

## 1

## An Introduction to Clathrate Hydrate Science

John A. Ripmeester<sup>1</sup>, Saman Alavi<sup>1,2</sup>, and Christopher I. Ratcliffe<sup>1</sup>

<sup>1</sup>National Research Council of Canada, 100 Sussex Drive, Ottawa, ON, K1A 0R6, Canada

<sup>2</sup>University of Ottawa, Department of Chemistry and Biomolecular Science, STEM Complex, 150 Louis-Pasteur Pvt., Ottawa, ON, K1N 6N5, Canada

### 1.1 Introduction

The first intersection of clathrate hydrates and human endeavor took place in the late 1700s. A number of researchers (natural philosophers) working on the solubility of newly discovered airs (gases) observed unexpected ice-like solids formed above the freezing point of ice when certain gases were passed into cold water or when such a solution was frozen. Davy identified these solids as two-component water–gas compounds and named them “gas hydrates.” After some 140 years and much research, these solids were shown to be clathrates, materials where small molecules (guests) are trapped in an ice-like lattice (host) consisting of hydrogen-bonded water cages. During the time between initial discovery and final identification, gas hydrates confounded researchers by having a number of properties that countered concepts derived from mainstream chemistry. For instance, the hydrates were non-stoichiometric, the water-to-gas ratios were not small whole numbers, and they decomposed upon heating or depressurization to give back the unchanged starting materials. The lack of chemical bonds between the water and the gas in the hydrates suggested that these were not real chemical compounds and in fact were the first examples of “chemistry beyond the molecule” – supramolecular compounds.

From phase equilibrium studies, we now know that when many gases and water are in contact under appropriate pressure ( $P$ ) and temperature ( $T$ ) conditions, a solid hydrate will form. The gas hydrates store gases, including natural gas, very efficiently with one volume of solid hydrate storing some 160 volumes of gas at standard temperature and pressure (STP). Since a number of gas hydrates are found naturally, this class of materials can be taken to be an unusual type of mineral. There are many sites in the geosphere where natural gas and water are in contact under the conditions required to form gas hydrate. Locations where this occurs are in sediments offshore of continental margins, under permafrost, and in some deep freshwater lakes.

Well before the discovery of natural gas hydrate in the geosphere, oil and gas engineers encountered blocked natural gas pipelines during cold weather operation

*Clathrate Hydrates: Molecular Science and Characterization*, First Edition.

Edited by John A. Ripmeester and Saman Alavi.

© 2022 WILEY-VCH GmbH. Published 2022 by WILEY-VCH GmbH.

which was initially attributed to ice formation from moisture in wet gas. Knowledge of earlier work on solid methane hydrate led Hammerschmidt in the 1930s to the correct explanation for the pipeline blocks – they were made of solid methane hydrate rather than ice. Since then, during the exploration, production and transport phases of hydrocarbon resources, blockage by natural gas hydrate formation has become a well-known hazard, resulting in possible serious damage and loss of life, for example in the Deepwater Horizon oil spill of 2010. Much research has been carried out to prevent or manage hydrate formation in pipelines. Other problems related to gas hydrates have been identified, including marine geohazards, such as submarine landslides, and sudden gas releases from hydrate formations.

Because of the vast amounts of trapped natural gas in hydrate form globally, gas hydrates have been evaluated to be a significant unconventional natural gas resource. Hydrate deposits have been mapped in many locations around the world, usually using geotechnical methods that depend on the location of unexpected solid hydrate–liquid water interfaces which act as seismic reflectors. Test wells for gas production have been drilled in the Mackenzie Delta, Canada (Mallik 2L38), Alaska, the Nankai trough offshore Japan, and offshore China. Many problems have been encountered in producing gas from hydrate reservoirs, including the development of the best techniques for destabilizing the solid hydrate and capturing the resulting gas. Some hydrate deposits, often associated with hydrocarbon seeps or vents, exist as outcrops on the seafloor. Whereas most of the methane in hydrate reservoirs is of biogenic origin, hydrates associated with seeps or hot vents are formed from thermally altered hydrocarbons originally residing in deeper reservoirs. Some hydrate outcrops are home to specialized biological ecosystems where microbes feed on hydrocarbons and these in turn become a food source for “ice-worms.”

Besides the marine and terrestrial natural gas hydrates, there are gas hydrates of air (mainly  $N_2$  and  $O_2$ ) deep inside glaciers. The hydrate zone starts at pressures where gas bubbles in the ice disappear. There has been much speculation regarding the existence of hydrates in extra-terrestrial space, that is, on Mars, Titan, Enceladus, and the heads of comets. One of the best candidates for finding such a hydrate would appear to be that of  $CO_2$ . Although lots of spectroscopic data exist for free solid  $CO_2$  and ice in extra-terrestrial space, no sign of  $CO_2$  hydrate has been found, see Chapters 3 and 13 for possible reasons.

The large gas capacity and water as cheap working fluid make gas hydrates interesting materials for industrial applications. Gas hydrates are generally selective for guest molecule adsorption which allows the separation of gas mixtures. Much as salt is excluded when brine is frozen in desalination processes, gas hydrates have the same ability, but now the properties of the solid phase can be adjusted. For example, depending on the choice of guest, the hydrate freezing point can be well above the ice point, so saving on refrigeration costs. The same principle applies to cool energy storage where the freezing point of the hydrate can be tuned to minimize operational costs. Further applications include dewatering of fruit juices,

sewage sludge and wood pulp, and the storage of unstable molecules such as ozone and chlorine dioxide. A more exotic application was the separation of radioactive radon gas from a gas mixture.

The gentler conditions required for the formation and storage of methane in solid hydrate form as compared to the low temperature required for liquid nitrogen storage of liquefied methane has resulted in the evaluation of transport by these two means. Indeed, some cost advantages become apparent for solid hydrate transport if methane has to be transported from stray fields where construction of a liquid natural gas (LNG) plant is not cost effective. Other applications for storage have been explored, e.g. for hydrogen as fuel gas and CO<sub>2</sub> for greenhouse gas separation and storage.

Gas hydrates, because of their unique properties, have demonstrated some entertainment value. The “burning snowball” results when methane from decomposing methane hydrate is ignited and this phenomenon has been admired by many, both live and in print. In the early 1980s, it was proposed that sudden, massive decomposition of marine methane hydrates could be the cause of disappearances of ships and planes in mythically mysterious areas such as the Bermuda triangle. It appears the mystery novel “Death by gas hydrate” still needs to be written: hydrates have great potential as difficult to track murder weapons. The media also have frequently given news coverage of “burning ice” which is rediscovered every 10 years or so.

From the earlier examples, it is clear that gas hydrates are interesting and unusual materials partly because nature makes them and partly because there are many potential uses which unfortunately remain largely prospective. This book will emphasize the molecular chemical, physical, and material aspects of clathrate hydrates, that is, the many details needed to understand the macroscopic properties and processes mentioned earlier. Engineering and geological aspects of the gas hydrates have been covered admirably in a number of previous books mentioned later.

In Section 1.2 of this chapter, we highlight milestones of clathrate hydrate science up to the present. The history and context of some of these earlier developments are discussed in greater detail in Chapter 2 and in chapters that follow and the relevant references can be found there. From their beginning and in the decades that followed, many centers of clathrate hydrate research emerged in different parts of the world. From the early 1960s with the work of Don Davidson and coworkers, the National Research Council (NRC) of Canada in Ottawa emerged as one of the active centers of research in this field. In Section 1.3, we give a summary of the contributions to clathrate hydrate science made in the NRC of Canada during this time period. Contributors to the clathrate hydrate research at the NRC are acknowledged in Section 1.4. Some influential books and review articles on clathrate hydrates that appeared during this period and up to the current time are introduced in Section 1.5. International conferences focusing on clathrate hydrate science are listed in Section 1.6.

## 1.2 Selected Highlights of Clathrate Hydrate Science Research Up to the Present

In this section, we summarize selected highlights of clathrate hydrate research, emphasizing contributions to molecular science. Not all engineering and geological discoveries are covered in detail in this selection. Full author names and references for most of these highlights are given in the following chapters.

