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# 6 Experimental Methods and Measurements of Hydrate Properties

Chapters 4 and 5 were concerned with the fitting and prediction of hydrate thermodynamic data. Those two chapters indicate how hydrate theoretical developments have dramatically changed over their history, particularly due to advances in knowledge of molecular structure, statistical thermodynamics, kinetics, and computing capability. Yet the powerful tools provided by all of these predictive methods are only as good as the measurements upon which they are based.

In addition to the change in the theoretical methods applied to hydrates, there have been significant advancements and widespread use of meso- and microscopic tools in hydrate research. Conversely, the typical static experimental apparatus used today to measure macroscopic properties, such as phase equilibria properties, is based on the same principles as the apparatus used by Deaton and Frost (1946). In part, this is due to the fact that the simplest apparatus is both the most elegant and reliable simulation of hydrate formation in industrial systems. In Section 6.1.1 apparatuses for the determination of hydrate thermodynamic and transport macroscopic properties are reviewed.

The traditional methods have involved experimentalists measuring the fluid phases, and predicting the hydrate phase. However, over the last 15 years there have been significant advancements in applying mesoscopic (micron-scale) and molecular-level ( $\leq$  nanometer scale) tools to measure the hydrate phase. In the case of mesoscopic tools, these include laser scattering, x-ray computed tomography (CT), and electron microscopy to investigate the morphology and distribution of the hydrate phase. These and other mesoscopic tools are discussed in Section 6.2.1. On the molecular level, tools such as Raman and nuclear magnetic resonance (NMR) spectroscopy and x-ray and neutron diffraction are applied to determine the molecular properties and structure of the hydrate phase directly. These and other molecular-level tools are discussed in Section 6.2.2.

Thermodynamic data form the basis for future theoretical developments, because the data represent the physical reality and they have been painstakingly obtained. Usually a period of several months (or even years) is required to construct an experimental apparatus and, due to long metastable periods, it is not uncommon to obtain only one pressure–temperature data point per 1 or 2 days of experimental effort. Phase equilibria data are presented in Section 6.3.1 for simple hydrates (Section 6.3.1.1), binary (Section 6.3.1.2), ternary (Section 6.3.1.3),

and multicomponent (Section 6.3.1.4) gas mixtures, and systems with inhibitors (Section 6.3.1.5).

Thermal conductivity data are even more difficult to obtain. In the case of calorimetric data of heat capacity and heats of dissociation, the measurements though still reasonably challenging are aided by significant improvements in commercial calorimeters that can operate at high pressures. Thermal property data are presented in Section 6.3.2.

This chapter deals with macro-, meso-, and molecular-level thermodynamic and transport hydrate properties of natural gas and condensate components, with and without solute. The feasibility of using these tools to measure the kinetics of hydrate formation and decomposition are also briefly discussed, while the results of these measurements have been discussed in [Chapter 3](#). The results for insoluble substances such as porous media are discussed in [Chapter 7](#).

For quick reference, [Tables 6.1](#) through [6.3](#) provide a summary of the key features, capabilities, limitations, and advantages of different experimental apparatuses for macro- ([Table 6.1](#)), meso- ([Table 6.2](#)), and molecular-level ([Table 6.3](#)) measurements of hydrate thermodynamic and kinetic properties.

## 6.1 EXPERIMENTAL APPARATUSES AND METHODS FOR MACROSCOPIC MEASUREMENTS

The experimental apparatuses for hydrate phase equilibria underwent considerable evolution during the nineteenth century. During the last half century the standard methods for measuring macroscopic equilibria have not changed considerably. Table 6.1 summarizes the different macroscopic experimental methods used to study hydrate properties.

The usual protocol in obtaining phase equilibria data involves observing the hydrate phase by indirect means, such as an associated pressure decrease or temperature increase in the fluid phase. Visual observation is typically the only direct evidence of the hydrate phase. However, the need to measure the hydrate phase directly is becoming increasingly recognized, for example, macroscopic phase equilibria data and guest size may indicate a homogenous hydrate formation, while microscopic (spectroscopy/diffractioin) measurements of the hydrate phase could show a very heterogeneous hydrate composition.

Section 6.1.1 deals with the evolution of the current apparatuses for the measurement of phase equilibria. Section 6.1.2 deals with the methods for measurement of macroscopic calorimetric and transport properties that relate to gas transmission, storage, and phase change due to heating and cooling.

### 6.1.1 Measurement Methods for Hydrate Phase Equilibria and Kinetics

In the first century after their discovery, hydrates were regarded as a scientific curiosity. Researchers worked either with gases that were highly soluble, or under conditions that enabled hydrate formation at low pressures. With the notable

**TABLE 6.1**  
**Macroscopic Experimental Methods for Studying Hydrate Properties**

Method	Capabilities				Key information/ advantages
	Phase equilibria data	Kinetic data (time-dependent)	$P, T^a$ Limits, stirred/unstirred		
High pressure visual autoclave cell (Turner, 2005; Turner et al., 2005a)	Yes: $P, T$	Yes: $P, T$ , film growth rate vs. time	Sapphire/quartz window limits: typically 5000 psi Stirred		$P_{\text{diss}}, T_{\text{diss}}$ , gas consumption rate during growth/decomposition, visual imaging of growth/decomposition
High pressure “Blind” (no windows) autoclave cell	Yes: $P, T$	Yes: $P, T$ vs. time	Typically 10,000 psi Stirred		$P_{\text{diss}}, T_{\text{diss}}$ , gas consumption rate during growth/decomposition
Quartz Crystal Microbalance (QCM) in high pressure cell (Burgass et al., 2002; Mohammadi et al., 2003)	Yes: $P, T$ (with $P$ transducer, thermocouple in cell)	Yes: $P, T$ vs. time	Typically 6000 psi		$P_{\text{diss}}, T_{\text{diss}}$ Advantages: mg samples so equilibration times (hence experimental time) reduced
Cailletet (Peters et al., 1993; Jager et al., 1999)	Yes: $P, T$		Typically 2000 psi		Accurate $P_{\text{diss}}, T_{\text{diss}}$
Rocking cell (Oskarsson et al., 2005)	Yes: $P, T$	Yes: $P, T$ vs. time	Typically 10,000 psi (blind cell); 5000 psi (visual cell) Stirred		$P_{\text{diss}}, T_{\text{diss}}$ , gas consumption rate during growth/decomposition. Typically used for LDHI testing
High pressure rheometer (Camargo et al., 2000)		Yes: $P, T$ , viscosity vs. time	Typically 1000 psi		Viscosity changes vs. time

(Continued)

**TABLE 6.1**  
**Continued**

<b>Method</b>	<b>Capabilities</b>			
	<b>Phase equilibria data</b>	<b>Kinetic data (time-dependent)</b>	<b><math>P, T^a</math> Limits, stirred/unstirred</b>	<b>Key information/advantages</b>
Flow wheel (Rasch et al., 2002)		Yes: $P, T$ vs. time, hydrate agglomeration	With plexiglass window 1450 psi, without window 2175 psi	$P_{\text{diss}}, T_{\text{diss}}$ , gas consumption rate during growth/decomposition, visualize agglomeration/slugging (window). Larger scale than autoclave cell. Typically used for LDHI testing
Pilot flow loop (Turner et al., 2005b)		Yes: $P, T$ vs. time	Typically <2000 psi Shear from flow/pump	$P_{\text{diss}}, T_{\text{diss}}$ , gas consumption rate during growth/decomposition, visualize agglomeration/slugging (if optical window present). Larger scale than autoclave cell or flow wheel
High-pressure differential scanning calorimetry (Handa, 1986d; Le Parlour et al., 2004; Palermo et al., 2005)	Yes: $P, T$	Yes: Hydrate phase vs. time	Typically up to 5800 psi, 230 to 400 K	$T_{\text{diss}}$ , heat capacities, heat of dissociation. Emulsion stability and hydrate agglomeration

<sup>a</sup> If  $T$  limits not given, this is just a function of the cooling bath, cryostat being used.

**TABLE 6.2**  
**Mesoscopic Experimental Methods for Studying Hydrate Properties**

Method	Capabilities			Key information/ advantages
	Phase equilibria data	Kinetic data (time-dependent)	$P, T^a$ Limits, stirred/unstirred	
Laser scattering—focused beam reflectance method, FBRM with high P cell (Clarke and Bishnoi, 2004)		Yes: $P, T$ , particle formation (min)	1500 psi; size range: 1–1000 $\mu\text{m}$ ; stirred	Hydrate particle size distribution during growth/decomposition
Particle video microscope, PVM with high P cell		Yes: $P, T$ , particle formation and agglomeration (min)	1500 psi; size range: 10–300 $\mu\text{m}$ ; stirred	Hydrate particle size imaging during growth/decomposition
Micromechanical force measurement apparatus (Taylor, 2006; Taylor et al., 2007)	Particle adhesive forces	Yes: Adhesive forces vs. time (min)	15 psi; >5 $\mu\text{m}$	Adhesive forces between hydrate–hydrate particles, hydrate particle-surface
Glass micromodels, in high $P$ cell (Tohidi et al., 2002)	Hydrate, gas, water phase distribution	Yes: $P, T$ hydrate phase vs. time (min)	Typically up to 5000 psi; >50 $\mu\text{m}$ channels	Visual location of hydrate phase during growth

(Continued)

**TABLE 6.2**  
**Continued**

<b>Method</b>	<b>Capabilities</b>			<b>Key information/ advantages</b>
	<b>Phase equilibria data</b>	<b>Kinetic data (time-dependent)</b>	<b>P, T<sup>a</sup> Limits, stirred/unstirred</b>	
X-ray computed tomography (CT) (Kneafsey et al., 2005)	Hydrate, water, gas phase distribution	Yes: P, T, hydrate, water vs. time (min)	Typically up to 1000 psi; microns	Density profile of hydrate plug contained in cell. Phase fractions, thermal conductivity with ITOUGH2 modeling
Scanning electron microscopy (SEM) (Stern et al., 2005)	Hydrate morphology	No	15 psi, 77 K; microns	Meso-scale imaging of hydrate morphology
Magnetic resonance imaging (MRI) (Moudrakovski et al., 2004)	Liquid, hydrate phase distribution	Yes: Hydrate conversion from ice particles or water droplets in oil (min)	Typically 3000 psi; microns	Direct visualization of droplet conversion to hydrate crystallites and hydrate shells
Infrared imaging (Long, 2003)	Hydrate phase distribution and texture		15 psi	Identify hydrate bearing zones and texture in core samples

<sup>a</sup> If T limits not given, this is just a function of the cooling bath, cryostat being used.

