formation pressure, given a temperature and gas gravity (gas molecular weight divided by that of air). The original work also enabled the determination of the hydrate formation limits due to expansions of natural gases, as in throttling gas through a valve. This method and its limitations are discussed in detail in Section 4.2.1 as a useful first approximation for hydrate formation conditions.

Katz's two predictive techniques provided industry with acceptable predictions of mixture hydrate formation conditions, without the need for costly measurements. Subsequently, hydrate research centered on the determination of the hydrate crystal structure(s). Further refinements of the K_{vsi} values were determined by Katz and coworkers (especially Kobayashi) in Chapter 5 of the *Handbook of Natural Gas Engineering* (1959), by Robinson and coworkers (Jhaveri and Robinson, 1965; Robinson and Ng, 1976), and by Poettmann (1984).

1.2.3 Hydrate Crystal Structures and Hydrate Type Definitions

In the late 1940s and early 1950s, von Stackelberg and coworkers summarized two decades of x-ray hydrate crystal diffraction experiments at the University of Bonn. The interpretation of these early diffraction experiments by von Stackelberg (1949, 1954, 1956), von Stackelberg and Müller (1951a,b), Claussen (1951a,b), and Pauling and Marsh (1952) led to the determination of two hydrate crystal structures (sI and sII) shown in [Figure 1.5](#).

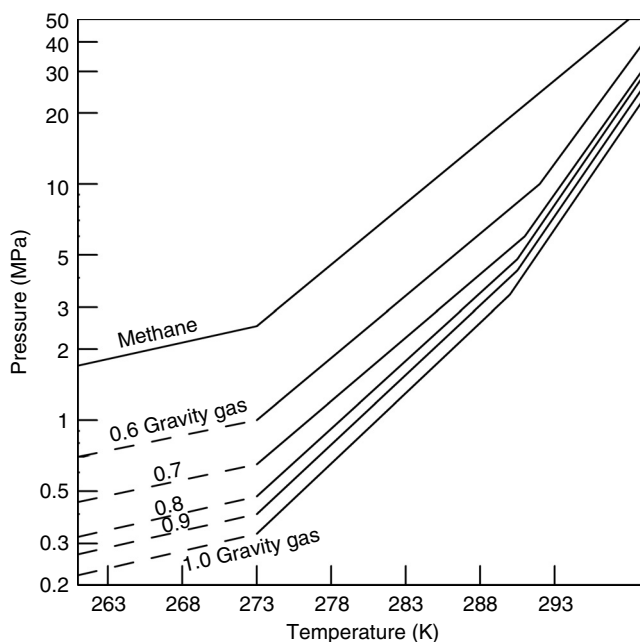


FIGURE 1.4 Gas gravity chart for prediction of three-phase (L_W -H-V) pressure and temperature. (Reproduced from Katz, D.L., *Transactions AIME*, **160**, 140 (1945). With permission.)

During the period from 1959 to 1967, an extensive series of crystallographic studies were performed on sI and sII clathrate hydrates by Jeffrey and coworkers (Mak and McMullan, 1965; McMullan and Jeffrey, 1965) resulting in summary reviews (Jeffrey and McMullan, 1967; Jeffrey, 1984). These studies showed hydrates to be members of the class of compounds labeled “clathrates” by Powell (1948)—after the Latin “clathratus” meaning “to encage.”

The existence of a third hydrate structure, structure H (sH) was not discovered until 1987 (Ripmeester et al., 1987). The unit cell of sH is shown in [Figure 1.5c](#). Details of all three unit cells and their constituent cages are given in [Chapter 2](#). Structure H requires both a small molecule such as methane and larger molecules typical of a condensate or an oil fraction. Just after their discovery, Ripmeester et al. (1991) reported the formation of sH with components of gasoline and a light naptha fraction.

About the same time as the initial measurements of sH with methane and adamantane in the Colorado School of Mines (CSM) laboratory by Lederhos et al. (1992), Becke et al. (1992) surmised that they measured the sH equilibrium for methane + methylcyclohexane. Structure H phase equilibria data were reported for binary systems with methane as the help gas (Mehta and Sloan, 1993, 1994, 1996; Thomas and Behar, 1994), with methane and nitrogen as the help gas (Danesh et al., 1994), and binary systems with salt (Hutz and Englezos, 1995).

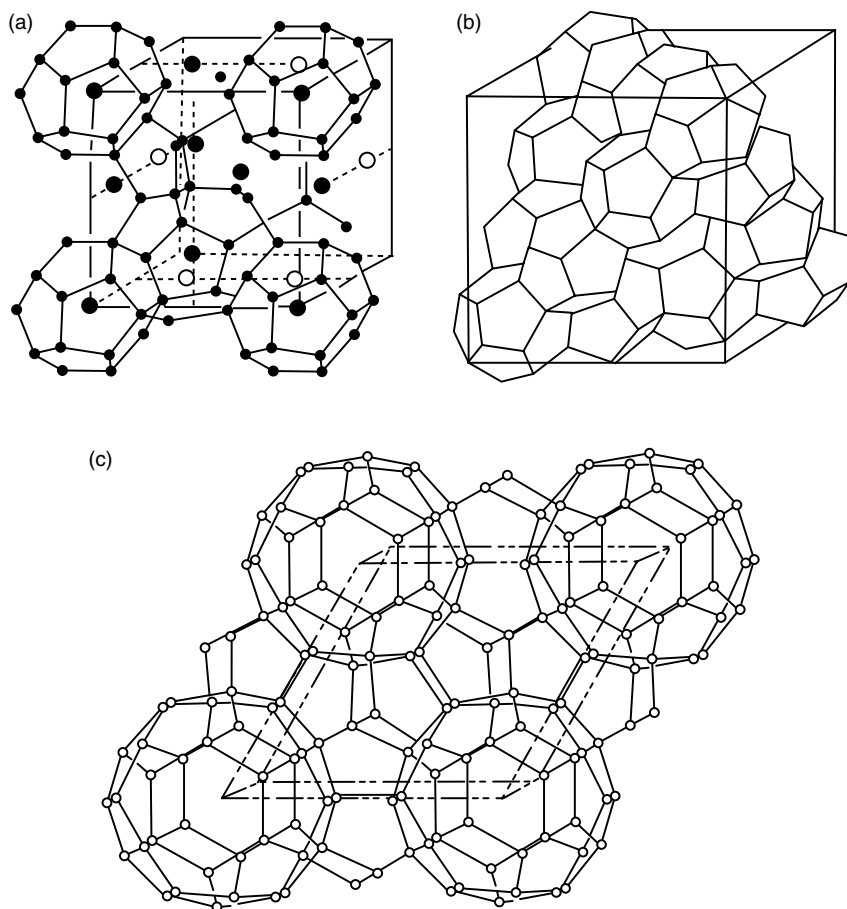


FIGURE 1.5 Hydrate crystal unit structures: (a) sI (McMullan and Jeffrey, 1965), (b) sII (Mak and McMullan, 1965), and (c) sH. (Both figures (a) and (b) were reproduced from the *J. Chem. Phys.* by the American Institute of Physics. With permission.)