---

1810	Sir Humphrey Davy correctly identified a solid material, previously thought to be solid chlorine, as a compound of chlorine and water and called it “gas hydrate.”
1823	Faraday determined the composition of chlorine hydrate to be $\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ .
1823	Faraday acting upon a suggestion by Davy, used decomposition of gas hydrates in confined vessels as a method of liquefying gases.
1828	Löwig prepared bromine hydrate and determined the formula $\text{Br}_2 \cdot 10\text{H}_2\text{O}$ for the compound.
1829	de la Rive prepared $\text{SO}_2$ hydrate, $\text{SO}_2 \cdot 14\text{H}_2\text{O}$ , and proposed that all common gases form hydrates.
1840	Wöhler prepared $\text{H}_2\text{S}$ hydrate.
1843	Millon prepared chlorine dioxide hydrate, the first example of the preservation of an unstable chemical species, $\text{ClO}_2$ , an explosive-free radical.
1852	Loir prepared solid binary hydrates from water, $\text{H}_2\text{S}$ , or $\text{H}_2\text{Se}$ and halogenated hydrocarbons like chloroform, their composition remained unknown for some 30 years.
1856	Berthelot prepared the first pure hydrates of organic compounds, namely, those of methyl chloride and methyl bromide. He also claimed that $\text{CS}_2$ formed a hydrate, starting a controversy about its existence that lasted 40 years.
1863	Wurtz prepared ethylene oxide (EO) hydrate, the first example of a water-soluble guest. Its composition and melting point diagram were not determined until 1922.
1878	Isambard showed that the equilibrium pressure of chlorine hydrate is univariant.
1878	Cailletet designed and built apparatus suitable for working at high pressure and low temperature. This was of great value for the preparation of new gas hydrates and the determination of phase equilibria. He illustrated this by preparing new hydrates of acetylene and phosphine.
1882	Wróblewski prepared $\text{CO}_2$ hydrate.
1882	de Forcrand prepared and characterized 33 double hydrates of $\text{H}_2\text{S}$ with a variety of guests and established similarities of composition, $\text{M} \cdot 2\text{H}_2\text{S} \cdot 23\text{H}_2\text{O}$ . Studies were extended to double hydrates with $\text{H}_2\text{Se}$ as well as a simple hydrate of $\text{H}_2\text{Se}$ .
1882	Cailletet and Bordet showed that mixed hydrates of $\text{CO}_2$ and $\text{PH}_3$ were not simply physical mixtures of simple $\text{CO}_2$ and $\text{PH}_3$ hydrates but hydrates with unique properties.
1883	de Forcrand applied calorimetry to gas hydrates and assigned most of the thermal effects to the dominant presence of water in the hydrate.

---

---

1883	de Forcrand observed that a number of double hydrates had well-defined cubic, cubo-octahedral, or truncated octahedral morphologies which were not acted on by polarized light.
1884–1885	Bakhuis Roozeboom provided hydration numbers for $\text{SO}_2$ , $\text{Cl}_2$ , and $\text{Br}_2$ hydrates and his phase equilibrium diagrams clearly showed the pressure–temperature fields of hydrate stability. Cailletet, Wróblewski, and Bakhuis Roozeboom observed a memory effect that increased the reformation rate of hydrate from solutions of decomposed hydrate.
1884	Le Châtelier used the Clausius–Clapeyron equation for the variation of vapor pressure of the hydrates with temperature and was the first to use the equation to determine gas hydrate compositions.
1885	Chancel and Parmentier reported a simple hydrate of chloroform. This was one of the first so-called “liquid hydrates” whose guest components are liquids at ambient temperature.
1887–1888	Bakhuis Roozeboom applied the Gibbs phase rule to heterogeneous equilibria and systematically classified chemical and physical processes according to number and nature of the components and phases present. He published on the treatment of the invariant points at which equilibrium lines meet.
1888	Villard prepared hydrates of $\text{CH}_4$ , $\text{C}_2\text{H}_6$ , $\text{C}_2\text{H}_4$ , $\text{N}_2\text{O}$ , and propane (1890).
1890	Villard recognized the stabilizing effect of air on the decomposition of gas hydrates. In the search for other “help-gases” he identified both hydrogen at 23 atm and oxygen at 2.5 atm as increasing the decomposition temperature of ethyl chloride.
1897	On the basis of careful measurements on the large number of hydrates then available, Villard presented a definition of the composition of gas hydrates (Villard’s law).
1897	de Forcrand and Thomas discovered new help-gases ( $\text{CO}_2$ , $\text{C}_2\text{H}_4$ , $\text{C}_2\text{H}_2$ , and $\text{SO}_2$ ).
1902	de Forcrand used calorimetric data and a generalization of Trouton’s rule to calculate hydrate compositions for 15 hydrates. About half had compositions in agreement with Villard’s law.
1923	Bouzat produced summary statements giving the then current definition of hydrates, their structure, and composition.
1926	Schroeder wrote an influential monograph summarizing the state of knowledge of gas hydrate to that date.
1934	Hammerschmidt, after reading Schroeder’s book, showed that gas hydrates are more likely to form plugs in natural gas pipelines than ice.
1936–1937	Nikitin prepared mixed hydrates of noble gases and $\text{SO}_2$ and showed that the noble gases could be separated by partitioning between the solid hydrate and the gas. His observations were first consistent with the “solid solution” nature of hydrates.
1946	Deaton and Frost presented experimental data on hydrate phase equilibria of natural gas components and methods of hydrate prevention.
1946	Miller and Strong proposed natural gas storage in hydrate form.

---

---

1947	Powell coined the term “clathrate” for materials having a guest molecule residing in a cavity formed in a host lattice.
1949	von Stackelberg used X-ray diffraction data to propose a structure for a gas hydrate of chloroform and H <sub>2</sub> S. Although the structure, based on a lattice with holes for guests, was incorrect, it was a radical departure from the molecular structure current up until that time. von Stackelberg had studied the X-ray diffraction of gas hydrates prior to this time, but his original photographic plates had been destroyed in aerial bombardment during World War II.
1951	Clausen introduced the pentagonal dodecahedron as a structural component of gas hydrates, and von Stackelberg and Muller’s X-ray diffraction data confirmed the crystal structure of the “structure II” (sII or CS-II) hydrate proposed by Clausen.
1952	Clausen, von Stackelberg, and Pauling and Marsh provided a structure for “structure I” (sI or CS-I) gas hydrates.
1952	Delsemme and Swings suggested the presence of gas hydrates in comets and interstellar grains. Delsemme later suggested that the outgassing of comets on approaching the sun could be due to decomposition of hydrates.
1957–1967	Barrer and coworkers studied hydrate thermodynamics, kinetics, and separation of gas mixtures with hydrate formation.
1959–1970	Jeffrey and coworkers used single-crystal X-ray diffraction to obtain structural data for clathrate hydrates, semi-clathrates, and salt hydrates.
1959	van der Waals and Platteeuw presented the “solid solution” statistical thermodynamics model for clathrate hydrates.
1961	Miller and Pauling hypothesized hydrate formation as a mechanism for anesthesia arising from inert noble gases, in particular xenon.
1961	Miller suggested the presence of gas hydrates in the planets, planetary rings, and interstellar space in the solar system.
1963	Davidson used dielectric methods to study clathrate hydrates. He discovered new water-soluble (polar) guests for clathrate hydrates, measured the dynamics of guest and host molecules, found that water molecule reorientation rates depend on the nature of the guest molecule, and postulated the presence of guest–host hydrogen bonding capable of generating Bjerrum defects.
1965	Makogon reported on natural gas hydrates found in the Siberian permafrost.
1965	Kobayashi and coworkers applied the Kihara intermolecular potential to van der Waals–Platteeuw theory to represent the guest–cage interactions.
1965	Davidson and coworkers started nuclear magnetic resonance (NMR) measurements on clathrate hydrates and demonstrated that the SF <sub>6</sub> guest in sII clathrate rotates isotropically even at 77 K.
1966	Glew and Rath showed that the equilibrium compositions of Cl <sub>2</sub> and EO clathrate hydrates are variable, in accordance with van der Waals–Platteeuw theory.
1968	Glew and Haggett studied EO hydrate growth kinetics and showed that the process is governed by heat transfer over a wide range of concentrations.
1969	Miller predicted air hydrates should be present in glacier ice, CO <sub>2</sub> hydrates on Mars, and CH <sub>4</sub> hydrates on the outer planets and moons.

---

---

1969	Ginsburg studied natural gas hydrates in geological settings.
1971	Stoll, Ewing, and Bryan found that anomalous wave velocities (bottom-simulating reflectors) are associated with marine offshore natural gas hydrate deposits.
1972	Parrish and Prausnitz developed convenient computer code for applying the van der Waals–Platteeuw theory to the calculation of gas hydrate phase diagrams.
1972	Tester, Bivins, and Herrick performed the first Monte Carlo simulation of gas hydrates of noble gases, N <sub>2</sub> , O <sub>2</sub> , CO <sub>2</sub> , and CH <sub>4</sub> to test some of the assumptions made regarding guest–cage interactions in using the van der Waals–Platteeuw approach.
1973–1983	Bertie and coworkers studied clathrate hydrates with infrared spectroscopy at low temperatures.
1974	Bily and Dick encountered gas hydrates below the permafrost in the Mackenzie Delta, Northwest Territories, Canada.
1974	Davidson, Garg, and Ripmeester reported broadline and pulsed NMR experiments on tetrahydrofuran (THF) hydrate from 4 to 270 K, showing regions of anisotropic and isotropic motions of the guest, relaxation minima for guest anisotropic rotation, water molecule reorientation, and diffusion.
1974	Davidson et al. showed that polar as well as non-polar guests show reorientational guest motions that can be described by very broad distributions in reorientational correlation times at low temperatures. It led to a model for a guest–host potential determined by short range interactions between the guest and the disordered hydrogen atoms of the host water molecules.
1974	Dyadin was appointed to lead a research group that over some 40 years provided new information on structure, stoichiometry, and stability of clathrates and high-pressure research on clathrate hydrates.
1975	Sloan and coworkers initiated work on two-phase hydrate equilibria.
1976	Holder calculated that small guests are more likely to form sII (CS-II) hydrate than sI (CS-I).
1976–1987	Nakayama studied phase equilibria of salt hydrates.
1976	Peng and Robinson developed an accurate equation of state which is widely used to describe the vapor–liquid equilibria of hydrocarbons and small gases for hydrate equilibrium calculations.
1977	Ripmeester and Davidson reported 17 new clathrate guests mainly from NMR measurements.
1979–1993	Bishnoi and coworkers initiated a program of natural gas hydrate kinetic measurements and modeling and phase equilibrium modeling.
1981–1985	Cady measured hydrate compositions as a function of pressure, obtaining values which are in agreement with van der Waals–Platteeuw theory.
1981	Ross, Anderson, and Backström measured the anomalously low thermal conductivity of hydrates of clathrate hydrates.
1983	Tse, Klein, and coworkers initiated molecular dynamics simulations of clathrate hydrates.