**TABLE 6.3**  
**Molecular-Level Experimental Methods for Studying Hydrate Properties**

<b>Method</b>	<b>Capabilities</b>			<b>Key information/ advantages</b>
	<b>Phase equilibria data</b>	<b>Kinetic data (time-dependent)</b>	<b><math>P, T^a</math> Limits</b>	
Solid-state NMR spectroscopy (Kini et al., 2004)	Hydrate phase	Yes: hydrate phase vs. time (mins)	Typically 15 psi, or use glass bulbs up to 1000 psi	Guest occupancy, structure, structural transitions, dynamics, hydration number, hydrate formation and dissociation kinetics
Liquid-state NMR spectroscopy (Davidson and Ripmeester, 1984)		Yes: Water mobility vs. time (mins)	15 psi	Reorientation and diffusion
Raman spectroscopy with high pressure windowed cell (Sum et al., 1997; Thieu et al., 2000)	$P, T$ and hydrate phase	Yes: $P, T$ , hydrate phase vs. time (mins)	Typically for sapphire window <10,000 psi (for capillary tubes <60,000 psi; diamond anvil cell GPa's)	Guest occupancy ratios, structure, structural transitions
Neutron spectroscopy (Tse et al., 1997a,b)	Hydrate phase	No: Several hours	15 psi	Dynamics, lattice and guest vibrational/rotational modes
Neutron diffraction—single crystal	Hydrate phase	No: Several hours	Typically 1 atm., 20–5 K	Definitive structure determination
Neutron powder diffraction (Halpern et al., 2001)	Hydrate phase	Yes: $P, T$ , hydrate phase vs. time (mins)	Typically <30,000 psi	Guest occupancy, structure determination, structural transitions

(Continued)

**TABLE 6.3**  
**Continued**

<b>Method</b>	<b>Capabilities</b>			<b>Key information/ advantages</b>
	<b>Phase equilibria data</b>	<b>Kinetic data (time-dependent)</b>	<b>P, T<sup>a</sup> Limits</b>	
Small angle neutron diffraction (Koh et al., 2000)	Hydrate phase	Yes: $P, T$ , hydrate phase vs. time (h)	Typically up to 5000 psi; Stirred	Structure factors, hydration shell structure
Small angle neutron scattering (SANS) (King et al., 2000)	Hydrate phase	No: Several hours	Typically 15 psi	Inhibitor adsorption
Single crystal x-ray (synchrotron/lab) (Udachin et al., 2001b)	Hydrate phase	No: Several hours	Typically 15 psi	Structure determination, guest occupancy
X-ray diffraction (lab/synchrotron) (Koh et al., 1996)	Hydrate phase	Yes: $P, T$ , hydrate phase vs. time (synchr.: secs; lab: mins)	15–2000 psi; Stirred (synchrotron only)	Structure determination, structure transitions, hydrate crystal growth, decomposition, thermal expansivity
Extended x-ray fine structure spectroscopy (EXAFS, Synchrotron) (Bowron et al., 1998)	Hydrate phase	No		Hydration structure
Dielectric spectroscopy (Davidson, 1973)	Hydrate phase	No	15 psi	Dynamics, reorientation of guest molecules

<sup>a</sup> If  $T$  limits not given, this is just a function of the cooling bath, cryostat being used.

exception of Roozeboom (1884), very early workers had two concerns: (1) that hydrates of certain compounds did exist and (2) the determination of the number of water molecules associated with each gas molecule. Those research objectives, combined with a few low pressure measurements of hydrate formers, necessitated only the use of hand-blown glass apparatuses. While such apparatuses are of historic interest, they are considered costly, fragile, and unsafe to simulate industrial or *in situ* gas hydrate conditions.

Beginning in the 1880s, de Forcrand and his collaborator Villard began a 45 year study of hydrates. Using an ingenious glass apparatus, de Forcrand and Villard (1888) were able to exclude most water when H<sub>2</sub>S formed so that the hydrate number (gas–water) for hydrogen sulfide was reduced from the previous value of H<sub>2</sub>S · 12H<sub>2</sub>O to H<sub>2</sub>S · 7H<sub>2</sub>O. As indicated in Chapter 1, Villard was the first to determine hydrates of methane, ethane (1888), and propane (1890), but he was not successful in the formation of nitrogen hydrates. In order to form methane and ethane hydrates, he replaced the glass container of the Cailletet (which was not suitable for use at very high pressures) with a round metal jar, and formed hydrates of methane at 26.9 MPa and 293.4 K. Models of the Cailletet apparatus are in current use at the Technical University of Delft, Netherlands (Peters et al., 1993; Jager et al., 1999).

### 6.1.1.1 Principles of equilibrium apparatus development

While these early workers did not have apparatuses suitable for very high pressure, the experimentalists during the first half of the century of hydrates did prove three important principles to guide the development of succeeding apparatuses and methods:

1. *Vigorous agitation is necessary for complete water transformation.* With minor exceptions, the early results (as determined by Villard) showed that an increase in agitation caused a decrease in the number of water molecules in the hydrate.

Such agitation is necessary for three reasons:

- To provide surface renewal and exposure of liquid water to the hydrate former.
- To prevent water occlusion. Without agitation, Villard (1896) showed, for example, that nitrous oxide hydrate formation was continuous for a period longer than 15 days under a pressure of 2 MPa. Villard also determined that in previous research the ratio of water to guest molecules had been analyzed as greater than G · 6H<sub>2</sub>O (Villard's Rule) due to either occlusion of water within the hydrate mass, or due to the loss of the guest component.
- Hammerschmidt (1934) added that some agitation in the form of flow fluctuations, pressure cycles, bubbling gas through water, and so on was necessary to initiate hydrate formation, in order to decrease the metastability.

2. *Hydrate dissociation is used to measure the hydrate equilibrium point.* Wroblewski (1882) was one of the first researchers to form ( $\text{CO}_2$ ) hydrates, using equilibrium pressures higher than atmospheric through Joule–Thompson expansions. Cailletet (1877) found that the pressure must be increased beyond the hydrate equilibrium value and that hydrate formation results in a relaxation of the metastable pressure. With slow heating or depressurization for hydrate dissociation, however, metastability did not occur. The endpoint of hydrate dissociation was thus much more reproducible and was taken as an indication of the upper limit to formation metastability. [It is now recognized that metastability can occur on dissociation if too high a heating rate is used (Tohidi et al., 2000; Rovetto et al., 2006), or if the conditions are within the anomalous self-preservation region of 242–271 K at 0.1 MPa (see Chapter 3, [Section 3.3.3](#)].

Half a century later, the work of Carson and Katz (1942) provided a second reason for considering the dissociation condition of the hydrate equilibrium point (see Chapter 3, [Figure 3.1b](#) for more details). Their work clearly showed the solid solution behavior of hydrates formed by gas mixtures. This result meant that hydrate preferentially encapsulated propane from a methane + propane gas mixture, so that a closed gas volume was denuded of propane (or enriched in methane) as more hydrates formed. On the other hand, upon hydrate dissociation, when the last crystal melted the initial gas composition was regained, minus a very small amount to account for solubility in the liquid phase.

3. *A rapid decrease in pressure or an increase in temperature indicates hydrate formation in a constant volume apparatus.* All of the early workers noted a concentration of the gas as it was encapsulated in the hydrate, which led to a decrease in pressure. Conversely on dissociation with heating, visual observation of the disappearance of the last hydrate crystal was accompanied by a decrease in the slope of a pressure versus temperature trace. This provided a means of obtaining higher hydrate equilibrium pressures without visual observation of crystal disappearance, simply by measuring the intersection point of the cooling and heating isochors, given as Point D in Figure 3.1b. Exothermic formation causes the temperature to increase because hydrated molecules have a lower energy of translation than those in the vapor and liquid.

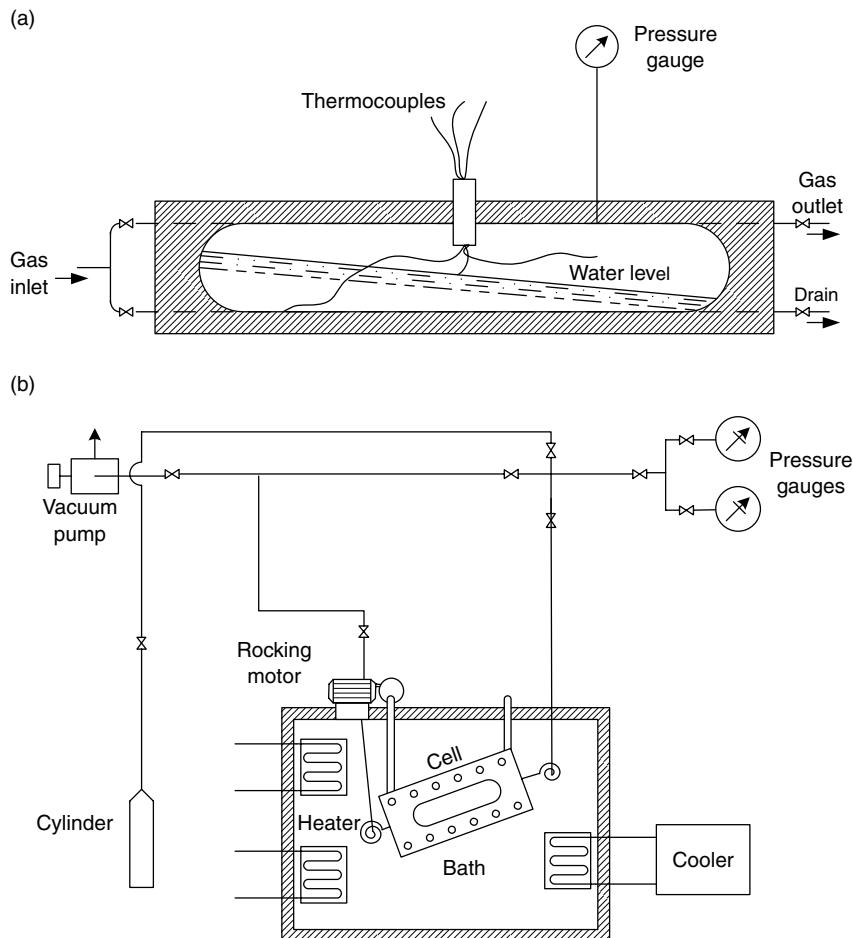
The following two subsections consider the apparatuses used for most phase equilibria measurements, namely, the three-phase ( $\text{L}_\text{w} - \text{H} - \text{V}$  and  $\text{I} - \text{H} - \text{V}$ ) regions, respectively. Similar equipment have been used to measure three-phase ( $\text{L}_\text{w} - \text{H} - \text{L}_\text{HC}$ ), and four-phase ( $\text{L}_\text{w} - \text{H} - \text{V} - \text{L}_\text{HC}$ ) conditions. For two-phase ( $\text{H} - \text{L}_\text{HC}$  and  $\text{H} - \text{V}$ ) regions, different apparatuses have been used as discussed in [Section 6.1.1.4](#).

### 6.1.1.2 Apparatuses for use above the ice point

In general, stirred autoclave cells with  $P, T$  control are used for hydrate phase equilibria measurements. Over the last 50 years, hydrate phase equilibria apparatuses have been developed with the above three principles. As a consequence of reading

Schroeder's (1927) hydrate monograph (Katz, Personal Communication, 1988), Hammerschmidt (1934) constructed a Pyrex tube flow apparatus for visual observation of simulated pipeline formations. After the gas flow stopped, slow heating enabled visual confirmation of hydrate disappearance, with measurement of temperatures and pressures. While numerous hydrate equilibria data were obtained using the above apparatus, Hammerschmidt reported a correlation rather than data, thereby inhibiting analysis of his data by others.

In 1937 Deaton and Frost constructed a static hydrate equilibrium apparatus that was to be the prototype for many others. The essential features of the apparatus are cited below and shown in Figures 6.1a,b, with a chronological



**FIGURE 6.1** (a) Detail of Deaton and Frost hydrate formation equilibrium cell. (Reproduced courtesy of U.S. Bureau of Mines (Deaton and Frost, 1946).) (b) Typical rocking hydrate equilibrium apparatus.