A detailed summary of extant sH phase equilibria data and statistical predictions up to 1996 is in the doctoral dissertation of Mehta (1996). Since 1996, more than 30 new sH phase equilibria data sets have been reported, notably from the laboratories of Peters in Delft, the Netherlands; Tohidi in Edinburgh, Scotland; Mori in Yokohama, Japan; and Ohgaki in Osaka, Japan. The different components that form sH hydrate are given in [Table 2.7](#).

All hydrate structures have repetitive crystal units, as shown in Figure 1.5, composed of asymmetric, spherical-like “cages” of hydrogen-bonded water molecules. Each cage typically contains at most one guest molecule, held within the cage by dispersion forces. The hydrate crystalline structures and mechanical properties are discussed in [Chapter 2](#). Throughout this book the common name

“natural gas hydrate(s)” may be used interchangeably with the correct designation “clathrate hydrate(s) of natural gas.”

Von Stackelberg and coworkers classified hydrates in a scheme that is still used:

- “Mixed” is the term reserved for hydrates of more than one component, in which cages of the same kind are occupied by two types of molecules, with the restriction of at most one molecule per cage.
- “Double” hydrates was initially reserved for structure II hydrates in which one component is hydrogen sulfide or hydrogen selenide. It has come to mean hydrates in which each size cage is primarily occupied by a different type of molecule. Von Stackelberg proposed that double hydrates were stoichiometric due to their almost invariant composition. Van der Waals and Platteeuw (1959) suggested this invariance was caused instead by azeotropic composition (i.e., hydrate and gas phase compositions are the same).
- A hiflgase or “help gas” hydrate is composed of small components such as nitrogen or methane that would aid in hydrate formation of a second larger component.
- To complete these common definitions, Davidson (1973) proposed that the term “simple” hydrate denote only one guest species.

While sI, sII, and sH are the most common clathrate hydrates, a few other clathrate hydrate phases have been identified. These other clathrate hydrates include new phases found at very high pressure conditions (i.e., at pressures of around 1 GPa and higher at ambient temperature conditions). Dyadin et al. (1997) first reported the existence of a new methane hydrate phase at very high pressures (500 MPa). This discovery was followed by a proliferation in molecular-level studies to identify the structure of the high pressure phases of methane hydrate (Chou et al., 2000; Hirai et al., 2001; Kurnosov et al., 2001; Loveday et al., 2001, 2003).

Up until 1997, it was considered that a maximum of one guest could occupy a hydrate cage. Kuhs et al. (1997) first reported that nitrogen doubly occupies the large cage of sII hydrate. Multiple occupancies were then subsequently reported for argon (Yu et al., 2002), oxygen (Chazallon and Kuhs, 2002), and hydrogen (Mao et al., 2002) in sII hydrate. Further details of the common hydrate structures, new hydrate structures, high pressure hydrate phases, and multiple guest occupancy are given in [Chapter 2](#).

1.2.4 Basis for Current Thermodynamic Models

With the determination of hydrate structure, more rigorous predictive methods were formulated for hydrate thermodynamic property predictions. Barrer and Stuart (1957) initially suggested a statistical thermodynamic approach to determining gas hydrate properties. In a similar yet more successful approach,

van der Waals and Platteeuw (1959) proposed the foundation of the method currently used. This method is perhaps the best modern example for the use of statistical thermodynamics to predict macroscopic properties, such as temperature and pressure, using microscopic properties such as intermolecular potentials. It represents one of the few routine uses of statistical thermodynamics in industrial practice.

The advantage of the method in addition to accuracy is that, in principle, it enables the user to predict properties of mixtures from parameters of single hydrate formers. Since there are only eight natural gas components (yet an infinite number of natural gas mixtures) that form hydrates, the method represents a tremendous saving in experimental effort for the natural gas industry. The modified van der Waals and Platteeuw method is detailed in [Chapter 5](#).

McKoy and Sinanoglu (1963) and Child (1964) refined the van der Waals and Platteeuw method using different intermolecular potentials such as the Kihara potential. Workers at Rice University, such as Marshall et al. (1964) and Nagata and Kobayashi (1966a,b), first fit simple hydrate parameters to experimental data for methane, nitrogen, and argon. Parrish and Prausnitz (1972) showed in detail how this method could be extended to all natural gases and mixed hydrates.

Efforts to improve the original assumptions by van der Waals and Platteeuw were detailed in a review by Holder et al. (1988). Erbar and coworkers (Wagner et al., 1985) and Anderson and Prausnitz (1986) presented improvements to inhibitor prediction. Robinson and coworkers introduced guest interaction parameters into their prediction scheme, as summarized by Nolte et al. (1985). At Heriot-Watt University, the group of Tohidi and Danesh generated another prediction extension, with emphasis on systems containing oil or condensate (Avlonitis et al., 1989; Avlonitis, 1994; Tohidi et al., 1994a).

The van der Waals and Platteeuw method has been extended to flash programs by a number of researchers (Bishnoi et al., 1989; Cole and Goodwin, 1990; Edmonds et al., 1994, 1995; Tohidi et al., 1995a; Ballard and Sloan, 2002). These flash calculations predict the equilibrium amount of the hydrate phase relative to associated fluid phases.

Several companies (D.B.R. Oilphase/Schlumberger, Infochem Computer Services, Ltd., Calsep) have commercially available computer programs (DBR hydrate, Multiflash, PVTsim) for the prediction of hydrate properties, and such methods are incorporated into process flowsheeting programs such as ASPENTM, HYPERCHEMTM, and SIMCITM. Researchers in the CSM laboratory (Sloan and Parrish, 1983; Sloan et al., 1987; Mehta and Sloan, 1996) generated new parameters for the prediction of sI, sII, and sH hydrates, which were incorporated into the program, CSMHyd.