---

---

1984	Handa prepared pure hydrocarbon hydrates under equilibrium conditions and obtained their thermodynamic properties from calorimetry.
1984	Davidson et al. experimentally showed very small guests form CS-II rather than CS-I.
1986	Davidson et al. provided the first laboratory analysis of recovered gas hydrate samples obtained from the Gulf of Mexico and identified both CS-I and CS-II hydrates.
1986	Davidson, Handa, and Ripmeester provided the first measurement of absolute cage occupancy of Xe hydrate.
1987	Ripmeester and coworkers discovered a new clathrate hydrate family, structure H (HS-III).
1988	Whalley showed that octahedral melt figures are produced in THF clathrate hydrate crystals.
1988	Ripmeester and Ratcliffe introduced low-temperature magic angle spinning $^{13}\text{C}$ NMR spectroscopy to measure the relative occupancy of methane and methane/propane hydrate and used van der Waals–Platteeuw theory to obtain hydration numbers.
1988	Makogon and Kvenvolden independently provided estimates of the total volume of worldwide in situ hydrated natural gas at $10^{16}$ m <sup>3</sup> . Kvenvolden recognizes the decomposition of natural gas hydrates as potential contributor to global climate change.
1990	Collins, Ratcliffe, and Ripmeester used NMR spectral properties of several different nuclei, including $^2\text{H}$ , $^{19}\text{F}$ , $^{31}\text{P}$ , and $^{77}\text{Se}$ to measure hydration numbers.
1990	Rodger studied hydrate stabilities with molecular dynamics simulations.
1990	Hallbrucker and Mayer formed clathrate hydrates by vapor deposition of amorphous solid water.
1990	Ripmeester and Ratcliffe discovered numerous new guests which form HS-III and CS-II using $^{129}\text{Xe}$ NMR of xenon co-guest.
1991	Sloan proposed a molecular mechanism for hydrate formation with implications for inhibition.
1991	Handa et al. applied high pressure at 77 K to amorphize CS-I and CS-II clathrate hydrates, much as was observed for ice itself. Unlike, the amorphous ice phase, this amorphous phase recrystallized to the original hydrate phase when the applied pressure was reduced to ambient at 77 K.
1992	Handa and Stupin investigated hydrate phase equilibria in porous media.
1993	Inelastic incoherent neutron scattering (IINS) experiments on methane, Xe, and Kr hydrates were initiated at the NRC.
1993	Englezos and Hatzikiriakos used mathematical models to quantify how global temperature warming affects the stability of methane hydrates in the permafrost and in ocean sediments.
1993–2020	Tanaka and coworkers began a program of generalizing and improving on the assumptions of the van der Waals–Platteeuw theory.
1994	Edwards modeled winter flounder antifreeze peptide as a potential kinetic hydrate inhibitor.
1996	Sum measured clathrate hydration numbers with Raman spectroscopy.

---



---

1996	Koga and Tanaka studied the rearrangements of the water hydrogen bonding network in clathrate hydrates with polar guests using molecular dynamics simulation.
1997	Kuhs et al. reported double occupancy of large cages in CS-II nitrogen hydrate.
1997	Udachin et al. reported HS-III (sH) structure from single-crystal X-ray diffraction.
1997	Udachin et al. determined the tetragonal structure, TS1, of Br <sub>2</sub> hydrate from single-crystal X-ray diffraction.
1999	Dyadin et al. reported that H <sub>2</sub> forms a clathrate hydrate at high pressure.
1999	Moudrakovski et al. reported the first magnetic resonance imaging (MRI) of hydrate formation on ice particles.
2000	Huang, Walker, and Ripmeester showed that antifreeze proteins (AFPs) inhibit hydrate formation and, in some cases, eliminate the freezing memory effect for hydrate reformation.
2000–2001	Loveday et al., Hirai et al., Chou et al., and Manakov et al. prepared and characterized high-pressure phases of water, including a high-pressure HS-III clathrate phase.
2001	Moudrakovski et al. used hyperpolarized <sup>129</sup> Xe NMR to observe the nucleation, growth, and decomposition of Xe hydrate in real time.
2001	Udachin et al. determined a new structural type for dimethyl ether clathrate hydrate.
2001	Moudrakovski et al. observed a metastable CS-II Xe hydrate phase.
2001	Loveday et al. discovered a high-pressure structure of CH <sub>4</sub> hydrate using diamond anvil diffraction methods.
2002	Ballard and Sloan developed CSMGem software for hydrate equilibrium prediction.
2002	Mao et al. synthesized the CS-II hydrogen hydrate under high-pressure and low-temperature conditions to observe high H <sub>2</sub> :H <sub>2</sub> O storage ratios.
2002	Servio and Englezos accurately measure the temperature dependence of the solubility of CH <sub>4</sub> and CO <sub>2</sub> gases in the aqueous phase in equilibrium with the corresponding clathrate hydrate phases.
2004	The mechanism of self-preservation of methane hydrate was studied with scanning electron microscope (SEM) imaging by Stern and coworkers. Falenty and Kuhs used SEM to study self-preservation of CO <sub>2</sub> hydrate in 2009.
2005	Lee et al. developed a method for tuning the H <sub>2</sub> content of the mixed CS-II hydrate with THF.
2005	Clarke and Bishnoi developed a focused beam reflectance method for in situ, time-dependent hydrate particle size analysis under conditions of hydrate nucleation and growth.
2007–2016	Bačić and coworkers performed quantum mechanical calculations to determine discrete translation-rotational states of H <sub>2</sub> and CH <sub>4</sub> in different CS-I and CS-II cages with single and multiple occupancies.
2007	Celli, Ulivi, and coworkers initiated IINS studies on H <sub>2</sub> /D <sub>2</sub> /HD dynamics in CS-I and CS-II clathrate hydrates

---

---

2007	Linga, Kumar, and Englezos provided the thermodynamic and kinetic basis for CO <sub>2</sub> capture from post-combustion flue gas and pre-combustion fuel gas.
2009	Detailed characterization of hydrogen bonding of hydrates was determined using molecular dynamics simulations by two groups: Buch et al. and at the NRC.
2009	Simulation work initiated by Jordan and coworkers determined the stepwise (layer by layer) decomposition mechanism for methane hydrate.
2010	Walsh et al. carried out millisecond molecular dynamics simulations of CH <sub>4</sub> hydrate nucleation and growth.
2010	Following an early proposal by McTurk and Waller, Mori, and coworkers formed ozone hydrate in an apparatus incorporating in situ ozone generation.
2012–2014	Shin et al. characterized clathrate hydrates incorporating NH <sub>3</sub> and CH <sub>3</sub> OH synthesized using vapor deposition.
2013	Udachin et al. performed single-crystal X-ray diffraction and molecular dynamics simulations on halogen hydrates which indicated the possibility of halogen bonding between these guests and water molecules of the cages.
2014	Falenty, Hanssen, and Kuhs prepared a metastable ice phase (Ice XVI) with the structure of the empty CS-II lattice.
2015	NMR spectroscopy gave direct evidence of cage-to-cage transfer of hydrate guests CO <sub>2</sub> in THF-CO <sub>2</sub> CS-II hydrate and for CH <sub>4</sub> and CH <sub>3</sub> F in double hydrates of THF and <i>tert</i> -butylmethylether.
2015	Molecular dynamics simulations performed at the NRC and University of British Columbia showed the formation of nanobubbles of methane upon decomposition of methane hydrate.

---

### 1.3 Clathrate Hydrate Research at the NRC Canada

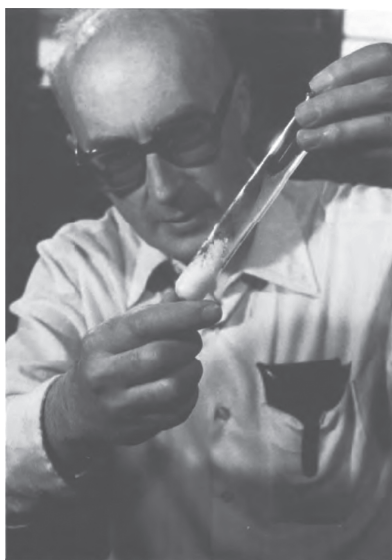
For about 50 years, gas hydrate research was a supported project at the NRC in Ottawa. It had its start in the early 1960s when Don Davidson, working in the Colloid Section of the Division of Applied Chemistry (Figure 1.1), took the initiative to follow up on a fundamental question that arose during his investigation of the dielectric properties of liquids: in the dielectric properties of liquids, is it possible to separate the contributions from molecular reorientation and diffusion? This led to the first studies on clathrate hydrates where molecules are trapped in pseudo-spherical molecule-sized cages so that one may well expect that contributions from diffusion should be reduced or eliminated.

Clathrate hydrate science was at a stage of development where two hydrate structures were known, confirming their clathrate nature. Statistical thermodynamics had provided a model of clathrate hydrates based on weak guest–host interactions; however, many of the features of the model remained untested.