**TABLE 6.4**  
**Development of High Pressure Visual Hydrate Cell**

Date	Investigator(s)	Modification
1937	Deaton and Frost	Basic cell with options for gas flow above liquid, or sparged through liquid, option for rocking cell in thermostatted bath
1940	Roberts, Brownscombe, and Howe	Mercury (Hg) displacement of liquids, agitation
1942	Carson and Katz	Rocking hydrate cell, displacement of liquids; hydrate decomposed for composition
1952a	Reamer, Selleck, and Sage	Capillary sight glass, hydrocarbons and water over Hg; agitation
1956	Scauzillo	Cooling coils adjacent to sight glass; Hg displacement; rocking
1960	Otto and Robinson	Double window cell; rotated or agitated (after 1960)
1961	van Welie and Diepen	Hg pressurization; $P > 25$ MPa; electromagnetic agitation
1969	Andryushchenko and Vasilchenko	100 cm <sup>3</sup> steel-coated organic glass cylinder, magnetic agitation
1974	Y. Makogon	$P < 20$ MPa without agitation; filming capability
1974	Berecz and Balla-Achs	Single and double chamber multivibrator mixer
1980	Dharmawardhana, Parrish, and Sloan	Bronze cell, plexiglass windows, ultrasonic agitation
1981	John and Holder	Glass windowed cell without mixing used below the ice point
1983	Vysniaukas and Bishnoi	Cylinder with sight ports magnetically stirred

listing of the modifications provided in Table 6.4. Note that Table 6.4 represents only the initiation of such apparatuses in each laboratory, with a chronology of modifications. Most designs have been used by many other investigators. For example, the apparatus type designed by Carson and Katz (1942) enjoyed longevity in the University of Michigan laboratory, and was used by Holder and Hand (1982).

The salient features of the apparatus are as follows:

- The heart of the apparatus consists of a sight glass (typically 300 cm<sup>3</sup>) for visual confirmation of hydrate formation and disappearance. Normally only 20–150 cm<sup>3</sup> of the cell volume contains water, with the remainder being gas and hydrate.
- The cell is enclosed in a thermostat bath but thermocouples are placed in the cell interior to measure the thermal lag between the cell and the bath.
- The pressure is usually measured with the use of Bourdon tube gauges or transducers.

- Mixing at the gas–liquid interface is provided in a variety of ways, such as by mechanical or magnetic agitators, by rotation or rocking of the cell, by bubbling gas through water in the cell, or by ultrasonic agitation.

#### *Operation of standard static formation apparatus*

With the fundamental apparatus established, normal operation above 273 K proceeds in one of three static modes:

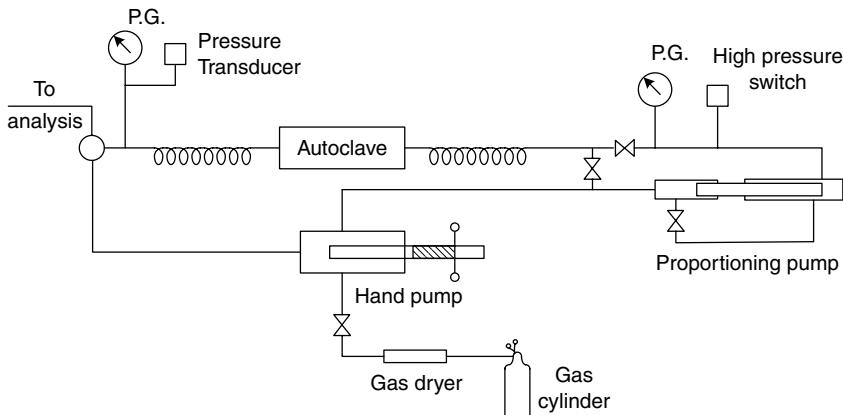
1. In isothermal (constant temperature) operation the gas–liquid system is originally set at a pressure higher than the hydrate formation value. As hydrates are formed the temperature increases at the hydrate interface because fluid (gas and water) molecules must discharge translational energy as they are solidified. However, such energy must be dissipated through conduction or convection/agitation to the surrounding phases and bath.

Encapsulation of the gas decreases the pressure to the three-phase (L<sub>w</sub>–H–V) condition. The system pressure may be controlled by an external reservoir for addition or withdrawal of gas, aqueous liquid, or some other fluid such as mercury. After hydrate formation, the pressure is reduced gradually, the equilibrium pressure is observed by the visual observation of hydrate crystal disappearance. Upon isothermal dissociation, the pressure will remain constant for a simple hydrate former until the hydrate phase is depleted.

2. In isobaric operation the system pressure is maintained constant, by the exchange of gas or liquid with an external reservoir. The temperature is decreased until the formation of hydrate is indicated by significant addition of gas (or liquid) from a reservoir. After hydrate formation the temperature is slowly increased (maintaining constant pressure by fluid withdrawal) until the last crystal of hydrate disappears. This point, taken as the equilibrium temperature of hydrate formation at constant pressure, may be determined by visual observation of hydrate dissociation or at a constant temperature as simple hydrates dissociate with heat input.

3. Isochoric (constant volume) operation of the hydrate formation cell is illustrated by the pressure–temperature trace of [Figure 3.1b](#). The temperature of the closed cell is lowered from the vapor–liquid region, and isochoric cooling of the gas and liquid causes the pressure to decrease slightly. Hydrates form at the metastability limit B, causing a marked pressure decrease, ending at the three-phase (L<sub>w</sub>–H–V) pressure and temperature. The temperature is then slowly increased to dissociate the hydrates. On a pressure–temperature plot, the hydrate dissociation point is taken as the intersection of the hydrate dissociation trace with the initial cooling trace (Point D in Figure 3.1b). This procedure is commonly used for high pressure hydrate formation, and provides an alternative to visual observation, which is the primary option in the previous two procedures.

In the mid-1940s a sight glass rupture resulted in the death of a hydrate researcher. Consequently, there was a revival of interest in non-visual means of hydrate detection, especially at high pressures. The development of



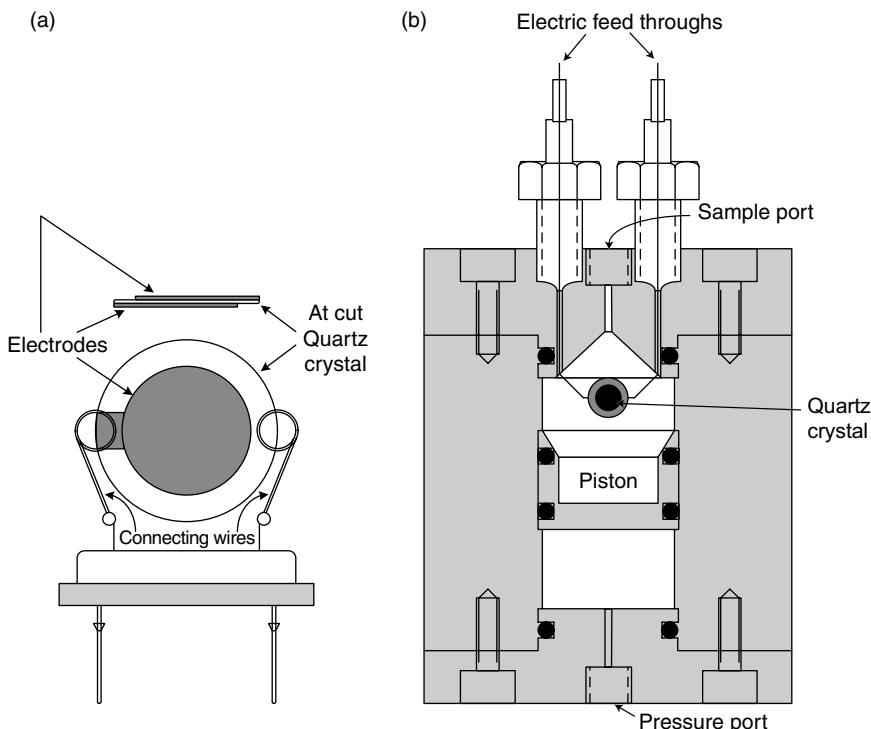
**FIGURE 6.2** Kobayashi's ball mill hydrate apparatus for three-phase and for two-phase hydrate equilibria. (Reproduced, from Aoyagi, K., Song, K.Y., Kobayashi, R., Sloan, E.D., Dharmawardhana, P.D., *Gas Proc. Assn. Res. Report*, No. 45, Julsa, OK (December 1980). With permission from the Gas Processors Association.)

the van der Waals and Platteeuw statistical theory in 1959 also rekindled interest in high pressure experimental work to complement and test the theory.

In the 1950s Kobayashi extended a series of studies he had begun with Katz at the University of Michigan. The new work represented high pressure nonvisual experimental studies that continued for half a century at Rice University. Of particular note are the high pressure studies of Kobayashi and coworkers (Marshall et al., 1964a,b; Saito et al., 1964) and the advances in the theory made by Nagata and Kobayashi (1966a,b) and Galloway et al. (1970). The apparatus consisted of a high-pressure stainless steel cylinder, which rotated about its axis. Inside the cylinder Galloway inserted stainless steel balls, suggested by Barrer and Edge (1967), to renew the surface area upon rotation, and to enable all water to be converted to hydrate. Aoyagi and Kobayashi (1978) modified the apparatus, as shown in Figure 6.2, to allow for gas recirculation through the cell in semibatch operation.

More recently, Tohidi and coworkers (Burgass et al., 2002; Mohammadi et al., 2003) have applied a novel method for measuring gas hydrate phase equilibria (Lw–H–V), which is based on a Quartz Crystal Microbalance (QCM). Figure 6.3 shows a schematic of the QCM set up and the QCM placed in a high pressure cell. The QCM consists of a thin disk of quartz sandwiched between two electrodes. The crystal will oscillate at a particular resonant frequency when an electric current is passed across the electrodes. This frequency is a function of the properties of the crystal. Any mass (from hydrate formation) attached to the surface of the crystal disk will cause a change in the resonant frequency, and hence be detected. The pressure and temperature of the system is measured using conventional methods, namely, a pressure transducer and a thermocouple in the high pressure cell.

The QCM is extremely sensitive and measures small changes in mass, that is, 1 ng mass change gives a 1 Hz frequency change (Lu and Czanderna, 1984).



**FIGURE 6.3** (a) Schematic illustration of the Quartz Crystal Microbalance (QCM), and (b) the QCM mounted within a high pressure cell. (Reproduced from Mohammadi, A.H., Tohidi, B., Burgass, R.W., *J. Chem. Eng. Data*, **48**, 612 (2003). With permission from the American Chemical Society.)

Therefore, key advantages of the QCM method are that much smaller samples (one drop of water) and hence shorter times (15 min/temperature step versus several hours for conventional methods) are required for these hydrate phase equilibria measurements. The authors applied this system to measure dissociation temperatures of gas hydrates, such as methane, nitrogen, and oxygen hydrates.

The procedure involved adding a drop of water onto the surface of the quartz crystal, and then lowering the system temperature to freeze the water. The cell was then evacuated and the gas system was introduced into the cell. The temperature and pressure conditions required for hydrate formation were then adjusted. The cell temperature was raised stepwise, and pressure and electrical parameters of the QCM were recorded at each step. The formation of a small amount of hydrate (causing a change in mass) is readily detected from the significant reduction in resonant frequency at conductance at the resonant frequency of the quartz crystal. However, the QCM method requires that hydrates adhere to the surface of the quartz crystal, and in some cases this may not occur, thereby making these measurements unfeasible.

### 6.1.1.3 Apparatus for use below the ice point

Hydrate experimental conditions have been defined in large part by the needs of the natural gas transportation industry, which in turn determined that experiments be done above the ice point. Below 273.15 K there is the danger of ice as a second solid phase (in addition to hydrate) to cause fouling of transmission or processing equipment. However, since the development of the statistical theory, there has been a need to fit the hydrate formation conditions of pure components below the ice point with the objective of predicting mixtures, as suggested in [Chapter 5](#).

Because most of the upper quadruple points of the hydrocarbon hydrate formers limit the temperature range of simple hydrate formers to a few degrees above the ice point, the region below 273 K was measured to provide more extensive data. However, as recorded in Section 6.3, substantially fewer data below 273 K exist than at higher temperatures. An increasing need for hydrate phase equilibria data below the ice point is evolving as oil/gas exploration move to Arctic conditions, where typically temperatures can be well below 273 K.