The next generation prediction tool to CSMHyd is the Gibbs energy minimization program, CSMGem (Ballard and Sloan, 2002). CSMGem accounts for the water nonideality in the hydrate phase because of volume expansion. A comparison of the absolute hydrate formation temperature error of five common prediction programs is given in Chapter 5, [Figures 5.7](#) and [5.8](#). The average

absolute errors in temperature for all these prediction programs varied between 0.4 and 0.66 K, which is acceptable for engineering purposes. (The CSMGem program and User's guide are given in the attached CD accompanying this book and the Users' Examples are given in [Appendix A](#).)

Further improvements to the van der Waals and Platteeuw model were to account for the experimental observations of lattice distortion by various guest molecules (von Stackelberg and Müller, 1954; Berecz and Balla-Achs, 1983). Westacott and Rodger (1996) removed the assumption that there is no lattice relaxation by calculating the free energy of the water lattice directly from the phonon properties of crystals. Zele et al. (1999) also accounted for the effect of lattice stretching due to guest size by calculating a new reference chemical potential using molecular dynamics simulations.

The formation of sII hydrate from two sI guests was first measured by von Stackelberg and Jahns in 1954. Detailed studies of the sI/sII transition with natural gas mixtures were performed by Subramanian (2000). Several models have been shown to successfully predict the sI/sII transition of two sI guests (Hendricks et al., 1996; Ballard and Sloan, 2000, 2001; Klauda and Sandler, 2003; Anderson et al., 2005).

The application of *ab initio* quantum mechanical calculations to determine the guest–host intermolecular potential parameters was performed in a parallel effort by the group of Sandler et al. (Klauda and Sandler, 2000, 2003) and the groups of Trout and Tester et al. (Anderson et al., 2004, 2005). Klauda and Sandler (2005) extended their model to predict in-place hydrate formation in nature.

Two heuristics of hydrate formation are as follows:

1. The guest molecule fit within each cavity determines the hydrate stability pressure and temperature.
2. Hydrate formation is a surface phenomenon, when formed on an artificial (laboratory) timescale.

Fundamentals of phase equilibria (i.e., phase diagrams, early predictive methods, etc.) are listed in [Chapter 4](#), while [Chapter 5](#) states the more accurate, extended van der Waals and Platteeuw predictive method. [Chapter 6](#) is an effort to gather most of the thermodynamic data for comparison with the predictive techniques of Chapters 4 and 5. [Chapter 7](#) shows phase equilibria applications to *in situ* hydrate deposits. [Chapter 8](#) illustrates common applications of these fundamental data and predictions to gas- and oil-dominated pipelines.

1.2.5 Time-Dependent Studies of Hydrates

In the mid-1960s, driven by the promise of natural gas hydrates as a substantial energy resource in the USSR, a large experimental effort was begun in a research group led by Makogon (1965, 1981) at the Gubkin Petrochemical and Gas Industry Institute. The area of hydrate kinetics and thermodynamics had priority in the Soviet research program, because the same physics can be applied to problems of

hydrate formation in transmission/processing equipment as well as those of *in situ* hydrates, the third major area of hydrate study. The Russian studies from the 1960s are the first to place emphasis on the kinetics of hydrate formation, both in the bulk phases and in porous environments.

Up until around the mid-1990s, there were only a limited number of groups investigating the time-dependent properties of hydrates. These groups include:

- Lubas (1978) and Bernard et al. (1979) who investigated the formation of hydrates in gas wells.
- Bishnoi and coworkers, who have had the longest tenure in the Western Hemisphere for investigating macroscopic kinetics of hydrate growth and decomposition. The experiments were restricted to low hydrate concentrations in an attempt to avoid heat and mass transfer phenomena (Vysniauskas and Bishnoi, 1983a,b; Kim, 1985; Englezos et al., 1987a,b; Englezos and Bishnoi, 1988a,b; Parent, 1993; Natarajan et al., 1994; Malegaonkar et al., 1997).
- Holder et al. (Holder and Angert, 1982a,b; Holder and Godbole, 1982; Holder et al., 1984a,b).
- Sloan and coworkers (Selim and Sloan, 1985, 1987, 1989; Ullerich et al., 1987; Yousif et al., 1990; Long and Sloan, 1996; Long et al., 1994; Lederhos et al., 1996; Lekvam and Ruoff, 1997).

Since around the mid-1990s, there has been a proliferation of hydrate time-dependent studies. These include macroscopic, mesoscopic, and molecular-level measurements and modeling efforts. A proliferation of kinetic measurements marks the maturing of hydrates as a field of research. Typically, research efforts begin with the consideration of time-independent thermodynamic equilibrium properties due to relative ease of measurement. As an area matures and phase equilibrium thermodynamics becomes better defined, research generally turns to time-dependent measurements such as kinetics and transport properties.

This growth in activity, investigating the time-dependent hydrate properties, has also been largely driven by hydrate technology in oil/gas flowlines (flow assurance) shifting from hydrate avoidance to hydrate risk management. Hydrate avoidance involves preventing hydrates from forming by avoiding the hydrate thermodynamic stability zone. Hydrate risk management, however, involves the use of transient methods to delay hydrate formation or prevent hydrate particles from agglomerating, thus preventing pipeline blockages. A further motivation for performing time-dependent hydrate studies is the increasing interest in assessment and production of energy from natural hydrates in permafrost and oceanic deposits.

Measurement and modeling of time-dependent hydrate properties is clearly far more challenging than time-independent (thermodynamic) hydrate properties. Although significant advances have been achieved in measurement and modeling

of hydrate formation, there are still significant knowledge gaps in this area to be filled before a reliable transient hydrate model can be developed.

Macroscopic measurements that have been applied to hydrate formation and decomposition include light scattering and calorimetry. Light scattering has been applied to measure the hydrate particle size distribution during formation and decomposition (Nerheim et al., 1992, 1994; Monfort and Nzihou, 1993; Parent, 1993; Yousif et al., 1994; Parent and Bishnoi, 1996; Clarke and Bishnoi, 2000, 2001, 2004; Turner, 2005). Differential scanning calorimetry has been used to measure hydrate formation and hydrate particle agglomeration in water-in-oil emulsions (Dalmazzone et al., 2005; Lachance, J., unpublished results) and water-in-porous glasses (T. Varma-Nair, Personal Communication, March 23, 2006).

Mesoscale imaging techniques have been applied to hydrate formation and decomposition processes. Specifically, scanning electron microscopy (SEM) has been used to investigate the hydrate grain texture and pore structure recovered at different stages of hydrate formation (Staykova et al., 2003; Stern et al., 2005). Magnetic resonance microimaging has also been performed to obtain spatial, time-resolved images during hydrate formation (Moudrakovski et al., 2004). X-ray computed tomography (CT) has been applied to track the spatial progression of the dissociation front in hydrate samples and to characterize the heterogeneity of a hydrate core during formation and decomposition (Freifeld et al., 2002; Gupta et al., 2006).