Early work on guest dynamics in clathrates at the University of British Columbia (by Charles McDowell) convinced Don, Figure 1.2a, that NMR spectroscopy would be another useful technique for the study of guest motion, as it provided the means to study the effect of polar versus non-polar guests. It was an opportune time to initiate



**Figure 1.1** National Research Council of Canada Building M-12 on the NRC Montreal Road campus in Ottawa, home of the Colloid Chemistry (later Colloid and Clathrate Chemistry) group until 1990. Source: Reproduced with permission from the National Research Council.

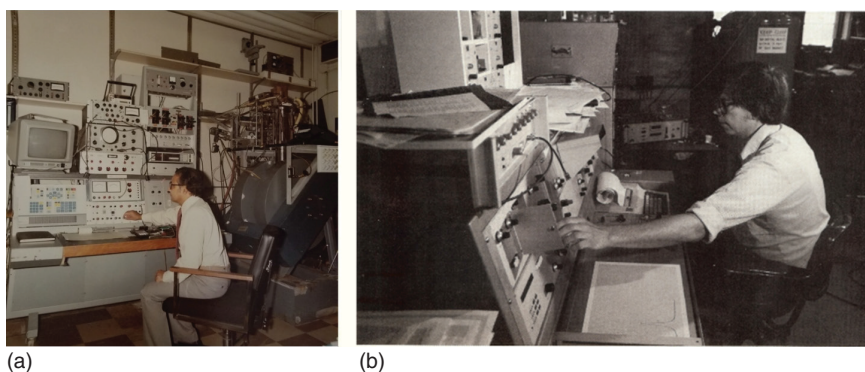


(a)



(b)

**Figure 1.2** (a) Donald Davidson observing a clathrate hydrate sample; (b) William Schneider in the official portrait as president of the NRC. Source: Photographs by the authors.



**Figure 1.3** (a) S. K. Garg at the controls of the Bruker 1.4 T SXP spectrometer as modified for broadline and pulsed NMR experiments at low temperatures (2 K). (b) J. A. Ripmeester at the console of the Bruker CXP180 NMR spectrometer. Source: Photographs by the authors.

an NMR capability, as a 12" NMR electromagnet became available from William G. Schneider's lab. Dr. Schneider, FRS (Figure 1.2b), was an internationally known pioneer in NMR spectroscopy who had taken on the Directorship of the Division of Pure Chemistry in 1963 and the Presidency of NRC in 1967.

With his associates S. R. Gough and S. K. Garg, post-doctoral, and technical staff, Don Davidson designed and built equipment to carry out dielectric and broadline NMR measurements over a temperature range from 2 to 295 K.

John Ripmeester joined the group (1972), arriving at the same time as a commercial pulsed NMR spectrometer (Bruker Bkr). The instrument was modified and upgraded (Bruker SXP, see Figure 1.3) so that both broadline and pulsed NMR experiments could be carried out down to 2 K.

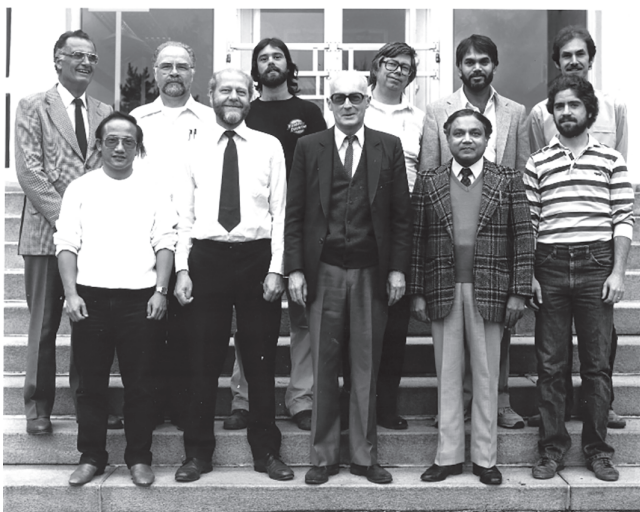
During this period, Don Davidson published "Clathrate Hydrates" an overview of clathrate hydrate science from 1810 to 1972, which appeared in *Water, A Comprehensive Series*, Vol. 2, edited by Felix Franks. This chapter summarized much of the knowledge on these substances up to that time and is still cited as a source of fundamental information on clathrate hydrates.

As NMR and dielectric measurements were extended down to 2 K to characterize guest molecule motional dynamics, by 1980, dielectric and NMR properties of clathrate hydrates had been thoroughly investigated and resulted in a good overall understanding. With these techniques, a considerable number of new guests forming structure I and structure II hydrates were identified.

The first direct measurements of hydrate cage occupancies ( $^{129}\text{Xe}$  NMR and calorimetry) were made, confirming the general correctness of the van der Waals–Platteeuw solid solution theory. This pioneering development of  $^{129}\text{Xe}$  NMR spectroscopy which illustrated the sensitivity of NMR chemical shift parameters to the size and shape of the clathrate cages became a widely used method to characterize porous materials. A review summarizing the new results "NMR, NQR and dielectric properties" was published in *Inclusion Compounds*, Vol. 3, edited by J. Atwood, J.E.D. Davies, and D. D. MacNicol in 1984.

As natural gas hydrate research advanced, the period of 1970–1980 saw publication of initial reports with results from both offshore and under permafrost locations. Davidson was invited to join a committee with members from the Canadian Federal Departments of Energy, Mines and Resources (EMR) and Indian and Northern Affairs (DINA) to learn about the gas hydrate potential of the Canadian Arctic. At the NRC, this new interest sparked a dielectric and NMR study of a number of hydrocarbon clathrate hydrates over a broad temperature range. These developing interests gave the NRC group an entry into the energy research field and the clathrate group benefited by being able to expand their clathrate hydrate program with funding from the National Energy Program. In recognition of the importance of the clathrate hydrate work, the Colloid Section was renamed the Colloid and Clathrate Section of the Division of Applied Chemistry.

Other members joining the group were John Tse (computation and diffraction, 1980), Chris Ratcliffe (NMR spectroscopy, 1982), and Paul Handa (calorimetry, 1982), see Figure 1.4. Funds for equipment were also received, leading to acquisitions of a Tian–Calvet calorimeter, a powder X-ray diffractometer, and a multinuclear FT NMR instrument dedicated to solid-state experiments. A reorganization of the Chemistry Division (1984) brought Dennis Klug, Ted Whalley, and Graham McLaurin to the Clathrate Group, bringing with them expertise in high-pressure techniques and Raman spectroscopy. Yuri Makogon, who documented the Messoyakha natural gas hydrate deposit, and a delegation from the USSR became regular visitors to Ottawa to visit the NRC, EMR, and other hydrate labs in



**Figure 1.4** Clathrate group, Division of Chemistry, National Research Council Canada circa 1984. Back row, left to right, Tony Antoniou, Ron Hawkins, Gerry McIntyre, John Ripmeester, Paul Handa, Chris Ratcliffe; front row, left to right, John Tse, Roger Gough, Don Davidson, Surendra Garg, Michael Collins. Source: Reproduced with permission from the National Research Council.

Canada to share new findings on natural gas hydrates. In 1986, Don Davidson passed away after a lengthy illness and John Ripmeester became section head in his place.

With the new group members and capabilities, a number of important contributions to understanding of hydrate solid-state properties were made, including the confirmation of the anomalously low thermal conductivity as a general property of clathrate hydrates. Also, the first lattice dynamics calculations on hydrates, including the hydrate of methane, were conducted. To measure thermodynamic properties of hydrocarbon hydrates, it became necessary to learn how to synthesize the hydrates under carefully controlled three-phase equilibrium conditions.

In 1987, a new hexagonal clathrate hydrate, structure H (HS-III or sH), was reported. It was characterized with an early version of an approach now known as NMR crystallography. It was the first new family of hydrate structures since the CS-I and CS-II hydrates were recognized. Among the pentagonal and hexagonal rings that form the sH cages, it also features square faces constructed from four water molecules with highly strained hydrogen bonds. In 1990, the first inventory of structure H hydrate formers was created, also extending the number of guests suitable for sII hydrate and noting guests which did not form ternary hydrates.

The synthesis and characterization of structure I carbon monoxide hydrate were reported and its clathrate hydrate nature was demonstrated from dielectric and  $^{13}\text{C}$  NMR measurements. Much later, a CS-II hydrate of CO was reported.

The 1980s saw some further advances in the science of natural gas hydrates. The success of the multi-technique approach to hydrate characterization led to collaboration with the US Geological Survey (USGS), Morgantown WV, to characterize natural gas hydrate recovered from the Gulf of Mexico. X-ray diffraction confirmed the existence of structure II hydrate for the natural gas; the calorimetry revealed delayed melting/decomposition as an example of a self-preservation effect, and  $^{13}\text{C}$  NMR techniques showed the distribution of methane over large and small cages in CS-II hydrate.  $^{13}\text{C}$  Magic Angle Spinning (MAS) NMR was used as a means of identification of structure I and structure II hydrates. Knowledge of cage occupancies proved to be the key to the determination of better parameters for the guest-host potential.

In 1990, NRC underwent a major reorganization that saw the disappearance of the familiar Division and Section structure. Most of the Clathrate Group members joined a larger group entitled Molecular Structure and Dynamics in the newly minted Steacie Institute for Molecular Sciences at the Sussex Drive location of the NRC (Figure 1.5). This group, led by Keith Preston, had a broader outlook on materials and also brought new expertise and capabilities.