Deaton and Frost (1946) suggested the same apparatus could be used for conditions below the ice point. In these experiments, gas was first bubbled through water above 273 K, to form a “honeycomb mass” of hydrate. Then free water was drained before the cell was cooled below the ice point. After the temperature was stabilized, gas was removed in small increments until a region of constant pressure was obtained, which indicated dissociation of the hydrate phase. Deaton and Frost used this procedure only for equilibria of simple hydrates, since the hydrated mass of guest mixtures was not constrained to be of uniform composition, and consequently would have decomposed at different pressures.

For glass-tube hydrate equilibria below the ice point, Barrer and coworkers (Barrer and Ruzicka, 1962a,b; Barrer and Edge, 1967) and later Falabella and Vanpee (1974) and Falabella (1975) used glass beads or stainless steel balls to provide surface renewal in a shaken glass tube. At the ice point Cady (1981, 1983a,b, 1985) was able to condense hydrates from mixtures of water and guest molecules in a visual glass apparatus. In other innovative experiments below the ice point, Holder and coworkers (Godbole, 1981; John, 1982; Kamath, 1984) performed low pressure measurements below 273.15 K using an electrobalance, a non-visual sampling cylinder, and a static sight glass, respectively.

The experiments of Hwang et al. (1990) indicated that hydrates from ice are readily formed when the sample temperature is raised just above the ice point. Stern et al. (1996) successfully converted ice to hydrates. They raised the temperature of 200–500  $\mu\text{m}$  ice grains to 289 K and 31 MPa within the L<sub>w</sub>–H–V region (beyond the almost vertical I–H–V line). Ice melted and converted all but 3% of the sample into hydrate within 8 h, as determined by x-ray diffraction. The method of Stern et al. (1996) has been widely adopted by hydrate researchers to achieve complete/near complete conversion of ice to hydrate.

At temperatures below the ice point more time is required to equilibrate the two solid phases, ice and hydrate. Byk and Fomina (1968) suggested that water molecule rearrangement is very difficult between the ice nonplanar hexagonal

structure and the hydrate planar pentagonal cage faces. Since many molecules in each structure must have some mobility to allow the transition necessary, a liquid-like structure may be required on a molecular scale. This liquid-like (quasi-liquid) layer has been more recently proposed based on neutron diffraction data to be a key part of the conversion process of ice to carbon dioxide hydrate (Henning et al., 2000).

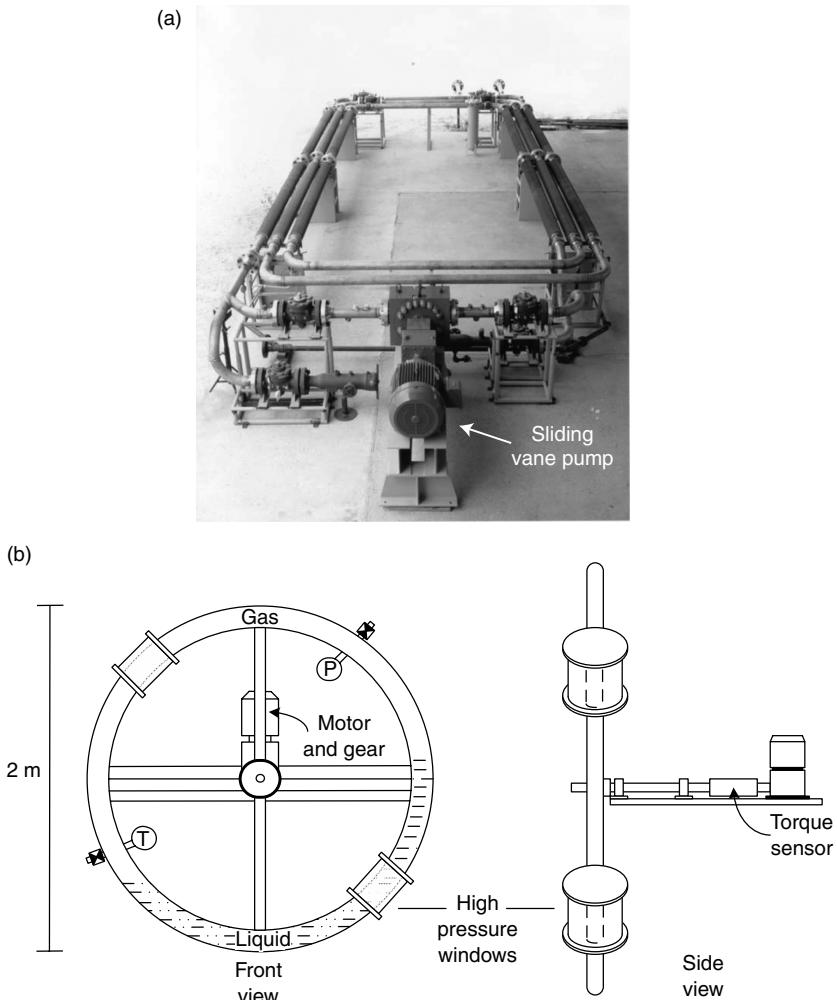
#### 6.1.1.4 Apparatuses for two-phase equilibria

In two-phase (H–V or H–L<sub>HC</sub>) equilibria, one less phase is present than in the more common three-phase measurements; therefore, an additional intensive variable (in addition to temperature or pressure) must be measured. Typically the water concentration of the hydrocarbon fluid phase is determined; the fluid phase contains very low concentrations of water, and a special means must be used to measure minute water concentrations, such as the special chromatograph developed by Ertl et al. (1976) in Kobayashi's laboratory. Alternatively, the hydrocarbon concentration of the aqueous phase in equilibrium with hydrates is determined; these concentrations are also very low and require special techniques.

The most productive two-phase (H–V or H–L<sub>HC</sub>) equilibrium apparatus was developed by Kobayashi and coworkers. The same apparatus has been used for two-phase systems such as methane + water (Sloan et al., 1976; Aoyagi and Kobayashi, 1978), methane + propane + water (Song and Kobayashi, 1982), and carbon dioxide + water (Song and Kobayashi, 1987). The basic apparatus described in Section 6.1.1.2 was used in a unique way for two-phase studies. With two-phase measurements, excess gas was used to convert all of the water to hydrate at a three-phase (L<sub>w</sub>–H–V) line before the conditions were changed to temperature and pressures in the two-phase region. This requires very careful conditioning of the hydrate phase to prevent metastability and occlusion. Kobayashi and coworkers equilibrated the hydrate phase by using the ball-mill apparatus to convert any excess water to hydrate.

#### 6.1.1.5 Flow loops for hydrate formation kinetics

A number of large temperature-controlled pilot flow loops have been constructed to study hydrate formation under simulated field conditions. For example, pilot flow loops have been constructed by ExxonMobil (Reed et al., 1994), Texaco (Notz, Personal Communication, 1996), Shell (Muijs et al., 1991), and l'Institut Francais du Petrole, IFP (Behar et al., 1994). The IFP loop at Solaize is 2 in. (ID; 5.1 cm) and 140 m in length, and is rated to 10 MPa (Palermo et al., 2000). ExxonMobil (Talley, Personal Communication, March 18, 2005) developed a pilot flow loop for hydrate testing and research that is 3.8 in. (ID; 9.7 cm) and 95 m in length, rated to around 10.3 MPa (see [Figure 6.4a](#)). The whole flow loop and peripheral equipment is housed in a large temperature controlled room. This flow loop has the advantage of having a particle size analyzer (focused beam reflectance method, FBRM) to monitor changes in the hydrate particle size distribution during



**FIGURE 6.4** (a) ExxonMobil flow loop for hydrate formation, before installing the FBRM instrument, peripheral equipment and housing. (From Turner, D., *Clathrate Hydrate Formation in Water-in-Oil Dispersions*, Ph.D. Thesis, Colorado School of Mines, Golden, CO 2005. With permission.) (b) Flow wheel apparatus for hydrate formation during flow simulation. (Reproduced from Bakkeng, S.E., Fredriksen, A.E., in *Proc. First International Conference on Natural Gas Hydrates*, 715, 502 (1994). With permission from the New York Academy of Sciences.)

hydrate formation/decomposition (see [Section 6.2.1](#) for more details on the FBRM system). It has been suggested that the loop diameter needs to be about equal to or larger than 4 in. internal diameter in order to be able to scale-up flow results to large (e.g., at least 10 in. internal diameter) multiphase gas/oil transmission lines.

Results obtained in the Texaco flow loop (1.93 in. or 4.9 cm ID, 14 m in length, rated to 13.8 MPa) and in field tests at Werner-Bolley, Southern Wyoming

showed there was good transferability between the flow loop and field. The flow loop results indicated the most probable locations for plug formation (Matthews et al., 2000).

Another flow loop facility used to test hydrate formation is the flow loop at Tulsa University (3 in. or 7.6 cm ID, 48.8 m in length, operating at pressures up to 15.2 MPa). This flow loop can be set at different slope inclines (e.g., from 5° to 30°). The concept of using a rocking loop originated from the desire of chemical companies to scale-up their laboratory rocking cell tests on low dosage hydrate inhibitors (LDHIs) to a pilot-scale facility. However, the ability to set the flow loop at different inclines enables simulation of different field flowline geometries.

Camargo and Palermo (2002) also investigated the transferability of hydrate slurry rheology measurements obtained in the “Lyre” flow loop in Solaize (2 in. or 5.1 cm ID, 140 m long) and in a laboratory high pressure rheometer. The results showed good agreement between the two apparatuses for relative viscosity versus shear rate data. The transferability between hydrate rocking cells, a mini loop (0.5 in. or 1.3 cm ID) and a pilot-scale flow loop (4 in. or 10.2 cm ID) for screening low dosage inhibitors was examined by Talley et al. (2000). Good correlation was found between the mini loop and flow loop, although it was concluded that flow loops give different subcoolings from rocking cells.

Herri and coworkers (Fidel-Dufour et al., 2005) have developed a flow loop reactor (in Saint Etienne, France) operating at pressures of 1–10 MPa at 0–10°C. The flow section is 36.1 m long, 1.0 cm internal diameter, and has a constant slope of 4°. The unique feature of this flow loop is that the exit of the flow section is connected to a gas lift riser (10.6 m long and 1.7 cm internal diameter) in which gas coming from a separator located at the top of the column is re-injected. The gas lift is thereby able to move an emulsion or suspension slurry without any pump or mechanical system.

An alternative that is less resource-intensive than the flow loop is the flow wheel apparatus (Bakkeng and Fredriksen, 1994; Lippmann et al., 1994) shown in [Figure 6.4b](#). The wheel (torus) is nominally a 2–5 in. (5.1–12.7 cm) pipe, 2 m in diameter that rotates at 0.3–5.0 m/s while filled with gas and less than 50 vol% liquid. Conceptually, the wheel is spun past the gas and liquid rather than the reverse. Therefore, the flow wheel apparatus does not require circulating devices such as pumps or compressors. Hydrate formation is deduced visually, or by a sharp increase in torque required to turn the wheel. Urdahl et al. (1995) and Lund et al. (1996) report good field transferability from results obtained with this apparatus. Pilot flow loops and flow wheels have been also used to simulate shut-in/start-up conditions (12 h stagnant period) and to test kinetic inhibitors (e.g., Palermo and Goodwin, 2000; Rasch et al., 2002).