Microscopic time-resolved measurements of the hydrate phase during gas hydrate formation, decomposition, and inhibition began only in the mid-1990s. These techniques include *in situ* synchrotron x-ray diffraction (Koh et al., 1996; Klapproth et al., 2003; Uchida et al., 2003), neutron diffraction (Henning et al., 2000; Koh et al., 2000; Halpern et al., 2001; Staykova et al., 2003), Raman spectroscopy (Subramanian and Sloan, 2002; Komai et al., 2004), and NMR spectroscopy (Moudrakovski et al., 2001; Kini et al., 2004; Gupta et al., 2007).

Computer simulations provide a means of examining the early stages of hydrate formation (nucleation) on a molecular level (Baez and Clancy, 1994; Radhakrishnan and Trout, 2002; Moon et al., 2003, 2005). Computer simulation has also been applied to study hydrate dissociation (Baez and Clancy, 1994; English and MacElroy, 2004) and the effects on dissociation kinetics of external electromagnetic fields (English and MacElroy, 2004).

The state-of-the-art of the fundamentals of hydrate formation and decomposition processes is reviewed in [Chapter 3](#). Because many time-dependent data appear to be a function of different apparatuses, time-dependent data are not listed in a separate chapter analogous to [Chapter 6](#) for thermodynamic data. However, applications of transient methods for preventing or remediating hydrate blockages in pipelines are discussed in [Chapter 8](#). In addition, a computer program, CSMPlug, and a User's Guide are provided on the CD accompanying this book (with Users' Examples in [Appendix B](#)) to determine the time for plug removal in flowlines.

1.2.6 Work to Enable Gas Production, Transport, and Processing

Since 1970, hydrate research has been motivated by production and processing problems in unusual environments, such as the North Slope of Alaska, in Siberia, in the North Sea, and in deep ocean drilling. For example, problems of hydrate formation in drilling applications reported by Barker and Gomez (1989) stimulated measurements of hydrate formation in oil-based drilling fluids (Grigg and Lynes, 1992) and in water-based drilling fluids (Cha et al., 1988; Hale and Dewan, 1990; Kotkoskie et al., 1992; Ouar et al., 1992), resulting in a prediction method to prevent future occurrences.

Kobayashi and coworkers (Sloan et al., 1976; Song and Kobayashi, 1982, 1984) and workers in the CSM laboratory (Sloan et al., 1986, 1987) have measured concentrations of water in hydrate-forming fluid phases in equilibrium with hydrates (when there is no free-water phase present) for application in single phase pipelines in cold regions, such as the North Slope or subsea. The trend in deepwater pipelines appears to be toward multiphase transmission (Shoup and Shoham, 1990) and their inhibition.

In Scotland, Danesh, Todd, and coworkers measured the inhibition of multiphase systems with methanol (Avlonitis, 1994) and mixed electrolyte solutions (Tohidi et al., 1993, 1994a, 1995b,c). They also performed the most comprehensive study of systems with heavy hydrocarbons such as might be produced/transported in the North Sea (Avlonitis et al., 1989; Tohidi et al., 1993, 1994b, 1996) including systems with structure H hydrate formers.

In Canada, Ng and Robinson (1983, 1984) and Ng et al. (1985a,b, 1987) have performed the most comprehensive measurements of aqueous phase concentrations of methanol and glycols needed to inhibit hydrates formed from both the gas and condensed hydrocarbon phases. Ng and Chen (1995) have provided data for solubility of inhibitors in other phases. Inhibition of methane and carbon dioxide hydrates by mixed electrolytes has been studied by Englezos and Bishnoi (1988a,b) and Dholabhai et al. (1991), and separately in Bishnoi's laboratory (Dholabhai et al., 1993a,b, 1994, 1996; Tse and Bishnoi, 1994) and in Englezos' laboratory (Englezos, 1992a,b,c,d; Englezos and Ngan, 1993).

Bishnoi's laboratory has measured hydrate formation under shutdown conditions (Jamaluddin et al., 1991) and in gas and condensate pipelines (Dholabhai et al., 1993a,b). Norsk Hydro's experience with hydrate formation in pipeline design and operation is described by Stange et al. (1989), Lingelem and Majeed (1992), and Lingelem et al. (1994). Dorstewitz and Mewes (1993, 1995) present German experiences with hydrate formation in small flow loops. At the SINTEF multiphase flow facility, extensive measurements of hydrate formation and dissociation have been carried out by Austvik (1992), Lund et al. (1996a,b), and Lysne (1994, 1995). A comprehensive study of hydrate formation in pipelines involved the formation/dissociation of 17 hydrate plugs in the Tommeliten Field (Austvik et al., 1995). Hydrate blockage formation was also studied in the Werner-Bolley gas line (Hatton and Kruka, 2002). Conceptual models and case studies

of how industrial hydrate plugs are formed and how they can be prevented are described in [Chapter 8](#).

In the 1990s, two types of chemical inhibitor technologies (antiagglomerants and kinetic inhibitors) were introduced, as a means of methanol replacement. The antiagglomerant method, for emulsifying the water phase internal to a liquid hydrocarbon phase using a surfactant, was pioneered by Behar et al. (1991). The second technology requires kinetic inhibition by preventing crystal growth for a period exceeding the free-water residence time in a pipeline, and was first proposed by the CSM laboratory (Sloan, 1991) with chemical inhibitors listed by Long et al. (1994) and Lederhos et al. (1996). Details of both methods are given in Chapter 8.

Hydrate formation is a substantial problem in deepwater production and flowlines. Pipelines that transport condensed hydrocarbon phases such as gas condensate or crude oil have limited possibilities for removing hydrates once the plugs have formed. Earlier work by Scauzillo (1956), indicating that formation may be inhibited by the input of hydrocarbon liquids, cannot be confirmed by thermodynamic calculations, and Skovborg (1993) has found counter-examples. Thus, the construction of large-scale pilot flow loops have been completed by large corporations such as ExxonMobil (Reed et al., 1994), Tulsa University, and Institut Francais du Petrole. Such experiments are discussed briefly in [Chapter 6](#).