For the hydrate work, the most significant changes were the inheritance of a single-crystal X-ray diffractometer. Gary Enright (1990) and Konstantin Udachin (1995) joined the group and developed a high level of expertise in solving highly disordered crystal structures, including clathrate hydrates. Structures of note included those of structure H hydrate, confirming the initial structural features determined from powder diffraction experiments, and that of CS-I  $\text{CO}_2$  hydrate, giving the distribution of  $\text{CO}_2$  over the large and small cages. In 1998, the single-crystal structure of tetragonal bromine hydrate was reported. Four different crystal



**Figure 1.5** National Research Council Canada building at 100 Sussex Drive, Ottawa, the home of much of the clathrate hydrate research 1990–2015. Source: Reproduced with permission from the National Research Council.

morphologies were observed depending on synthesis conditions. All crystals had the same microscopic crystal structure, but with different cage occupancies. This work was seen as a further vindication of the “solid solution” model. In a paper published in *Nature* entitled, “A complex clathrate hydrate structure showing bimodal hydration,” Udachin and Ripmeester showed that a new hydrate structure formed which consists of alternating stacks of structure H and structure II hydrates. This structure is just one example of the many possible hydrate structures that can be formed from stacked layers.

From phase equilibrium studies, dimethyl ether was known to form two hydrates, one having the CS-II structure, the second was thought to be isostructural with bromine hydrate. However, it, was discovered that the second hydrate had a novel, dense trigonal structure. Unique among the simple hydrate structures, it did not have any pentagonal dodecahedral cages, although some novel cage geometries were observed.

In collaboration with Satoshi Takeya, a major advance was made in the diffraction of powdered hydrate samples (2009). Direct methods for the analysis of powder X-ray diffraction (PXRD) patterns, dealing with molecular fragments rather than atoms, reduced the number of parameters to be refined and were able to give detailed structural information, including cage occupancies.

The NMR facilities were renewed and improved and Igor Moudrakovski, joining initially as a post-doctoral fellow (1992), was able to develop a number of unique capabilities suitable for clathrate hydrate work. One of these, MRI, was used to image hydrate layers on ice particles, which, on melting leave intact water droplets inside a hydrate coat. Another new technique, NMR spectroscopy with hyperpolarized  $^{129}\text{Xe}$  was developed to give unprecedented signal enhancement to allow the time-dependent studies of structural and compositional changes. Applications to hydrate formation kinetics showed evidence for a precursor structure before nucleation of crystalline hydrate with the primacy of a small cage environment. Also, a transient structure II hydrate of Xe was identified. Time-resolved MRI

studies of hydrate formation kinetics revealed that the formation process is locally very inhomogeneous even though the spatially averaged kinetics in the bulk system may look homogeneous. Nucleation and crystal growth are simultaneous rather than sequential processes, with multiple nucleation sites forming during the crystal growth process.

The Clathrate Group joined a Canada–Japan project (JAPEx/JNOC/GSC) on the exploration of natural gas hydrate deposits in the Mallik site in the Canadian Arctic. The NRC group contributed laboratory analysis of recovered hydrate samples from the Mallik 2L-38 site:  $^{13}\text{C}$  NMR, Raman, diffraction, calorimetry, gas, and saturation analyses were conducted on samples. Hailong Lu joined the group, first as a visiting scientist (2002), bringing his expertise on the geochemical analysis of natural gas hydrates. One outcome was the establishment of a protocol for the characterization of hydrate from natural sources, including the determination of structure and composition. Collaboration with members of a number of hydrate cruises followed. Samples from many worldwide hydrate locations were shipped to NRC in liquid nitrogen containers. One highlight, published in 2007, was the discovery of naturally occurring structure H hydrate on the Cascadia margin, offshore Vancouver Island. The synthetic version was first reported 20 years before by the hydrate group. The structure is capable of trapping large hydrocarbon molecules and is far more stable than CS-I hydrate. The findings were published in *Nature* entitled, “Complex gas hydrate from the Cascadia Margin.”

The van der Waals–Platteeuw theory was developed to describe hydrate formation from water and small non-polar guests. Potentials to describe guest–host interactions in this case tend to be of the Lennard–Jones or Kihara type. Differences due to guest chemistry tend to be hidden because of the limited number of potential parameters which ultimately are obtained by fitting to experimental observables. This procedure effectively captures all guest–host interactions (e.g. van der Waals interactions, dipolar interactions, hydrogen bonding interaction, etc.) even though only the non-directional van der Waals interactions are explicitly taken into account when developing the approach. At the NRC, efforts to look for explicit effects of guest chemistry on hydrate properties were spread over many years and involved a number of techniques and contributions from Davidson, Alavi, Udachin, Ratcliffe, Moudrakovski, and Ripmeester, among others.

A most evident guest observable is its water solubility, a property enabled by hydrogen bonding between the water and the guest species. One can then ask: Does hydrogen bonding just disappear once the guest is incorporated from the bulk aqueous solution into the hydrate lattice? In the 1960s Don Davidson, using dielectric relaxation to study water motions in hydrates noted that water reorientational dynamics for hydrates of non-polar guests were very similar to those for ice Ih. On the other hand, water dynamics for hydrates of water-soluble guests were much faster with smaller activation energies. He attributed this to transient host–guest hydrogen bonding. For THF, this would be hydrogen bonding of the oxygen atom in the rapidly rotating guest with the water molecules forming the cage wall. Bjerrum defect injection was proposed as a suitable mechanism for this process, as discussed previously by Onsager and Runnels for water molecule reorientation



in ice. From the relatively small differences in guest reorientational activation energies for hydrogen-bonded versus non-hydrogen-bonded guests, it can be seen that the interactions tend to be weak, e.g. for THF  $\sim 3.9 \text{ kJ mol}^{-1}$  as compared to cyclopentane with  $\sim 2.8 \text{ kJ mol}^{-1}$ . Insight from molecular dynamics computational studies gave the dependence of the defect concentration for different guest types on temperature. One effect of guest–host hydrogen bonding is the transfer of electron density from the host lattice to guest–host units, thus affecting lattice stability. Another is that in a guest–host  $\text{O} \cdots \text{H} - \text{O}$  hydrogen bond, the  $\text{O} \cdots \text{O}$  distance is less than the sum of the van der Waals radii. This makes some of the guests appear to be too large for the cage in which they reside, according to calculations of the free van der Waals volume in the cage, e.g.  $\text{CO}_2$  in the small cage of CS-I  $\text{CO}_2$  hydrate. Whereas the oxygen in guests with ether or ketone functions are hydrogen bond acceptors, guests with OH, NH, or  $\text{NH}_2$  functions can also be hydrogen bond donors, giving rise to complex guest–host hydrogen-bonding geometries.

Stronger hydrogen bond formation, such as for methanol in the double CS-II THF-methanol hydrate and for *t*-butylamine in the CS-II *t*-butylamine +  $\text{H}_2\text{S}$  binary hydrate, can lead to displaced or vacant water positions in the hydrate lattice. It can be surmised that a sufficient number of such defects can destabilize the hydrate lattice.

Since water-soluble molecules affect the activity of aqueous solutions, it is clear that water-soluble guests will also act as inhibitors, as accounted for by a modified van der Waals–Platteeuw equation. Thus, it is important to recognize that hydrate instability may have two origins – one from strong liquid water–guest interactions accounted for by the altered activity, the other by insufficiently strong guest–hydrate cage interactions as accounted for by the magnitude of potential function parameters. Note that the first of these effects can be “turned off” by eliminating the liquid aqueous phase and producing hydrate from an ice–guest molecule reaction. Clathrate hydrates of formaldehyde and ammonia were made this way. On the other hand, so far it has not been possible to produce a binary methanol hydrate. Another interesting observation was the catalyst-like behavior when small quantities of methanol or ammonia were added to the reaction of methane and ice. These molecules, while being excluded from bulk ice, function as catalysts by disrupting the ice surface by hydrogen bonding to surface water molecules. This greatly enhances the rate of clathrate hydrate formation. This is not a true “catalytic” effect since a small amount of the methanol or ammonia may be incorporated into the hydrate phase.

Halogen–water interactions have proven to give chlorine and bromine hydrates unusual properties. Although the chlorine van der Waals diameter is far too large to fit into the CS-I hydrate small D cage, cage occupancies of  $\sim 30\%$  have been measured. Compositional analysis by Cady has shown that chlorine hydrate is more stable than expected from applications of the van der Waals–Platteeuw equation.

Bromine by forming a unique hydrate structure illustrates the strong structure-directing effect of the halogen–water interaction. One feature that stands out is the bromine guest in the tetrakaidecahedral (T) cage of the structure where, considering the accepted van der Waals diameter of  $\text{Br}_2$ , this guest is far too large to

fit into the T cage. Another feature is the presence of the pentakaidecahedral (P) cage in Br<sub>2</sub> hydrate, rarely observed in other hydrate structures. The halogen–water interaction in bromine hydrate is reminiscent of the electrophilic electron acceptor Br<sub>2</sub> in the bromine-*p*-dioxane complex reported by Hassel many years ago.