### 6.1.2 Methods for Measurement of Thermal Properties

The number of measurements for natural gas hydrate thermal properties is several orders of magnitude lower than that for phase equilibrium properties. The experimental difficulties in thermal measurements center on the determination of

the composition of the system prior to measurement. The difficulty of system composition determination is due to two factors. First, at temperatures above the ice point, high equilibrium pressures cause decomposition when the apparatus is loaded with preformed hydrate. Second, hydrate metastability and component occlusion cause extreme difficulty in completely converting all the water to hydrate.

However, recent advances in commercially available high pressure calorimeters (e.g., by Setaram with the DSC 111, BT2-15 calorimeter, micro-DSC VII) have the potential to provide a more tractable method of obtaining thermal property data for hydrates. In particular, the problem mentioned above of incomplete conversion/decomposition of the hydrate sample during loading may be largely circumvented by using the following procedure. The gas hydrate sample is synthesized off-line and then quenched in liquid nitrogen to stabilize the hydrate at atmospheric pressure. The quenched hydrate is loaded into the high pressure DSC cell in a dry atmosphere (to avoid condensation). The sample is then pressurized with the appropriate gas system to allow any unconverted or partially decomposed hydrate to convert to hydrate [which is analogous to Handa's (1986b) method described in Section 6.1.2.1]. Another method is to add crushed ice particles into the high pressure cell and then on pressurizing the ice, freeze-thaw cycles are performed to fully convert the ice to hydrate [cf. Stern et al.'s (1996) method]. Using these methods, thermal property data at high pressures (above the ice point) have been obtained for methane hydrate by Gupta (2007).

Other attempts to avoid the experimental difficulties of measuring the thermal properties of gas hydrates have been to choose the easier route of thermal property measurements of cyclic ethers—ethylene oxide (EO) for structure I, or tetrahydrofuran (THF) for structure II. Since both compounds are totally miscible with water, liquid solutions can be made at the theoretical hydrate compositions ( $\text{EO} \cdot 7.67\text{H}_2\text{O}$  or  $\text{THF} \cdot 17\text{H}_2\text{O}$ ).

Hydrates of EO and THF may be formed at atmospheric pressure without problems of occlusion or mass transfer at temperatures of 285.7 and 277.4 K, respectively. In such measurements, the host or water contribution is correctly determined.

Table 6.5 lists the different thermal property measurements that have been performed on hydrates of cyclic ethers, other nonnatural gas components, and natural gas components.

### 6.1.2.1 Heat capacity and heat of dissociation methods

In a thorough review of calorimetric studies of clathrates and inclusion compounds, Parsonage and Staveley (1984) presented no direct calorimetric methods used for natural gas hydrate measurements. Instead, the heat of dissociation has been indirectly determined via the Clapeyron equation by differentiation of three-phase equilibrium pressure–temperature data. This technique is presented in detail in Section 4.6.1.

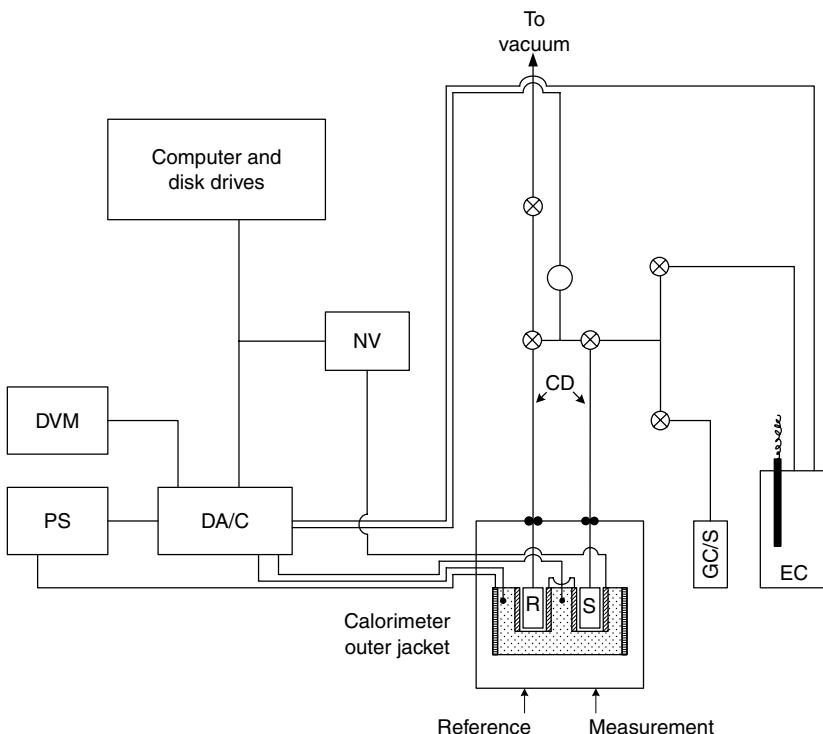
**TABLE 6.5**  
**Measurements of Hydrate Thermal Properties**

Investigator(s)/date	Component	Range of experiments
Heat capacity and heat of dissociation		
Ross and Andersson (1982)	Tetrahydrofuran	$C_v$ : 100–260 K; $P < 1.5$ GPa
Leaist et al. (1982)	Ethylene oxide	$\Delta H$ and $C_p$ : 120–260 K
	Tetrahydrofuran	$\Delta H$ and $C_p$ : 120–260 K
Callanan and Sloan (1983)	Ethylene oxide	$\Delta H$ and $C_p$ : 240–270 K
	Tetrahydrofuran	$\Delta H$ and $C_p$ : 240–270 K
	Cyclopropane	$C_p$ : 240–265 K
Handa (1984)	Tetrahydrofuran	$\Delta H$ and $C_p$ : 100–270 K
Handa (1985)	Trimethylene oxide	$\Delta H$ and $C_p$ : 85–270 K
Rueff et al. (1985)	Tetrahydrofuran	$\Delta H$ and $C_p$ : 240–265 K
White and MacLean (1985)	Tetrahydrofuran	$C_p$ : 17–261 K
Handa (1986c)	Xenon	$\Delta H$ : 273 K; $C_p$ : 150–230 K
Handa (1986a)	Xenon and krypton	$\Delta H$ and $C_p$ : 85–270 K
Handa (1986d)	Methane, ethane, propane	$\Delta H$ and $C_p$ : 85–270 K
Handa (1986b)	Isobutane	$\Delta H$ and $C_p$ : 85–270 K
Rueff et al. (1988)	Methane	$\Delta H$ : 285 K; $C_p$ : 245–259 K
Kang et al. (2001)	Methane, Carbon dioxide, Nitrogen, Tetrahydrofuran	$\Delta H$ : 273.65
Gupta (2007)	Tetrahydrofuran	$\Delta H$ and $C_p$ : 240–277 K
	Methane	$\Delta H$ and $C_p$ : 243–283 K; $P \leq 20$ MPa
Thermal conductivity		
Cook and Laubitz (1981)	Ethylene oxide	Ambient freezing point
	Tetrahydrofuran	
Ross et al. (1981)	Tetrahydrofuran	100–277 K; 0.1 GPa
Ross and Andersson (1982)	Tetrahydrofuran	100–260 K; $P \leq 1.5$ GPa
Andersson and Ross (1983)	1,3-Dioxolane	100–260 K; $0.05 \leq P \leq 1.0$ GPa
	Cyclobutanone	100–260 K; $0.05 \leq P \leq 1.5$ GPa
Ashworth et al. (1985)	Tetrahydrofuran	45–160 K
Ahmad and Phillips (1987)	1,3-Dioxolane	$T < 200$ K; ambient pressure
Asher (1987)	Tetrahydrofuran	273 K; ambient pressure
Waite et al. (2005)	Tetrahydrofuran	250–270 K; ambient pressure
Waite et al. (2002)	Methane	250–293 K; 24.8 MPa
Huang and Fan (2004)	Methane	263–277 K; 6.6 MPa
Gupta et al. (2006b)	Methane	277–279 K; 4.6 MPa

However, as discussed by Barrer (1959), there is an inherent difficulty in the Clapeyron method, particularly when there is significant nonstoichiometry, as in the case for molecules that occupy the smaller cavities (see Example 5.1). Additionally, while the Clapeyron equation often provides satisfactory estimates of the heat of dissociation, no information about the hydrate heat capacity is directly determined by that equation.

The most accurate calorimetric measurements were made at the Canadian National Research Council by Handa, who modified a Setaram BT Tian-Calvet calorimeter for high pressures. In the Tian-Calvet calorimeter, the sample and reference cells are surrounded by a thermopile, allowing the heat flux to be measured directly. This device was used to measure the heat capacity and heat of dissociation between 85 and 270 K for methane, ethane, propane (Handa, 1986d), iso-butane (Handa, 1986b), and the heat of dissociation of two naturally occurring hydrates (Handa, 1988). A similarly modified BT Tian-Calvet instrument was used by Varma-Nair et al. (2006) to investigate kinetic inhibitor polymer–water interactions, and the relation of these interactions to hydrate inhibition. An abbreviated diagram of the calorimeter is provided in Figure 6.5.

Using this instrument in Figure 6.5, Handa (1986b) measured the heat input to a hydrate sample in the sample container S, relative to helium at ambient temperature and 5 kPa in reference cell R. The hydrate was externally prepared from ice in a rolling-rod mill, before a 4 g sample was loaded into the calorimeter at liquid nitrogen temperatures. For heat capacity measurements, a pressure greater than the hydrate dissociation pressure was maintained in the sample cell. By cycling



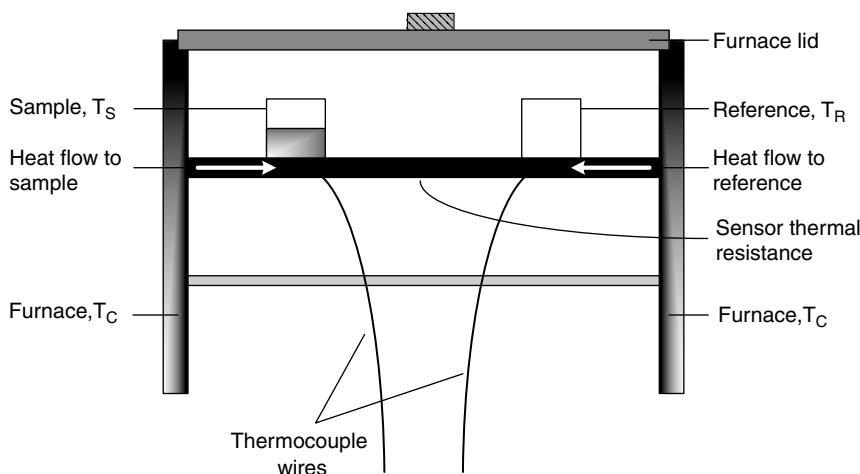
**FIGURE 6.5** Schematic of Tian-Calvet calorimeter at the Canadian National Research Council. (Reproduced from Handa, Y.P., *Calorimetric Studies of Laboratory Synthesized and Naturally Occurring Gas Hydrates*, paper presented at AIChE 1986 Annual Meeting Miami Beach, November 2–7, 28 (1986b). With permission.)

the temperature around 273.15 K, Handa was able to determine the amount of ice present in the sample, and to convert most of the ice to hydrate. For hydrate dissociation measurements, the amount of gas released from the hydrates was determined by PVT analysis. Handa estimated the precision to be  $\pm 1\%$  for all measurements; the accuracies for  $C_p > 100$  K and for  $\Delta H$  were  $\pm 1\%$ , while the accuracy for  $C_p < 100$  K was  $\pm 1.5\%$ .