Subsea gas and oil production, processing, and transportation since the past decade are moving to deeper waters (e.g., 6500–7200 ft in the Canyon Express system). These deepwater conditions are associated with higher pressures and lower temperatures, which are well within the hydrate stability zone. For these deepwater facilities, traditional thermodynamic methods (heating, thermodynamic inhibitor injection, line burial) for preventing hydrate formation in pipelines and related industrial equipment are becoming increasingly uneconomic. Therefore, the industry is moving to risk management approaches that are based on time-dependent phenomena. The risk management tools for preventing hydrate blockages include kinetic inhibitors, antiagglomerants, cold slurry flow, or combinations of these tools. The application of these methods to pipelines is discussed in Chapter 8, along with a number of industrial case studies. The application of plug remediation methods, such as depressurization, is also described in Chapter 8. A fundamental requirement for risk management is the availability of reliable and accurate transient formation and decomposition models to predict when hydrates will form and decompose, respectively. Fundamental knowledge on hydrate formation and decomposition, which is needed to develop such models, is discussed in [Chapter 3](#).

1.2.7 Hydrates in Mass and Energy Storage and Separation

Several researchers have studied hydrates as a means of separating gases and water, and as a means of storing mass and energy. Because many of these studies are not typically with natural gas components, they are only given cursory attention here. A few details of this section are to be found in [Chapters 4](#) and [8](#).

The storage and transportation of natural gas in hydrate form was investigated by Benesh (1942), Miller and Strong (1946), Parent (1948), and Dubinin and Zhidenko (1979). Hydrate storage of gases has assets of lower storage space and low pressures for safety. Methane hydrate has an energy density equivalent to a highly compressed gas, but is less dense than liquefied natural gas (LNG).

In the 1990s, Gudmundsson et al. (1994, 1995) and Gudmundsson and Parlaktana (1992) showed favorable economics for gas in hydrates using higher storage temperatures and suggested that this was enabled by the ice barrier formed by dissociated hydrates. Gudmundsson and Borrehaug (1996) proposed to ship natural gas in hydrated form, rather than in liquefied natural gas (LNG) tankers and suggested that the economics were favorable. The basic concept proposed by Gudmundsson to transport stranded gas in hydrated form has been extended by researchers from Mitsui Shipbuilding in conjunction with the Japanese Maritime Research Institute (Nakajima et al., 2002; Shiota et al., 2002; Takaoki et al., 2005). The hydrated gas is stored in pellet form at low temperatures, with the stability of the pellets aided by the concept of anomalous preservation first reported by Stern and coworkers (2001).

Hydrates as a storage material for hydrogen have been explored by a number of research groups. Dyadin et al. (1999) were the first to discover that hydrogen can form a clathrate hydrate at high pressures (1.5 GPa). Structure confirmation of hydrogen hydrate was performed by Mao et al. (2002), where hydrogen was shown to multiply occupy the cavities of structure II hydrate at high pressures (300 MPa at 350 K). Florusse et al. (2004) demonstrated that hydrogen can be stabilized in the clathrate framework at pressures over two orders of magnitude lower than for pure hydrogen hydrate by using a second guest, tetrahydrofuran.

The first Soviet hydrate separation available in the Western literature was that of Nikitin (1936, 1937, 1939, 1940), who developed a method for separating rare gases by using SO_2 hydrates. Nikitin was also the first to suggest a guest/host lattice structure for hydrates. In his review, Davidson (1973) notes that the capacity of host lattices for guests is equivalent to the best activated carbons or zeolites. Barrer and Edge (1967) showed fractionation to be effective when aided in hydrate formation by chloroform. Tsarev and Savvin (1980) and Trofimuk et al. (1981, 1982) suggested other hydrate separations of light gas components.

Kang and Lee (2000) showed that carbon dioxide could be removed from flue gas using hydrate-based gas separation. A small amount of tetrahydrofuran (THF) was added to promote hydrate formation and hence this separation process. Hydrate formation has also been used to separate hydrogen sulfide (Yamamoto et al., 2002), HCFCs, and HFCs (Okano et al., 2002) from waste streams.

Hydrates as a means of cool energy storage have been extensively investigated in the United States (Ternes and Kedl, 1984; Carbajo, 1985a,b; Ternes, 1985) and in Japan (Mori and Mori, 1989a,b; Tanii et al., 1990; Akiya et al., 1991; Mori and Isobe, 1991; Nakazawa et al., 1992; Ogawa et al., 2005). Conceptually, electrical “peak shaving” requires the use of excess electrical capacity to generate hydrates during evening hours. The cool energy is recovered by endothermic melting of hydrates in daylight hours. Hydrates are useful for energy storage and recovery,

because (1) their heat of fusion approximates that of ice and (2) hydrates can be formed at temperatures above the ice point for a better refrigeration coefficient of performance.

Another separation application of hydrates is the desalination of seawater. The 15-year effort of Barduhn and coworkers is particularly notable (Barduhn et al., 1962; Barduhn, 1967, 1968, 1975; Barduhn and Rouher, 1969; Vlahakis et al., 1972). Most of the early desalination work has been reported in six Desalination Symposia Proceedings (Udall et al., 1965; Delyannis, 1967; Delyannis and Delyannis, 1970, 1973, 1976, 1978). These early attempts to use gas hydrates for seawater desalination involved mixing gas and seawater so that all the gas was consumed. As a result, a hydrate–brine slurry was formed that was essentially unwashable. Researchers at Marine Desalination Systems have attempted to circumvent this problem by increasing the mass to surface area of hydrate crystallites formed, such that adsorption of salt becomes insignificant (Max, 2001, 2002; Osegovic et al., 2005).

Englezos and coworkers (Gaarder et al., 1994; Gaarder and Englezos, 1995) have used hydrates of propane and carbon dioxide to remove water from aqueous paper mill effluents. The process seems technically viable and the contaminants in the aqueous stream did not inhibit hydrate formation significantly.

Hydrates have also been applied to foodstuffs in Fennema's laboratory (Huang et al., 1965, 1966; van Hulle et al., 1966; van Hulle and Fennema, 1971, 1972; Scanlon and Fennema, 1972). A process for producing edible hydrates of carbon dioxide was patented by Baker (1993).

Hydrates have further applications in bioengineering through the research of John and coworkers (Rao et al., 1990; Nguyen, 1991; Nguyen et al., 1991, 1993; Phillips et al., 1991). These workers have used hydrates in reversed micelles (water-in-oil emulsions) to dehydrate protein solutions for recovery and for optimization of enzyme activity, at nondestructive and low-energy conditions.