Guest–guest interactions in hydrates with a single guest per cage rarely manifest themselves directly. The best-known example is the guest dipole ordering of trimethylene oxide in the large CS-I cage. From diffraction, the guest molecules are sterically constrained so that the guest dipoles lie along the symmetry axis of the T cages, but in disordered directions. Below ~105 K the dipole directions order, as evident from dielectric relaxation, NMR, and calorimetry.

Computational work has shown that longer range interactions exist between THF guests in the large CS-II cage and small guests in neighboring small cages. The number of Bjerrum defects generated by THF–water hydrogen-bonding appears to depend on the electron donating properties and size of the small molecule in binary THF+small gas CS-II hydrates. Most likely this interaction between guests is mediated by the intervening cage wall.

In the early 2000s, the US Department of Energy (DOE) set a target of 5 mass % as a target for onboard hydrogen storage in vehicles. In 2002, Mao and coworkers determined that multiple cage occupancies of the CS-II clathrate hydrate cages with H<sub>2</sub> molecules were possible at low-temperature and high-pressure conditions. In 2003, a paper published in the *Proceedings of the National Academy of Sciences (PNAS)* at the NRC by Patchkovskii and Tse examined the stability of the type II hydrogen clathrate with respect to hydrogen occupancy with a statistical mechanical model in conjunction with first-principles quantum calculations. These works suggested that the required mass % of H<sub>2</sub> gas in the hydrate phase was possible to attain, but at pressures and temperatures which would not be easily accessible to vehicles. To lower the pressure required to incorporate substantial amounts of H<sub>2</sub> gas into a clathrate hydrate phase, a joint Korean Advanced Institute of Science and Technology (KAIST) and NRC study was carried out and published in *Nature* in 2005. This study showed hydrogen storage capacity is enhanced by composition tuning with THF. When aqueous solutions of THF with less than stoichiometric amounts of THF relative to the pure CS-II phase were exposed to pressures of H<sub>2</sub> gas, it was found that the H<sub>2</sub> guests enter both the large and the small cages under milder conditions than the pure CS-II hydrate. These experimental studies were followed by a series of molecular dynamics simulations where the energies of different H<sub>2</sub> guest occupancies in pure and binary clathrate hydrates were determined.

A further development in this area was that it was experimentally realized that once pressure is relieved from an H<sub>2</sub> containing clathrate hydrate, the hydrogen content gradually decreases, even though the crystal structure of the hydrate phase remained intact. In 2007, a quantum chemical study at the NRC, the energy barriers and diffusion rates of H<sub>2</sub> molecules diffusing through the hexagonal and pentagonal faces of the CS-II cages were determined. The barriers to diffusion from the hexagonal faces can be overcome at lower temperatures, making the CS-II phase somewhat porous to the diffusion of this gas.

A unique method was described for producing high-occupancy hydrogen hydrate in 2012. Replacement of the nitrogen guest in CS-II nitrogen clathrate by hydrogen at high pressures was found to result in hydrogen clathrate where small cages are doubly occupied.

Following earlier work on the observation that organisms in cold climates use AFPs for protection against destructive freezing by a non-colligative mechanism, A. R. Edwards and coworkers suggested that such proteins may well have a similar action on solid hydrate formation. Because of the difficulty in obtaining significant quantities of AFPs, much effort was expended in searching for polymers that might mimic the antifreeze behavior of AFPs. This led to a burgeoning research area focused on discovering and testing of low-dosage kinetic inhibitors (LDKIs) and resulted in some early successes such as polyvinylpyrrolidone (PVP) and polyvinylcaprolactam (PVCap) by E. D. Sloan. With the greater availability of AFPs and related materials from V. Walker's (2005) group, a collaborative effort with the NRC group and later with P. Englezos' group was initiated to characterize the AFP function as a LDKI. This was carried out on a scale from the size of droplets to that of a stirred reactor with multiple techniques, including gas uptake and release, calorimetry, PXRD, solid-state NMR spectroscopy and micro-imaging, quartz crystal microbalance, and Raman spectroscopy. Some findings include there is no correlation between AFP function on ice or hydrate; some AFPs are as effective as polymers for antifreeze function; elimination of the memory effect for strong AFPs; and the presence of multiple decomposition temperatures for hydrate made in the presence of AFPs in calorimetric measurements. As explained in the chapter on kinetics of hydrate formation (Chapter 14), it is expected that the supercooling of hydrate forming solutions with inhibitor is mirrored by a superheating effect of the solid hydrate coated with inhibitor. What these effects have in common is that the processes are limited by the local radius of curvature of the advancing or retreating solid-liquid interface.

Molecular dynamics simulations were performed at the NRC and University of British Columbia to determine the mechanism of action of the winter flounder AFP as an inhibitor of methane hydrate nucleation and growth. These studies showed that the properly oriented dangling methyl groups on the amino acids of the AFP are incorporated into the half-formed hydrate cages on the hydrate surface, thus inhibiting local growth of the hydrate and inhibiting global growth of the hydrate through pinning to the hydrate surface and the action of the Kelvin effect.

In the early part of the twenty-first century, environmental concerns brought about an interest in the utilization of clathrate hydrates as a working medium for gas storage and transportation and separation of flue and fuel gases. The groups of P. Englezos and H. Lee had been active in the engineering research of the aforementioned processes and linked up with the NRC group to provide information on the molecular aspects using a multi-technique approach, in some cases with in situ time resolution. Some early results were obtained on "guest-swapping" where methane was recovered from methane hydrate by exposing the hydrate to CO<sub>2</sub> and "composition tuning" where the composition of binary hydrates can be varied over a wide range.

Studies reveal that vastly improved kinetics occur for the application of clathrate-based gas separation studies with water dispersed in stationary beds of either microporous or low-porosity silica gel. As well spatial resolution shows that nucleation and growth are simultaneous processes rather than time-separated events and are spatially highly heterogeneous. A number of experiments showed that spatially resolved kinetics are needed to develop an understanding of mechanisms. Results from spatially averaged experiment like gas uptake and NMR spectroscopy may be useful for measuring process parameters but cannot give the molecular scale details required for development of mechanisms. Molecular dynamics simulations and consideration of classical nucleation theory led to reconsideration of some well-established kinetic models. For instance, the assumption of hydrate processes being isothermal was shown to be incorrect, and taking hydrate processes to be phase changes are more consistent with observations than the often assumed chemical reaction – activated process model.

The ability of methane hydrate to exist outside its usual thermodynamic range of stability was first reported in a calorimetric study of hydrate decomposition (Davidson et al. studies on the naturally occurring hydrate from Gulf of Mexico, 1986). Later this property became an important feature (self-preservation or anomalous preservation) of the concept to use methane hydrate as a medium for the storage and transport of natural gas. Many laboratories contributed to the development of this concept, including contributions from NRC (Takeya 2001) on the guest dependence of the preservation process and the nature of the ice formed during the preservation process. A recent study showed that THF hydrate could be superheated by coating it with cyclopentane hydrate that has a higher melting point than THF hydrate.

As described earlier, a combination of powder diffraction and NMR spectroscopic results led to the characterization of HS-III as a previously unknown clathrate hydrate family. Another Xe hydrate structure, previously known only hypothetically, was characterized in a similar way as HS-III. The hydrate, known as HS-I, is of similar composition as the Xe hydrates CS-I and HS-III and demonstrates that the synthetic pathway is important in defining the structure of the product.

It is well known that ice Ih and ammonium fluoride are isostructural and form a solid solution with a maximum  $\text{NH}_4\text{F}$  concentration of ~22%. The  $\text{NH}_4^+$  and  $\text{F}^-$  ions replace two water molecules in the ice lattice. It was likely that clathrate hydrate lattices could be built with some water sites substituted with  $\text{NH}_4^+$  and  $\text{F}^-$  ions, although it is not possible to build pentagonal rings from only  $\text{NH}_4\text{F}$ . The NMR spectrum of the xenon guest in the  $\text{NH}_4\text{F}$ -substituted clathrate shows up to five distinguishable D cages because of different  $\text{NH}_4\text{F}$  distribution patterns, and the unit cell parameters shrink with increasing  $\text{NH}_4\text{F}$  content (2012). The CS-I version of the  $\text{NH}_4\text{F}$ -substituted hydrate lattice was shown to be a viable host lattice for methanol guests, an impossibility for the pure CS-I hydrate lattice. A new help-gas role for methanol was discovered so that unconventional guests such as alcohols and diols could be incorporated in the large cages of  $\text{NH}_4\text{F}$  substituted lattices of CS-I and HS-III hydrates.

Physical aspects of clathrate hydrates as solid-state materials have been studied at the NRC. In 1986, Don Davidson and coworkers measured the index of refraction of hydrate for the first time. They measured the index of refractive of water–THF solutions and THF clathrate hydrate crystals that formed upon cooling the solution up to  $-20^{\circ}\text{C}$ . The refractive index of the THF hydrate, which was greater than ice, was reproduced fairly accurately using a reactive field model where the THF molecule was assumed to lie in a cavity with the radius of the CS-II  $5^{12}6^4$  cage (Davidson et al. 1986). The elastic constants of ice in the high-pressure range of clathrate hydrate formation were measured by H. Kieft and coworkers (Memorial University of Newfoundland) and E. Whalley of the NRC in 1988. Inelastic neutron scattering studies were performed on methane hydrate under high-pressure conditions in 2000 as a collaboration between the University of Edinburgh and the NRC. At room temperature and high pressure (0.9 GPa), methane hydrate was found to form a hexagonal HS-III (MH-II) phase (Loveday et al. 2001, 2003). Further work on methane hydrate at even higher pressures was carried out by the same group in 2001. The structure of a new methane hydrate is solved from neutron and X-ray powder diffraction at pressures of 2.0 GPa and higher. A transition from a clathrate to a filled ice structure was observed and the structure of methane hydrate III was finally uncovered (Loveday 2001). In a follow-up paper published in *Nature* that year, neutron and synchrotron X-ray diffraction studies determined the thermodynamic nature of methane hydrate which probably exists on Saturn’s moon Titan, suggesting that the hydrate phases are a plausible source for the continuing replenishment of Titan’s methane atmosphere.