In the CSM laboratory, Rueff et al. (1988) used a Perkin–Elmer differential scanning calorimeter (DSC-2), with sample containers modified for high pressure, to obtain methane hydrate heat capacity (245–259 K) and heat of dissociation (285 K), which were accurate to within 20%. Rueff (1985) was able to analyze his data to account for the portion of the sample that was ice, in an extension of work done earlier (Rueff and Sloan, 1985) to measure the thermal properties of hydrates in sediments. At Rice University, Lievois (1987) developed a twin-cell heat flux calorimeter and made  $\Delta H$  measurements at 278.15 and 283.15 K to within  $\pm 2.6\%$ . More recently, at CSM a method was developed using the Setaram high pressure (heat-flux) micro-DSC VII (Gupta, 2007) to determine the heat capacity and heats of dissociation of methane hydrate at 277–283 K and at pressures of 5–20 MPa to within  $\pm 2\%$ . See [Section 6.3.2](#) for gas hydrate heat capacity and heats of dissociation data. Figure 6.6 shows a schematic of the heat flux DSC system. In heat flux DSC, the heat flow necessary to achieve a zero temperature difference between the reference and sample cells is measured through the thermocouples linked to each of the cells. For more details on the principles of calorimetry the reader is referred to Hohne et al. (2003) and Brown (1998).

### 6.1.2.2 Methods for thermal conductivity measurements

The two most common methods for thermal conductivity measurements for natural gas hydrates are the transient method and the steady-state method. Afanaseva



**FIGURE 6.6** Schematic of a heat flux DSC System.

and Groisman (1973) first measured hydrate thermal conductivity to be the same as ice with stated accuracy to within  $\pm 10\%$ . Stoll and Bryan (1979) first used the transient needle probe method on propane hydrates that have been compacted after formation, and showed the thermal conductivity of propane hydrate was about five times less than that of ice. The probe was modeled after the probe of von Herzen and Maxwell (1959) that had been used with marine sediments.

A slightly modified version of the probe comprised a stainless steel 20 gauge hypodermic tube containing a full length heater wire, a mid-tube thermistor, with epoxy filling the annulus. When a step power change is input to the heater, the probe temperature varies with the thermal conductivity of the material surrounding the probe. With good media contact at the probe boundary, the logarithmic increase of temperature with time gives an inverse relationship with the surrounding hydrate thermal conductivity. In the CSM laboratory the apparatus was used, and the mathematical model was refined and extended to short times by Asher (1987) for methane hydrates in sediments. The thermal conductivity accuracy was estimated to be within  $\pm 8\%$  for this transient method.

A conventional steady-state guarded hot-plate method for thermal conductivity measurement was used by Cook and Leaist (1983). Their apparatus was used to perform an exploratory measurement of methane hydrate to within  $\pm 12\%$ . A sample of methane hydrate was made externally, pressed, and placed in the hot-plate cell at the “Sample Disc.” The lower sample heater had thermocouples contacting the top and the bottom of the sample to determine the temperature gradient.

Waite et al. (2002, 2005) have measured thermal conductivities of hydrates using von Herzen and Maxwell’s (1959) needle probe method (see [Figure 6.7](#)). Waite et al. (2005) showed that THF hydrate (sII) and methane hydrate (sI) have similar thermal conductivities below 265.5 K. A novel method of determining the thermal conductivity of methane hydrate samples is to couple x-ray Computed Tomography (CT) measurements with numerical modeling using history matching of the data (Freifeld et al., 2002; Gupta et al., 2005; Moridis et al., 2005). See [Section 2.2.3.1](#) for more details.

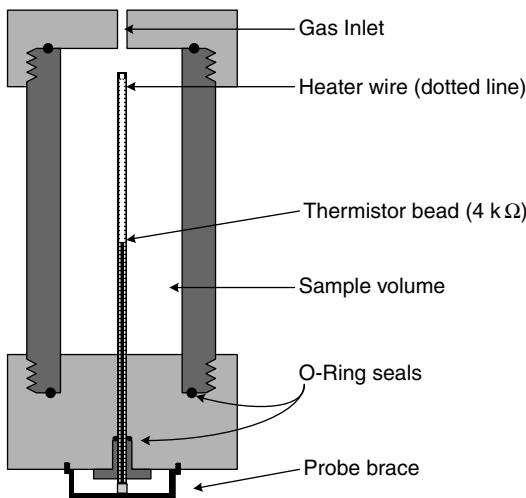
## 6.2 MEASUREMENTS OF THE HYDRATE PHASE

This section will outline the developments and significance of applying mesoscopic and molecular-level methods to measure hydrate thermodynamic and kinetic properties. The characteristics of these different techniques are also listed in [Tables 6.2](#) and [6.3](#).

### 6.2.1 Mesoscopic Measurements of the Hydrate Phase

Table 6.2 summarizes the mesoscopic methods that have been successfully applied to study hydrate properties. These are categorized as methods that provide a spatial resolution on the order of microns.

Laser scattering methods have been applied by the groups of Bishnoi and Sloan to measure changes in the hydrate particle size distribution during hydrate

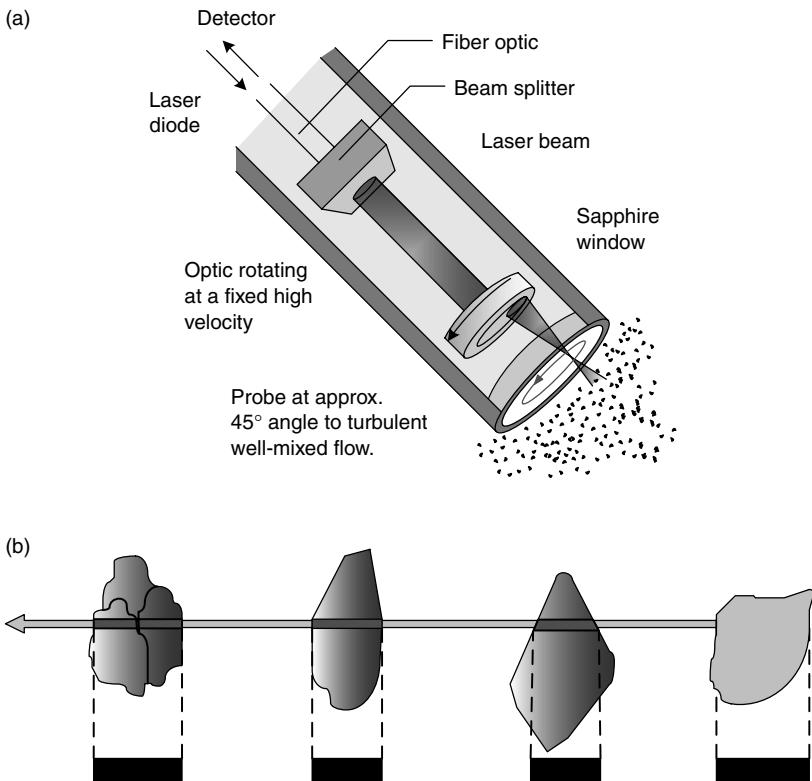


**FIGURE 6.7** Schematic of the pressure vessel and needle probe system used to measure thermal conductivity. (Reproduced from Waite, W.F., deMartin, B.J., Kirby, S.H., Pinkston, J., Ruppel, C.D., *Geophys. Res. Lett.*, **29**, 2229 (2002). With permission from the American Geophysical Union.)

formation and decomposition. One recent laser scattering method that has been applied to hydrate studies is the focused beam reflectance method, FBRM (Lasentec/Mettler Toledo) (Clarke and Bishnoi, 2000, 2001a,b; Turner et al., 2005a). The FBRM probe consists of a near-infrared laser with a wavelength of 785 nm, which is housed in a cylindrical probe. The laser rotates at high velocity (2–8 m/s) and is propagated through the sapphire window mounted on the probe tip. When the laser hits a particle, it is reflected and back propagated through the sapphire window. The corresponding chord length (distance between any two points on a particle surface) is thus the product of the rotating laser velocity and the measured intersecting time of the particle (Figure 6.8). From the chord lengths, the FBRM can be used to detect hydrate formation and monitor changes in particle size during hydrate growth and decomposition.

CSM has coupled the FBRM with a second probe, the particle video microscope, PVM (Lasentec/Mettler Toledo), which consists of six illuminating near-infrared lasers (850 nm) that are transmitted into the sample. While the FBRM provides precise quantitative tracking of the chord lengths, the PVM probe provides qualitative images of the hydrate particle size and degree of agglomeration. The size range scale of hydrate particles that can be measured with the PVM probe is 10–300  $\mu\text{m}$ .

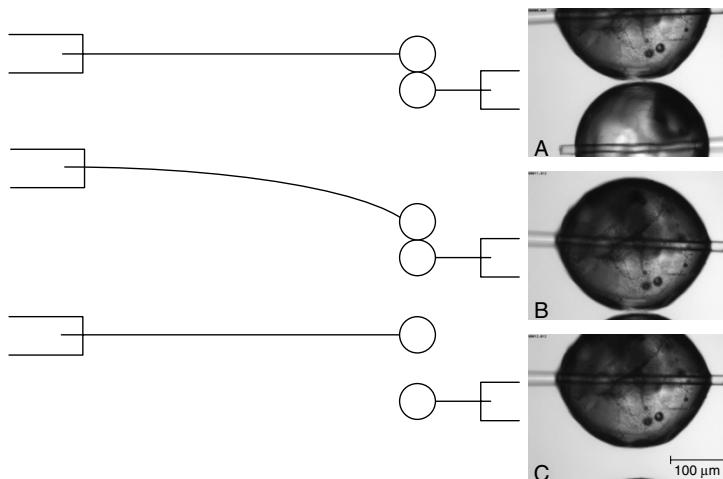
A micromechanical force apparatus has been developed at CSM to measure directly the adhesive forces between hydrate particles or between a hydrate particle and a surface (Yang et al., 2004; Taylor et al., 2007). Similar micromechanical force apparatus designs have been applied to measure adhesive forces between ice particles (Hosler, 1957; Hosler and Hallgren, 1961; Fan, 2003). This apparatus



**FIGURE 6.8** Schematic of the FBRM probe tip (a), and chord lengths (b). (Reproduced, with permission, from [www.lasentec.com](http://www.lasentec.com).)

consists of a stationary micromanipulator that holds a glass fiber cantilever ( $30\text{ }\mu\text{m}$  in diameter and  $3.5\text{ mm}$  in length). A hydrate particle is attached to the end of the glass fiber. The other glass fiber is attached to a moving micromanipulator and also has a hydrate particle on the end of the fiber (see Figure 6.9). The cantilevers and hydrate particles are immersed in a cooled surrounding fluid, such as decane and the moving manipulator pulls off/down, and depending on the attractive force between the particles, is displaced by a distance delta from the original position. The adhesive force is given as the spring constant of the glass fiber (determined from a previous calibration) multiplied by the displacement.