1.3 HYDRATES AS AN ENERGY RESOURCE

A world atlas, giving sites with evidence of hydrate deposits, both onshore and offshore, is presented in [Chapter 7](#), [Figure 7.2](#). Since each volume of hydrate can contain as much as 184 volumes of gas (STP), hydrates are currently considered a potential unconventional energy resource. [Table 1.4](#) lists the milestones accomplished to further our knowledge on naturally occurring hydrates.

Estimates of world hydrate reserves, given in [Chapter 7](#) are very high, but uncertain. This is reflected by the large variation in the estimated values over the period 1990–2005 (0.2×10^{15} – 120×10^{15} m³ of methane at STP). However, even with the most conservative estimates, it is clear that the energy in these hydrate deposits is likely to be significant compared to all other fossil fuel deposits. [Chapter 7](#) presents the concepts for hydrates in Earth. These concepts are illustrated with field case studies involving the assessment of the hydrate resource (in the Blake Bahama Ridge and Hydrate Ridge) and the production of energy from hydrates (in the Messoyakha and Mallik 2002).

TABLE 1.4
Hydrate Milestones since 1965—*Hydrates in Nature*

| | |
|------|--|
| 1965 | Makogon and coworkers announce hydrates in Siberian permafrost |
| 1969 | Ginsburg begins study of hydrates in geological environments |
| 1969 | Russians begin a decade of producing gas in Messoyakha, possibly from hydrates |
| 1972 | ARCO–Exxon recover hydrated core from Alaskan well |
| 1974 | Bily and Dick report hydrates in Canada’s MacKenzie Delta |
| 1980 | Kvenvolden publishes survey of worldwide hydrates |
| 1980 | Dillon and Paull begin work on hydrates in Atlantic Ocean |
| 1982 | Brooks begins recovery of <i>in situ</i> biogenic and thermogenic hydrates from Gulf of Mexico |
| 1983 | Collet presents analysis of ARCO–Exxon drilling logs study for hydrated core |
| 1988 | Makogon and Kvenvolden separately estimate <i>in situ</i> hydrated gas at 10^{16} m ³ |
| 1988 | Kvenvolden and Claypool estimate that hydrate decomposition does not contribute to greenhouse effect |
| 1994 | Sassen discovers <i>in situ</i> sH hydrates in Gulf of Mexico |
| 1996 | Microbiological study of 12 sites in Atlantic and Pacific Oceans and Mediterranean Sea from cores collected during 1986–1996 by Ocean Drilling Program (ODP) (Parkes et al., 2000) |
| 1998 | Pilot drilling, characterization, and production testing of hydrates began in permafrost regions (e.g., in Mallik 2L-38 well in Canada) |
| 2000 | Methane hydrate R&D Act of 2000 (U.S. Congress) |
| 2002 | Mallik 5L international permafrost field experiment on Richards island in MacKenzie Delta of Canada concluded that hydrates could be economically recovered at high concentrations |
| 2002 | ODP Leg 204 drilling off Hydrate Ridge in Oregon (Sahling et al., 2002, Tréhu et al., 2003, 2006a) |
| 2005 | IODP Expedition to Cascadia Margin (Riedel et al., 2006) |
| 2006 | First <i>in situ</i> ocean Raman measurements at Barkley Canyon off Vancouver Island (Hester 2007, Hester et al., 2007) |
| 2006 | Indian National Gas Hydrate Program (NGHP) expedition of ocean hydrates, recovering 493 core samples |

The following are three general heuristics for naturally occurring ocean hydrates (Tréhu et al., 2006a,b):

1. Water depths of 300–800 m (depending on the local bottom water temperature) are sufficient to stabilize the hydrate.
2. Only a few sites contain thermogenic hydrates (containing CH₄ + higher hydrocarbons), such as in the Gulf of Mexico and in the Caspian Sea. These deposits tend to comprise large accumulations near the seafloor.
3. Hydrates are typically found where organic carbon accumulates rapidly, mainly in continental shelves and enclosed seas. These are biogenic hydrates (containing CH₄, formed from bacterial methanogenesis).

1.3.1 *In Situ* Hydrates

An overview of the Soviet hydrate literature, with particular emphasis on natural occurrences, was published by Krasov and Ciesnik (1985). Later, Makogon (1994),

who has worked for five decades in hydrates, published a review of Soviet hydrates. He reported that the early Russian researchers hypothesized that hydrates existed in the northern permafrost, suggested *in situ* formation mechanisms, and discussed the possibility of hydrate formation associated with coals. A review of gas hydrates in the Okhotsk Sea in Russia proposes hydrate prone areas on the basis of seismic and core sampling measurements (Matveeva et al., 2004).

The work by Ginsburg and Soloviev (1995) has estimated worldwide hydrate reserves in amounts consistent with the most commonly cited Russian hydrate reserve estimations by Trofimuk et al. (1980); namely $5.7 \times 10^{13} \text{ m}^3$ of gas in continental hydrates and $3 \times 10^{15} \text{ m}^3$ of gas in hydrates in oceans. Note that, while both the estimated amounts are controversial, there are two orders of magnitude less hydrates on land than in the oceans.

In 1967, the Soviets discovered the first major hydrate deposit in the permafrost (Makogon, 1987). The hydrate deposit in the Messoyakha field has been estimated to involve at least one-third of the entire gas reservoir, with depths of hydrates as great as 900 m. During the decade beginning in 1969, more than $5 \times 10^9 \text{ m}^3$ of gas were produced from hydrates in the Messoyakha field. The information in the Soviet literature on the production of gas from the Messoyakha field is discussed in [Chapter 7. Table 7.4](#) in Chapter 7 also lists other locations in Russia, including the Black Sea, Caspian Sea, and Lake Baikal, where evidence for hydrates has been provided from sample recovery or BSR (bottom simulating reflectors) data.

The majority of the Soviet publications are by nine authors, listed here in decreasing order with respect to their number of publications: Y.F. Makogon, G.D. Ginsburg, N.V. Cherskii, V.P. Tsarev, A.A. Trofimuk, V.A. Khoroshilov, S. Byk, V.A. Fomina, and B.A. Nikitin. In a review of the Russian literature, Krason and Ciesnik (1985) indicate that other Soviet authors have only a small number (<5) of publications. Makogon (1994) notes that over ten monographs in Russian have been published on the topic; he has available a Soviet Bibliography (in Russian) that cites a number of hitherto unknown hydrate references.