High-pressure inelastic X-ray scattering was used to study the elastic properties of the high-pressure methane hydrate MH-II and MH-III structures in 2005 by the NRC staff and coworkers from Germany and France. These studies revealed how guest molecules interact with the cages in clathrates and filled ice structures and how under high pressures, the water–methane guest repulsive interactions lead to the elastic properties of the methane hydrate phases becoming significantly different from the ice phases at the same pressure.

A 2005 *Nature Materials* paper entitled, “Anharmonic motions of Kr in the clathrate hydrate,” determined the origins of the low thermal conductivity in clathrates using incoherent inelastic neutron scattering, nuclear resonant inelastic X-ray scattering (NRIXS) – a powerful new technique, and molecular dynamics simulations. The low thermal conductivity in the hydrate phase was related to the coupling of the local anharmonic guest rattling motions in the cages with the host lattice vibrations. This coupling leads to the scattering of the heat-carrying lattice phonons resulting in a glass-like anomaly in the clathrate phase thermal conductivity.

## 1.4 Contributors to NRC Clathrate Hydrate Research

### *NRC scientific staff*

Don Davidson, Surendra K. Garg, Roger Gough, John Ripmeester, John Tse, Paul Handa, Chris Ratcliffe, Igor Moudrakovski, Gary Enright, Konstantin Udachin, Hailong Lu, Dennis Klug.

*NRC technical staff*

Ron Hawkins, Graham McLaurin, Régent Dutrisac, Jamie Bennett, Steve Lang, Jeff Farnand.

*Other collaborators from the NRC*

Edward Whalley, B. Morris, Derek Leait, Michael Collins, Ian Cameron, Mike Desando, Litao Chen, Xu Zhu, Anivis Sanchez, Darren Brouwer, Marek Zakrzewski, Chris Tulk, Lee Wilson, Yong Ba, Luy Ding, Eric Brouwer, Andreas Brinkmann, Erik van Klaveren, Hidenotsuke Itoh, Serguei Patchkovskii, Vladimir P. Shpakov, Saman Alavi, D. Yu. Stupin.

*Scientific collaborators on clathrate hydrates*

Alan Judge, Scott Dallimore, Fred Wright, Michael Riedel (Geologic Survey of Canada).

George Spence, Ross Chapman (University of Victoria).

Peter Englezos, Robin Susilo, Rajnish Kumar, Praveen Linga, Nagu Daraboina, Alireza Bagherzadeh, Adebola Adeyemo, Hassan Sharifi (University of British Columbia) Virginia Walker, Huang Zeng, Hiroshi Ohno, Raimond Gordienko (Queens University), Harry Kiefte, Maynard J. Clouter, Robert E. Gagnon (Memorial University of Newfoundland), Tom K. Woo (University of Ottawa).

Richard Coffin, John Pohlman (Naval Research Laboratory, Washington), Jamie J. Molaison, António M. dos Santos, Neelam Pradhan, Bryan C. Chakoumakos, Ling Yang (Oak Ridge National Laboratory), Wolfgang Sturhahn, Esen E. Alp, Jiyong Zhao, Charles D. Martin (Argonne National Laboratory) W. F. Lawson (US Department of Energy, Morgantown), Peter Brewer (Monterey Bay Aquarium Research Institute).

Dendy Sloan, Ajay Mehta, Ramesh Kini, Siva Subramanian, Keith Hester, Carolyn Koh, Amadeu K. Sum (Colorado School of Mines), Lars Ehm, John B. Parise (Stony-Brook University).

Hirokazu Nakayama (Kobe Pharmaceutical University), Tsutomu Uchida (Hokkaido University), Satoshi Takeya, Saneshiro Muromachi (AIST), Ryo Ohmura (Keio University), Takuo Okuchi (Nagoya University).

Huen Lee, Yutaek Seo, Jongwon Lee, Kyuchul Shin (KAIST).

Deqing Liang (Chinese Academy of Sciences, Guangzhou), Changling Liu (China Geologic Survey, Qingdao).

Anbawaghan Krishnamoorthi (Gas Authority of India, Mumbai).

Cor Peters, Miranda Mooyer-van den Heuvel, Maaïke Kroon, Alondra Torres Trueba (TU Delft), Jan P. J. Michels, Johannes A. Schouten (University of Amsterdam).

Judith Schicks, Manja Luzi (GFZ Potsdam) Julian Baumert (Universität Kiel).

Werner Press (Institute Laue-Langevin), Micheal Krisch, Herwig Requart (European Synchrotron Radiation facility).

Stefan Janssen (Paul Scherrer Institute).

John S. Loveday, Richard J. Nelmes, Malcolm Guthrie (University of Edinburgh).

## 1.5 Review Articles and Books on Clathrate Hydrates

---

- 1926 W. Schroeder. Die Geschichte der Gas Hydrate, Sammlung chemischer und chemisch-technischen Vorträge. Vol. 29. Stuttgart, Verlag Ferdinand Enke.
- 1946 W. M. Deaton and E. M. Frost. Gas hydrates and relation to the operation of natural gas pipelines. United States Department of the Interior, Bureau of Mines. 1949.
- 1958 J. H. van der Waals, J. C. Platteeuw. Clathrate solutions. In *Advances in Chemical Physics*, Vol. II, Wiley.
- 1959 D. L. D. Katz, P. Cornell, R. Kobayashi, F. H. Poettman, J. A. Vary, J. R. Elenbaas and C. F. Weinang. Water-hydrocarbon systems in *Handbook of Natural Gas Engineering*. McGraw-Hill.
- 1963 University of Pittsburgh. *Bibliography of Publications on Compounds of the Gas Hydrate Type*. United States Department of the Interior, Office of Saline Water.
- 1967 G. A. Jeffrey, R. K. McMullan. The Clathrate Hydrates. In, *Progress in Inorganic Chemistry*, F. A. Cotton, Ed. Vol. 8. Wiley.
- 1973 D. W. Davidson. Clathrate Hydrates, In *Water, A Comprehensive Treatise*, F. Franks, Ed. Vol. 2. Plenum.
- 1974 Y. F. Makogon. *Hydrates of Natural Gas*. NEDRA (PennWell, Tulsa, 1981).
- 1977 E. Berecz, M. Balla-Achs. *Gas Hydrates*. Elsevier.
- 1983 J. L. Cox. *Natural Gas Hydrates: Properties, Occurrence and Recovery*. Butterworth.
- 1983 V. A. Kuuskraa, E. C. Hammershaimb. *Handbook of Gas Hydrate Properties and Occurrence*. Lewin & Associates.
- 1984 G. A. Jeffrey. Hydrate inclusion compounds, in *Inclusion Compounds*. J. L. Atwood, J. E. D. Davies, D. D. McNicol, Eds., Vol. 1. Academic Press.
- 1984 D. W. Davidson, J. A. Ripmeester. NMR, NQR and dielectric properties of clathrates, in *Inclusion Compounds*. J. L. Atwood, J. E. D. Davies, D. D. McNicol, Eds., Vol. 3. Academic Press.
- 1988 G. D. Holder, S. P. Zetts, N. Pradhan. Phase behaviour in systems containing clathrate hydrates: A Review. *Rev. Chem. Eng.* 5: 1–70.
- 1990 D. L. Katz and R. L. Lee. *Gas hydrates and their Prevention*. In *Natural Gas Engineering: Production and Storage*. McGraw-Hill.
- 1990 E. D. Sloan, Jr. *Clathrate Hydrates of Natural Gases*. CRC Press.
- 1991 J. A. Ripmeester, C. I. Ratcliffe. Solid state NMR Studies of Inclusion Compounds. In *Inclusion Compounds*. J. L. Atwood, J. E. D. Davies, D. D. McNicol, Eds. Vol. 5. Oxford University Press.
- 1992 P. M. Rodger. Computational Studies of Clathrate Hydrates. In *Spectroscopic and Computational Studies of Supramolecular Systems*. J. E. D. Davies, Ed. Springer.
- 1993 P. Englezos. Clathrate Hydrates. *Ind. Eng. Chem.* 32: 1251–1274.
- 1996 G. P. Johari. Dielectric Methods for Studying Supramolecular Clathrate Structures. In *Comprehensive Supramolecular Chemistry*, Vol. 8. *Physical Methods in Supramolecular Chemistry*. J. E. D. Davies, J. A. Ripmeester. Eds. Chapter 3. Elsevier.
-