A glass micromodel method has been developed to observe gas hydrate formation from the water-gas interface and water-containing dissolved gas (Tohidi et al., 2001, 2002). The glass micromodel consists of an etched glass base plate with a sealed glass cover plate (Figure 6.10). Geometric networks of pores or flow channels (width  $>50\text{ }\mu\text{m}$ ) were etched onto the glass micromodel with hydrofluoric acid. Fluid was pumped into channels/pores through the cover plate that has an inlet and outlet. The micromodel was then placed in a vessel that was pressurized up to  $40\text{ MPa}$  with gas (methane or carbon dioxide). The liquid water phase was dyed

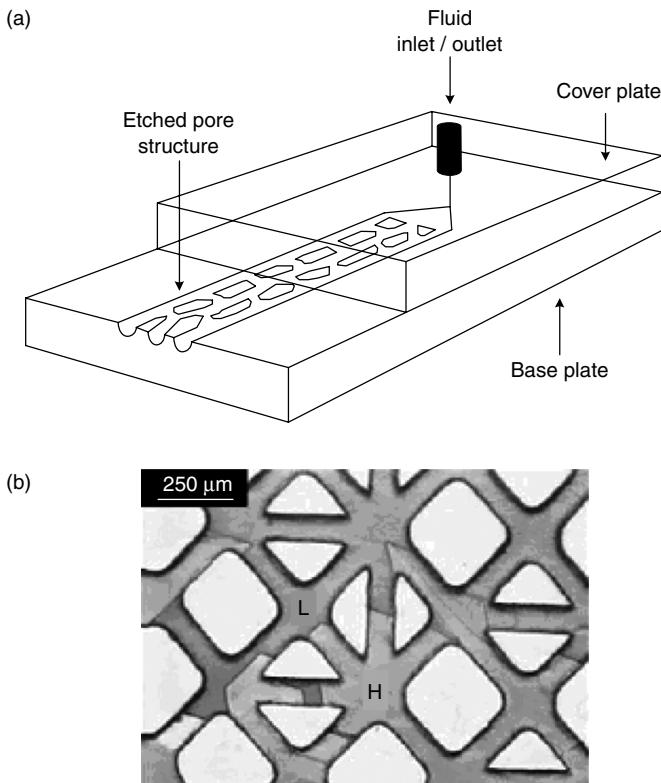


**FIGURE 6.9** A schematic of the micromechanical force measurement (left) and video images of hydrate particles during each stage of the adhesive force measurement. (From Taylor, C.J., *Adhesion Force between Hydrate Particles and Macroscopic Investigation of Hydrate Film Growth at the Hydrocarbon/Water Interface*, MS Thesis, Colorado School of Mines, Golden, CO (2006). With permission.)

with methyl blue to provide increased contrast between the liquid and gas/hydrate phases (hydrates and gas exclude the dye). The pore channels were only up to 50  $\mu\text{m}$  deep, and so phase changes from liquid water/gas to hydrate could be clearly observed. From these experiments, Tohidi et al. (2001, 2002) suggest that hydrate formation can occur at the liquid–gas interface, as well as from dissolved gas in water.

X-ray computed tomography (CT) measurements have been more recently applied to determine hydrate transport properties (thermal conductivity, thermal diffusivity, and permeability), and kinetic properties during hydrate core formation and dissociation (density profiling of the hydrate, gas, and water phases). The results illustrate the importance of spatially characterizing the hydrate core during transport and kinetic measurements to correctly interpret macroscopic data ( $P, T$ ). For example, the heterogeneous nature of a hydrate core has been clearly illustrated using x-ray CT analysis. Figure 6.11 illustrates the use of x-ray CT analysis to obtain visual images of the density profiles of slices of a hydrate core contained in a high pressure aluminum sample cell. Therefore, the application of x-ray CT analysis to hydrate cores presents a major advance to the measurement methods used for gas hydrates (Gupta et al., 2005; Kneafsey et al., 2005). Also see Section 2.2.3.1 for more details.

Other advances in mesoscopic measurements include the application of magnetic resonance imaging (MRI) to study real-time hydrate growth from ice particles and water droplets, and particle morphology (Moudrakovski et al., 2004). Scanning electron microscopy has also been shown to be a useful tool for studying natural



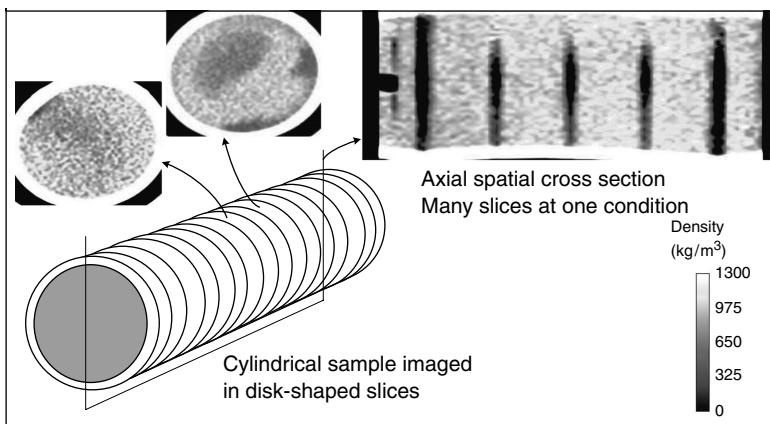
**FIGURE 6.10** Schematic of the glass micromodel apparatus (a) and the micromodel pore network (b). (Reproduced from Tohidi, B., Anderson, R., Clennell, B., Yang, J., Bashir, A., Burgass, R.W., in *Proc. Fourth International Conference on Gas Hydrates*, Yokohama, Japan, May 19–23, p. 761 (2002). With permission.)

and synthetic hydrate sample morphologies (Kuhs et al., 2000; Staykova et al., 2003; Stern et al., 2005). Also see Chapter 3, [Section 3.2.2.2](#) for more details.

### 6.2.2 Molecular-Level Measurements of the Hydrate Phase

Equilibrium measurements of the solid hydrate phase have been previously avoided due to experimental difficulties such as water occlusion, solid phase inhomogeneity, and measurements of solid phase concentrations. Instead, researchers have traditionally measured fluid phase properties (i.e., pressure, temperature, gas phase composition, and aqueous inhibitor concentrations) and predicted hydrate formation conditions of the solid phase using a modified van der Waals and Platteeuw (1959) theory, specified in [Chapter 5](#).

However, over the last decade there has been a significant shift in the number of researchers recognizing the importance of implementing mesoscopic and molecular-level methods to measure the hydrate phase directly. It is clear that



**FIGURE 6.11** (See color insert following page 390.) Schematic of the application of x-ray CT analysis to provide density profile images of different sections of a hydrate core contained in a cylindrical high pressure aluminum cell. (From Gupta, A., *Methane Hydrate Dissociation Measurements and Modeling: The Role of Heat Transfer and Reaction Kinetics*, Ph.D. Thesis, Colorado School of Mines, Golden, CO (2007). With permission.)

prediction without molecular-level measurements of the hydrate phase does not represent the state-of-the-art for hydrate equilibria, and must be considered as a less-than-optimal solution for at least three reasons:

1. The prediction of the hydrate phase is often mistaken. For example, over four decades ago Saito et al. (1964) published gas phase measurements of hydrate equilibria for methane, argon, and nitrogen at pressures to 690 MPa. When they fit the data with the van der Waals and Platteeuw model, they made the (then common) assumption that the single guest components formed sI hydrates. In 1984, however, x-ray diffraction data (Davidson et al., 1984) proved the Holder and Manganiello (1982) prediction that argon and nitrogen formed sII as single hydrate guests. The fact that the model could be fit to (and subsequently predict) the incorrect crystal structure suggests that the model is a means of data fitting, rather than an a priori prediction technique.

Since 1987, 39 sH hydrate formers have been reported, many of which are incorrectly listed in industrially important references such as the *API Databook* (Lippert et al., 1950), where methylcyclopentane and methylcyclohexane are listed as sII formers, and the *Handbook of Natural Gas Engineering* (Katz et al., 1959), where iso-pentane and methylcyclopentane are listed as non-hydrate formers.

2. In addition to the three known natural gas hydrates, several other hydrate structures exist. Dyadin et al. (1991) found four hydrate structures and Jeffrey (1984) proposed five additional hydrate structures. These structures have yet to be confirmed in natural gas systems, although new hydrate structures have been identified using x-ray diffraction such as a tetragonal structure for bromine (Udachin et al., 1997b), a trigonal structure for dimethyl ether (Udachin et al., 2001a),

a complex hydrate structure for choline hydroxide tetra-*n*-propylammonium fluoride (Udachin and Ripmeester, 1999), and high pressure (GPa range) hydrate phases (Dyadin et al., 1999; Mao et al., 2004).

The existence of other hydrate structures is also suggested by the striking analogy of hydrate cavities to the large Buckminsterfullerene family of carbon cavities. Both types of cavities obey Euler's Rule: cavities have exactly 12 pentagonal faces and any number of hexagonal faces, except one. Hydrates have the additional restriction that cavities should fill space continuously without excessive strain on the hydrogen bonds.

With the evolution of these new structures, the possibility of forming metastable hydrate phases (Section 3.2), and the fact that different structures form at different thermodynamic conditions (pressure, temperature, composition), it is clear that macroscopic methods cannot adequately predict the hydrate structure(s) present.

3. Prediction of the hydrate phase on a laboratory scale is analogous (in vapor–liquid equilibrium) to the prediction of the liquid phase concentration given only the vapor phase concentration, temperature, and pressure. Predictions of either the liquid phase or the hydrate phase are unacceptable because all experimental errors are transferred to prediction of the unmeasured phase.

It is clear from the above that molecular-level methods are required to determine the hydrate structure. Furthermore, these methods have identified several phenomena that shift the paradigm on our understanding of clathrate hydrates, including:

1. A binary mixture of methane + ethane, which are both sI hydrate formers, can form sII hydrate as the thermodynamically stable phase (Subramanian et al., 2000).
2. Metastable crystalline phases form during hydrate formation and decomposition (Staykova and Kuhs, 2003; Schicks et al., 2006).
3. Small molecules such as hydrogen form structure II hydrate (Dyadin et al., 1999; Mao et al., 2002; Lokshin et al., 2004).
4. At high pressures (>0.5 kbar) hydrate cavities can contain more than one guest for nitrogen, methane, or hydrogen (Chazallon and Kuhs, 2002; Mao et al., 2002; Loveday et al., 2003; Lokshin et al., 2004; Mao and Mao, 2004).

**Table 6.3** provides a summary of the different microscopic techniques that have been applied to hydrate studies and the type of information that can be obtained from these tools. The following discussion provides a brief overview of the application of diffraction and spectroscopy to study hydrate structure and dynamics, and formation/decomposition kinetics. For information on the principles and theory of these techniques, the reader is referred to the following texts on x-ray diffraction (Hammond, 2001), neutron scattering (Higgins and Benoit, 1996), NMR spectroscopy (Abragam, 1961; Schmidt-Rohr and Spiess, 1994), and Raman spectroscopy (Lewis and Edwards, 2001).

### 6.2.2.1 Diffraction methods

The classic method to obtain information on any crystal structure is via diffraction crystallography. Crystal structure information includes identification of the hydrate structure type, lattice parameters, guest occupancy, and guest position in the cavity. The earliest and most comprehensive x-ray diffraction studies were performed to define the crystal structure by von Stackelberg and coworkers (von Stackelberg, 1949, 1954; von Stackelberg and Müller, 1951a,b, 1954; von Stackelberg and Meinhold, 1954; von Stackelberg and Fruhbuss, 1954; von Stackelberg and Jahns, 1954) and confirmed by Jeffrey and coworkers (McMullan and Jeffrey, 1965; Jeffrey and McMullan, 1967; Jeffrey, 1984). More recent single crystal x-ray data were obtained for sI, sII, and sH by Udachin et al. (1997a, 2001b, 2002) and for sII by Kirchner et al. (2004). X-ray (Tse, 1987, 1990; Tse et al., 1987; Takeya et al., 2000; Udachin et al., 2001b) and neutron diffraction (Rawn et al., 2003) have been also used to determine the thermal expansion in sI, sII, sH hydrates.

It is worthwhile to note that the synchrotron x-ray facilities (e.g., ESRF in Grenoble, APS at Argonne, NSLS at Brookhaven) have significant advantages over laboratory x-ray instruments. The synchrotron x-ray source is significantly more intense than that from conventional sources. Therefore, this means the former measurements have far higher sensitivity than laboratory x-ray measurements, hence better *time resolution*, and the capability of using cells at higher pressures. The different x-ray methods available at a synchrotron source are summarized in Table 6.3. These methods range from x-ray scattering (EXAFS) to measure hydration structures or clustering during hydrate formation (Bowron et al., 1998; Montano et al., 2001) to x-ray powder diffraction for time-resolved hydrate structural studies (Koh et al., 1996; Mirinski et al., 2001).