In the Western Hemisphere, in 1972, a core of hydrates was recovered from the ARCO–Exxon Northwestern Eileen Well Number Two in West Prudhoe Bay, Alaska (Collett, 1983). Also in 1972, hydrates were found when drilling an Imperial well in Canada’s MacKenzie Delta (Bily and Dick, 1974). Instances such as the above have caused further geologic investigations of permafrost hydrates in Russia, Canada, and Alaska. Using logs from the ARCO–Exxon well, Collett (1983) evaluated possible hydrate occurrences in 125 wells in the North Slope of Alaska. Weaver and Stewart (1982) and Franklin (1983) indicated well log responses in several wells in the Arctic Archipelago region. Judge (1982) and Collett (1995) summarized *in situ* hydrate resources in North America.

The Deep Sea Drilling Project (DSDP), currently the Integrated Ocean Drilling Program (IODP) of the National Science Foundation, has undertaken the most systematic evaluation of ocean hydrate deposits. The DSDP has recovered hydrate cores in the deep oceans from both coasts of the United States, from the Mid-America Trench off Guatemala, and off the coast of Peru. A total of 23 oceanic hydrate cores have been recovered, including the Gulf of Mexico and three Soviet

water bodies. Even with these core recoveries, most of the evidence of hydrates in oceans had been inferential. Bottom Simulating Reflectors (BSRs) have been used to infer the existence of hydrates in most of the locations shown in [Figure 7.2](#). Much of the oceanic geochemical and geophysical research for these determinations has been done by Kvenvolden and McMenamin (1980), Kvenvolden and Claypool (1981), Kvenvolden (1982, 1983, 1985a,b, 1995), Kvenvolden et al. (1984, 1993a,b), Dillon et al. (1980, 1994), Dillon and Paull (1983), Paull and Dillon (1981), Paull et al. (1995, 1997, 2005), as well as extensive studies in the Gulf of Mexico by Brooks et al. (1984, 1985a,b, 1987).

Direct evidence of ocean hydrates has been obtained using *in situ* Raman measurements in Barkley Canyon, off Vancouver Island (Hester, 2007). The occurrence of sH in natural hydrate deposits has been inferred from gas analyses of recovered core samples from the Gulf of Mexico (Sassen and Macdonald, 1994; Yousuf et al., 2004) and confirmed by diffraction and NMR for samples from Barkley Canyon (Pohlman et al., 2005; Lu et al., 2007).

Drilling results in the Blake Bahama Ridge have given promise for recovery of energy from hydrate reserves. Hydrate recovery results from ODP Leg 164 in the Blake Bahama Ridge seem to confirm the large resource estimation (Paull et al., 1997, 2000; Lorenson and Collett, 2000).

Following on from the geochemical and geophysical work performed on ODP Leg 146 (Westbrook et al., 1994), Leg 204 focused on an area known as Hydrate Ridge, which is located in the southern Cascadia accretionary margin where the Juan de Fuca plate converges to the North American plate. Leg 204 was undertaken to help evaluate the economic potential of hydrates, the role of hydrates as a geohazard, and their impact on climate (Trehu et al., 2003). IODP Leg 311 then proceeded with hydrates being explored in the northern Cascadia accretionary margin (Riedel et al., 2005) in a similar geological setting to Hydrate Ridge. The primary goal of the IODP Leg 311 expedition was to constrain geological models for the formation of the gas hydrates.

Starting in 1998, pilot drilling, characterization, and production testing were performed in permafrost regions in the Mallik well in Canada, with the international field experiment concluding in 2002. The Mallik 2002 well demonstrated proof of concept that it is possible to recover energy from permafrost hydrates combining dissociation techniques of depressurization and thermal stimulation. Further details of sample recovery and detection and inference of in-place hydrates from BSRs from the above-mentioned locations and other sites (including the Mackenzie Delta, Hydrate Ridge, Northern Cascadia Margin, and many more) are given in [Chapter 7](#).

The Japanese initiated a National Project to drill hydrates in the Nankai Trough. This included coring and seismic work to assess the resource (Ministry of Economy, Trade and Industry, METI-sponsored project in 1999–2000; Japan National Oil Company, JNOC, and Japan Petroleum Exploration Corporation, JPEX, studies in 1997–2000). Remote operated vehicle and manned submarine explorations have been employed to perform the resource assessments (Marine Science and Technology, JAMSTEC). The energy potential of significant hydrate deposits in

the Okhotsk Sea and the Nankai Trough has led to the Japanese making substantial investments in hydrate research (JNOC, 2000).

The Indian National Gas Hydrate Program (NGHP) expedition of ocean hydrates was performed in 2006. During this expedition, over 494 cores were recovered at depths ranging from 952 to 2674 mbsf. The cores were distributed to a number of research laboratories (including USGS, GFZ, CSM, NRC) for meso- and molecular-level analysis on the hydrate samples (T. Collett and R. Boswell, Personal Communication, August 31, 2006).

1.3.2 Investigations Related to Hydrate Exploration and Recovery

The determination of *in situ* hydrates spawned a wave of research to measure hydrate properties needed for geological research and gas recovery. Several measurements were made of sonic velocity and thermal conductivity of hydrates in sediments (e.g., Stoll and Bryan, 1979; Pearson et al., 1984; Asher, 1987; Waite et al., 2005), while others measured the calorimetric properties (e.g., Rueff, 1985; Handa, 1986a,b,c,d; Rueff et al., 1988) needed to estimate dissociation energy. Davidson (1983) summarized hydrate properties as being similar to ice, with a few notable exceptions. [Chapter 2](#) presents comparisons of physical property measurements of ice and hydrate.

Along with the measurements of hydrate properties came several studies to determine the recoverability of gas from hydrates beneath the permafrost. Kamath and coworkers, in a research effort spanning over more than a decade, studied hydrate drilling and recovery in Alaska (Kamath, 1984; Kamath et al., 1984; Kamath and Godbole, 1987; Kamath and Holder, 1987; Roadifer et al., 1987a,b; Godbole et al., 1988; Nadem et al., 1988; Sira et al., 1990; Kamath et al., 1991; Sharma et al., 1991, 1992).

Soviet researchers indicated that thermal stimulation from above the ground was not economically viable. Trofimuk et al. (1982) suggested alternatives of pressure reduction, inhibitor injection, geothermal stimulation, or *in situ* combustion techniques. Recovery techniques modeled in the Western Hemisphere were by either pressure reduction or thermal stimulation. The first of these was by McGuire (1982), followed by Holder et al. (1984a), Burshears et al. (1986), and workers in the CSM laboratory (Selim and Sloan, 1985, 1987, 1989; Yousif et al., 1988, 1990).