- 
- 1996 J. A. Ripmeester, C. I. Ratcliffe. Solid-State NMR Spectroscopy: Applications to Supramolecular Chemistry. In *Comprehensive Supramolecular Chemistry*. J. L. Atwood, J. E. D. Davies, D. D. McNicol, F. Vogtle, J.-M. Lehn Eds. Vol. 8: 323–380. Pergamon.
- 1996 G. A. Jeffrey. Hydrate Inclusion Compounds. In *Comprehensive Supramolecular Chemistry*. J.-M. Lehn, J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vogtle, Eds. Vol. 6: 757–788. Elsevier.
- 1996 Y. A. Dyadin, V. R. Belosludov. Stoichiometry and Thermodynamics of Clathrate Hydrates. In *Comprehensive Supramolecular Chemistry*. J.-M. Lehn, J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vogtle, Eds. Vol. 6: 789–824. Elsevier.
- 1997 Y. F. Makogon. *Hydrates of Hydrocarbons*. Pennwell Books.
- 1999 S. R. Dallimore, T. Uchida, T. S. Collett, Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, NWT, Canada, *Geologic Survey of Canada Bulletin* 544.
- 2000 B. A. Buffett. Clathrate hydrates. *Annu. Rev. Earth Planet. Sci.* 2000; 28: 477–507.
- 2001 C. K. Paull, W. P. Dillon Eds *Natural Gas Hydrates: Occurrence, Distribution and Detection*. American Geophys. Union.
- 2004 C. E. Taylor, J. T. Kwan. Eds. *Advances in the Study of Gas Hydrates*. Springer.
- 2006 M. D. Max, A. H. Johnson, W. P. Dillon. *Economic Geology of Natural Gas Hydrates*. Springer.
- 2007 E. D. Sloan, Jr., C. A. Koh, *Clathrate Hydrates of Natural Gases*. 3<sup>rd</sup> Ed., CRC Press.
- 2009 C. A. Koh, A. K. Sum, E. D. Sloan. Gas hydrates: Unlocking the energy from icy cages. *App. Phys. Rev.* 2009; 106: 061101.
- 2010 J. F. Gabitto, C. Tsouris. Physical properties of gas hydrates: A review. *J. Thermodyn.* 2010; ID: 271291.
- 2012 S. Alavi, K. A. Udachin, C. I. Ratcliffe, J. A. Ripmeester. *Clathrate Hydrates. In Supramolecular Chemistry: From Molecules to Nanomaterials*. J. W. Steed, P. A. Gales, Eds. Wiley.
- 2012 Barnes BC, Sum AK. Advances in molecular simulations of clathrate hydrates. *Curr. Opin. Chem. Eng.* 2012; 2: 184–190.
- 2015 Special Issue of *Can. J. Chem.* 93 Part 1 and 2. Issues Dedicated to J. A. Ripmeester.
- 2015 L. Krishna, C. A. Koh. Inorganic and methane clathrates: Versatility of guest-host compounds for energy harvesting. *MRS Ener. Sustain. Rev. J.* 2015; doi:10.1557/mre.2015.9
- 2015 P. Babu, P. Linga, R. Kumar, P. Englezos. A review of the hydrate based gas separation (HBGS) process for carbon dioxide pre-combustion capture. *Energy* 85: 261–279.
- 2015 Tse JS. Computational Techniques in the study of the properties of clathrate hydrates. In *Reviews in Computational Chemistry*, Vol. 28. Edited by Parrill AL, Lipkowitz KB. Wiley, New York, 2015: 315–389.
- 2015 English NJ, MacElroy JMD. Perspectives on molecular simulation of clathrate hydrates: Progress, prospects and challenges. *Chem. Eng. Sci.* 2015; 121: 133–156.
- 2016 J. A. Ripmeester, S. Alavi. Some current challenges in clathrate hydrate science: Nucleation, decomposition and the memory effect. *Current Opinion, Solid State Mater. Sci.* 20: 344–351.
-



- 
- 2016 P. Warriar, N. N. Khan, V. Srivastava, C. M. Maupin, C. A. Koh. Overview: Nucleation of clathrate hydrates. *J. Chem. Phys.* 2016; 145: 211705.
- 2017 D. Broseta, L. Ruffine, A. Desmedt. *Gas Hydrates 1: Fundamentals, Characterization, and Modeling*. Wiley.
- 2017 M. Yang, Z. R. Chong, J. Zhang, Y. Song, P. Linga. Advances in nuclear magnetic resonance (NMR) techniques for the investigation of clathrate hydrates. *Renewable Sustain. Ener. Rev.* 2017; 74: 1346–1360.
- 2018 J. G. Beltran, R. Weir. Special Issue on Gas Hydrates. *J. Chem. Thermodyn.* Vol. 117.
- 2018 P. Babu, A. Nambiar, T. He, I. A. Karimi, J. D. Lee, P. Englezos, P. Linga. A review of clathrate hydrate based desalination to strengthen energy-water nexus. *ACS Sustain. Chem. Eng.* 6: 8093–8107.
- 2018 Tsimpanogiannis, Economou IG. Monte Carlo simulation of clathrate hydrates: A review. *J. Supercrit. Fluids* 2018; 134: 51–60.
- 2020 A. Hassanpourouzabad, E. Joonaki, M. Vasheghani Farahani, S. Takeya, C. Ruppel, J. Yang, N. J. English, J. M. Schicks, K. Edlmann, H. Mehrabian, Z. M. Aman, B. Tohidi. Gas hydrates in sustainable chemistry. *Chem. Soc. Rev.* 2020; 40: 5225–5309.
- 2020 H. N. Nagashima, T. Miyagi, K. Yasuda, R. Ohmura. Clathrate hydrates at temperatures below the freezing point of water: A review. *Fluid Phase Equilib.* 2020; 517: 112610.
- 

## 1.6 Conference Proceedings

### 1.6.1 Canadian Permafrost Conference

- 
- 1981 Proceedings of the 4<sup>th</sup> Canadian Permafrost Conference, Calgary, H.M French, Ed., National Research Council of Canada, Ottawa, 1983.
- 

### 1.6.2 Physics and Chemistry of Ice

- 
- 1972 *Physics and Chemistry of Ice*. Royal Society of Canada, Ottawa, 1973.
- 1986 7<sup>th</sup> Symposium on the Physics and Chemistry of Ice, Grenoble. *J. de Phys.* 48 C1-1987.
- 1992 *Physics and Chemistry of Ice*. Hokkaido University Press, Sapporo.
- 1996 *Physics and Chemistry of Ice*, Hanover, New Hampshire, USA, *J. Phys. Chem. B* 1997; 101: Issue No. 32.
- 2002 10<sup>th</sup> Conference of the Physics and Chemistry of Ice, 2002 St. Johns, Nfld., Can. *J. Phys.* 2003; 81: No. 1-2.
- 2006 11<sup>th</sup> Conference of the Physics and Chemistry of Ice, 2006 Bremerhaven, Germany. <https://epic.awi.de/id/eprint/26177/1/Wil2007b.pdf>
-

---

2010	12th International Conference on the Physics and Chemistry of Ice (PCI-2010), Sapporo, September 5–10, 2010
2014	13th International Conference on the Physics and Chemistry of Ice (PCI-2014), Hanover, NH, USA, 2014. <i>J. Phys. Chem. B</i> 2014; 118: Issue No. 47.
2018	14th International Conference on the Physics and Chemistry of Ice (PCI-2018), Zürich, Switzerland, 2018. <a href="https://indico.psi.ch/event/5120/attachments/9173/11708/Book_of_Abstacts_PCI_2018.pdf">https://indico.psi.ch/event/5120/attachments/9173/11708/Book_of_Abstacts_PCI_2018.pdf</a>

---

### 1.6.3 International Conference on Gas Hydrates (IGCH) Proceedings

---

ICGH 1	E. D. Sloan Jr., J. Happel and M. A. Hnatow, New Paltz, NY. <i>Natural Gas Hydrates</i> , <i>Ann. NY Acad. Sci.</i> , Vol. 715, 1994.
ICGH 2	J. P. Montfort, Ed. Toulouse, France, 1996.
ICGH 3	G. D. Holder and P. R. Bishnoi, Ed., Salt Lake City, <i>Gas Hydrates, Challenges for the Future</i> . <i>Ann. NY Acad. Sci.</i> Vol. 912, 2000.
ICGH 4	Y. H. Mori, Ed., Proc. 4 <sup>th</sup> ICGH Yokohama, Japan, 2002.
ICGH 5	T. Austvik, Proc 5 <sup>th</sup> ICGH Trondheim, Norway, 2005. <a href="http://toc.proceedings.com/05337webtoc.pdf">http://toc.proceedings.com/05337webtoc.pdf</a>
ICGH 6	P. Englezos and J. A. Ripmeester, Proc. 6 <sup>th</sup> ICGH, Vancouver, Canada, 2008. <a href="https://open.library.ubc.ca/cIRcle/collections/59278">https://open.library.ubc.ca/cIRcle/collections/59278</a>
ICGH 7	G. K. Westbrook and B. Tohidi, Ed., Proc. 7 <sup>th</sup> ICGH, Edinburgh, Scotland, 2011. <a href="http://toc.proceedings.com/28521webtoc.pdf">http://toc.proceedings.com/28521webtoc.pdf</a>
ICGH 8	Beijing, China, 2014.
ICGH 9	C. A. Koh, E. D. Sloan Jr., and T. S. Collett, Denver, Colorado, USA, 2017. <a href="https://icgh9.csmospace.com/docs/ICGH9_FinalProgram.pdf?062017">https://icgh9.csmospace.com/docs/ICGH9_FinalProgram.pdf?062017</a>

---