Hydrate dissociation models that were later developed to simulate hydrate recovery techniques include numerical models by Masuda et al. (1997), Moridis (2002), and Hong et al. (2003); analytical models by Makogon (1997) and Tsympkin (2000). The details of these models are given in [Chapter 7](#).

There have been significant developments in logging and coring tools for assessing amounts of hydrated gas in permafrost and oceanic locations. Logging tools including calliper, γ -ray density, resistivity, neutron porosity, drilling logs, and NMR are used to determine the hydrate depth and the concentration of hydrate gas to some extent. Secondary tools including infrared temperature sensing, gas evolution from cores, pore water chlorinity decrease, and x-ray computed

tomography (CT) of cores provide the extent and concentration of the hydrate reservoir. The use of pressurized coring tools is becoming increasingly recognized as a key (Tréhu et al., 2006b) to help maintain the integrity of the recovered sample core compared to unpressurized coring tools. Further details of the use of these logging and coring tools are given in [Chapter 7](#).

1.4 ENVIRONMENTAL ASPECTS OF HYDRATES

Other “natural” hydrates have been suggested during the past few decades. Miller (1974) concluded that hydrates of carbon dioxide were on Mars, and Pang et al. (1983) indicated that the E rings of Saturn were hydrates. Delsemme and Miller (1970), Mendis (1974), and Makogon (1987) suggested that hydrates exist in comets; in particular, carbon dioxide and water in comets were combined in the form of hydrates.

Shoji and Langway (1982) described air hydrates found with ice cores off Greenland, while Tailleux and Bowsher (1981) indicated the presence of hydrates associated with coals in permafrost regions. Hondoh (1996) suggested that deep ice hydrates of air in Antarctica can be used to predict the Earth’s ancient climate. Such hydrates are formed from air imbedded in snowfall and have been buried at pressure for hundreds of thousands of years. Rose and Pfannkuch (1982) have considered the applicability of the “Deep Gas Hypothesis” to the origin of methane in hydrates.

Kvenvolden (1988) provided the first estimates that hydrate decomposition should not contribute significantly to the greenhouse effect. Despite these estimates, there have been suggestions in the popular press (Leggett, 1990) that hydrates may contribute to an exponentially growing feedback loop for global warming. In 1996, a conference on hydrate decomposition and contribution to global warming (Henriet, 1996) indicated that the uncertainties in the existing climate models were significantly greater than the likely contribution of hydrates to global warming.

More recently, there has been renewed and increased interest in the role of methane hydrate as a potential source for climate change. Kennett et al. (2003) reported the somewhat controversial “clathrate gun” hypothesis (also known as the “late Quaternary climate change”), which suggests that methane released from methane hydrate around 15,000 years ago has resulted in immense global warming. Significant efforts have been initiated by German scientists to investigate the role of hydrates in climate change (Lovell, 2006). There are also ongoing investigations of the role of gas hydrates in the carbon cycle (Dickens, 2001, 2003; Milkov, 2004, 2005).

1.5 SAFETY ASPECTS OF HYDRATES

There are four safety aspects associated with hydrates that should be mentioned in order of decreasing importance:

1. When hydrates plug pipelines they are usually removed through depressurization, sometimes depressurizing only one side of the plug.

Chapter 8 gives the evidence that plugs dissociate first at the pipewall, thus becoming a projectile in a pipeline with substantial momentum, relative to the gas phase. Lysne (1995, p. 78) lists three such incidences in which hydrate projectiles erupted from pipelines at elbows and caused the loss of three lives and over US\$7 million in capital costs. Where possible, depressurization from both sides of a plug is recommended.

2. In drilling through hydrates (Roadifer et al., 1987a) and in drilling normal wells, hydrates have jeopardized the safety of drillers and plugged blowout preventers (Barker and Gomez, 1989) necessitating the use of special drilling precautions and drilling muds.
3. In the past, hydrates have been associated with significant movement of earth (seafloor slumps) in deepwater ocean environments. Notably, Bugge et al. (1988), Schmuck and Paull (1993), MacDonald et al. (1994), and Paull and Dillon (2001) have described both large and small Earth movements associated with hydrates. Concerns have been expressed (Campbell, 1991) about the effect of hydrates on foundations of platforms and pipelines, as well as offshore drilling. Hydrates as geohazards are discussed in Section 7.8.
4. Hydrates have also been the source of speculation of long-range climate change and safety in the greenhouse effect (Leggett, 1990). Hydrates in climate change are discussed in Section 7.8.

Speculations about the role of hydrates in disasters such as the Piper Alpha platform (Boniface, 1990) or Lake Nyos (Rogers and Yevi, 1996) are characterized as hypotheses that are not discussed in this book.

1.6 RELATIONSHIP OF THIS CHAPTER TO THOSE THAT FOLLOW

With the overview provided by the current chapter, the remainder of this book provides a detailed development of research conducted in the above areas, together with examples of industrial interest. A brief description of the following chapters is given as follows:

Chapter 2 presents a comprehensive description of the chemical structure of hydrates and, by inference, begins to consider molecular and macroscopic properties with emphasis on similarities and differences from ice. Discussion is also given to the transport properties of hydrates.

Chapter 3 presents the fundamentals of the time-dependent hydrate phenomena of nucleation, growth, and decomposition. These fundamentals are presented with an objective of understanding how hydrate formation and decomposition occur, such that this knowledge may be applied to a range of hydrate applications, such as flow assurance, storage, separation, or gas production from hydrate reservoirs.

Chapter 4 provides phase diagrams and simple prediction schemes for each of the hydrate phase diagram regions.

Chapter 5 details the modified statistical thermodynamic prediction method of van der Waals and Platteeuw (1959). The application of molecular simulation methods to hydrates is outlined in Section 5.3.

Chapter 6 provides a listing of the hydrate phase equilibria and transport property data since 1934 for natural gas pure components, mixtures, and inhibitors together with common measurement techniques. Details of hydrate phase measurements using spectroscopy and diffraction are also discussed.

Chapter 7 discusses *in situ* hydrates in the oceans and permafrost. Seven key concepts are presented for hydrates in nature. These concepts are illustrated in four field case studies for hydrate assessment (Blake Bahama Ridge, Hydrate Ridge) and production (Messoyakha and Mallik, 2002).

Finally, **Chapter 8** considers some common industrial problems (and solutions) concerning hydrates in processing, transportation, and production. The phenomena of how hydrate plugs form and how they are prevented or simulated are illustrated by several industrial case studies.

The appendices and the computer programs (on the accompanying CD-ROM) deal with predictions of hydrate plug dissociation (CSMPlug) and hydrate phase equilibria and structure (CSMGem).

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