Neutron diffraction studies have the advantage of being able to determine guest and host (both O and H/D) positions. With the difficulty of preparing single crystals of gas hydrates, most diffraction studies are performed on powder samples. Powder x-ray and neutron diffraction can be used with Rietveld analysis of the data for detailed structure determination (Rawn et al., 2003; Hester et al., 2006a).

Similar to the case of synchrotron x-ray diffraction, there are a number of different neutron scattering methods. These methods range from high resolution neutron powder diffraction for structure determination, to small angle neutron scattering, to neutron spectroscopy. Neutron powder diffraction has been applied by a number of researchers to study structural changes/transitions during hydrate formation (Halpern et al., 2001; Wang et al., 2002; Staykova and Kuhs, 2003).

Small angle neutron scattering instruments are specifically designed to examine disordered materials, such as to determine hydration structures during hydrate formation (Koh et al., 2000; Buchanan et al., 2005; Thompson et al., 2006), or to study kinetic inhibitor adsorption onto a hydrate surface (Hutter et al., 2000; King et al., 2000).

Neutron spectroscopy (also referred to as inelastic neutron scattering) has been used to measure the extent of guest–host interactions in a hydrate lattice, which help to explain the anomalous thermal behavior of hydrates (e.g., low thermal

conductivity). This work has been mostly performed by Tse and coworkers (1993, 1997a,b, 2001; Gutt et al., 2002).

### 6.2.2.2 Spectroscopic methods

Three main types of spectroscopy have been used to study hydrates. These are described below.

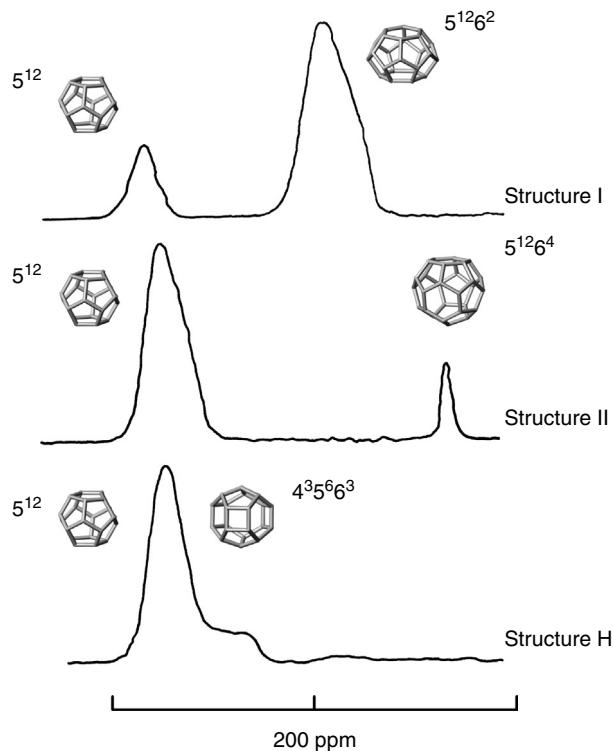
#### 6.2.2.2.1 Solid-state NMR spectroscopy

*Structure identification, quantifying relative cage occupancies.*  $^1\text{H}$  NMR has been used for ethane, propane, and isobutane hydrates (Davidson et al., 1977; Garg et al., 1977), while  $^2\text{H}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ , and  $^{77}\text{Se}$  NMR have been used for several sI guests (Collins et al., 1990).  $^{13}\text{C}$  cross-polarization and magic angle spinning (MAS) NMR techniques have been applied to study hydrates of carbon dioxide, methane, and propane (Ripmeester and Ratcliffe, 1988, 1999; Wilson et al., 2002; Kini et al., 2004).

$^{129}\text{Xe}$  NMR was shown to be capable of identifying ratios of xenon atoms in small and large cages (Pietrass et al., 1995; Moudrakovski et al., 2001). Subsequently, it was shown that there are unique chemical shifts for xenon in the cages of sI, sII, and sH hydrate (except for the  $5^{12}6^8$  cage which is not occupied by xenon) as shown in Figure 6.12.  $^{129}\text{Xe}$  is unique for NMR because, among hydrate guests, it has the largest chemical shift (100 ppm) compared to that for  $^{13}\text{C}$  (1–5 ppm) and can be used to resolve the shape of cages (Ripmeester and Ratcliffe, 1990). Some hydrocarbon chemical shifts are given in [Table 6.6](#).

*Kinetic studies during hydrate formation and decomposition, identifying changes in hydrate structure and relative cage occupancies.* Ripmeester et al. (Ripmeester and Ratcliffe, 1988; Ripmeester et al., 1994) introduced  $^1\text{H}$  cross-polarization techniques to enable relaxation times compatible with hydrate kinetic measurements. Pietrass et al. (1995) introduced techniques using optically polarized xenon to significantly increase the detection sensitivity to enable early stage hydrate formation to be monitored. Hyperpolarized Xe NMR has been applied to study Xe hydrate growth from ice (Moudrakovski et al., 2001). At CSM,  $^{13}\text{C}$  MAS NMR and non-spinning (NS) NMR have been used to study growth/decomposition of hydrates of methane (Gupta et al., 2006a), methane + propane (Kini et al., 2004), and methane + ethane (Bowler et al., 2005).

*Water mobility from molecular reorientation and diffusion.* Evidence for the motion of the water molecules in crystal structures is typically provided by  $^1\text{H}$  NMR (Davidson and Ripmeester, 1984). At very low temperatures (<50 K) molecular motion is “frozen in” so that hydrate lattices become rigid and the hydrate proton NMR analysis suggests that the first-order contribution to motion is due to reorientation of water molecules in the structure: the second-order contribution is due to translational diffusion.  $^2\text{H}$  NMR has been also used to measure the reorientational rates of water and guest molecules in THF hydrate (Bach-Verges et al., 2001). Spin lattice relaxation rates ( $T_1$ ) have been measured during THF hydrate



**FIGURE 6.12** Determination of ratios of xenon atoms in large and small hydrate cages using  $^{129}\text{Xe}$  NMR Spectroscopy at 77 K. (Reproduced from Ripmeester, J.A., Ratcliffe, C.I., *J. Phys. Chem.*, **94**, 8773 (1990).

formation and dissociation Gao et al. (2005). The authors suggest that close to the surface of the hydrate the liquid water is structured.

#### 6.2.2.2.2 Infrared spectroscopy

Bertie and co-workers (Bertie et al., 1975; Bertie and Jacobs, 1978) suggested that the strength of hydrogen bonds in hydrates is very similar to that in ice. Using FTIR (Fourier transform infrared) spectroscopy for low temperature growth of hydrate from the vapor phase, Bertie and Devlin (1983), Richardson et al. (1985a,b), and Fleyfel and Devlin (1988, 1991) showed that hydrates grow from the vapor phase only when Bjerrum L-type defects (induced by ethylene oxide) propagate through the crystal body to the surface.

However, IR spectroscopy has not been widely used for hydrate studies. This is largely due to the technical problems associated with sample preparation (e.g., vapor deposition of thin films) to avoid the high IR absorptivity of water, and the difficulties of performing *in situ* and high pressure measurements. Therefore, this technique will not be further discussed here.

### 6.2.2.2.3 Raman spectroscopy

Raman spectroscopy has been applied for the following.

*Structure identification and relative cage occupancies.* The hydration number and relative cage occupation for pure components and guests were measured by Sum et al. (1997), Uchida et al. (1999), and Wilson et al. (2002). Raman guest spectra of clathrate hydrates have been measured for the three known hydrate crystal structures: sI, sII, and sH. Long (1994) previously measured the kinetic phenomena for THF hydrate. Thermodynamic sI/sII structural transitions have been studied for binary hydrate systems (Subramanian et al., 2000; Schicks et al., 2006).

*Kinetic studies during hydrate formation and decomposition identifying changes in hydrate structure and relative cage occupancies.* (Subramanian and Sloan, 2000; Uchida et al., 2000; Schicks et al., 2006; Gupta et al., 2006a.) Among the different laser Raman spectrometers being used to study hydrates, three main configurations are used: a macro-cell without a fiber optics probe, a macro-cell with a fiber optics probe, and a micro-cell with a confocal Raman microscope. The fiber optics probe provides more flexibility in sampling. For example, a laser Raman spectrometer equipped with a fiber optics probe has been used during successful collaborative efforts between CSM and the Monterey Bay Aquarium Research Institute (MBARI) to measure natural hydrates on the ocean floor (at  $\sim 770$  m depths) in Hydrate Ridge in the Cascadia Margin (Hester et al., 2006b). The confocal Raman microscope is particularly powerful since it allows simultaneous micron-level visualization and Raman data to be collected on hydrate kinetics, as well as enabling fine control of the focus spot on the sample (Schicks et al., 2006).

The application of Raman spectroscopy becomes more challenging when samples exhibit significant fluorescence (e.g., sediment samples which are brown in color). Other difficulties occur when hydrate samples contain occluded gas (e.g., the vC–H peak for methane gas overlaps with that for methane in the small cage of structure I hydrate). In this case, care must be given to assignment of the spectra (Hester, 2007). The latter example illustrates the strength of combining Raman and NMR spectroscopy to ensure correct interpretation of the data.

In summary, spectroscopy and diffraction can provide important information about hydrates that are not accessible otherwise, namely,

- The hydration number
- Structure identification
- The relative occupancy of molecules in each cage
- Identification of metastable phases
- The kinetics of formation of various structures

NMR and Raman peak assignments for natural gas and non-natural gas hydrates are listed in [Tables 6.6](#) through [6.8](#), respectively. The NMR data presented are based on the works by Ripmeester and Ratcliffe (1998, 1999) and

**TABLE 6.6**  
**List of NMR Peak Assignments for Natural Gas Hydrates**

Guest molecule	Guest environment cage type	Chemical shift ppm
Methane	sI large	-6.1
	sI small	-4
	sII large	-7.7
	sII small	-3.95
Ethane	sI large	7.7
	sII large	6.5
Propane	sII large	17.7, 16.8 (18)
Iso-butane	sII large	26.6, 23.7

*Note:* Chemical shifts are from  $^{13}\text{C}$  MAS NMR using tetramethylsilane as a standard at 253 K.

Chemical shifts in parentheses are from  $^{13}\text{C}$  NS NMR.

**TABLE 6.7**  
**List of Raman Peak Assignments for Natural Gas Hydrates**

Guest composition	Vibrational mode	Guest environment ( $\text{cm}^{-1}$ )				
		Gas	Dissolved in water	Liquid	Cage type	Hydrate
CH <sub>4</sub>	v1 sym C—H stretch	2917 <sup>†</sup>	2911 <sup>†</sup>		sI large	2905 <sup>†</sup>
					sI small	2915 <sup>†</sup>
					sII large	2904 <sup>†</sup>
					sII small	2914 <sup>†</sup>
					sH medium	2905 <sup>†</sup>
					sH small	2913 <sup>†</sup>
CO <sub>2</sub>	v1 + 2v2	1266*	1274 <sup>§</sup>	1280 <sup>§</sup>	sI large	1276 <sup>§</sup>
	v1 + 2v2	1286*				
	v1 + 2v2	1389*	1382 <sup>§</sup>	1386 <sup>§</sup>	sI large	1381 <sup>§</sup>
	v1 + 2v2	1410*				
	v3 asym C—O stretch	2349 <sup>†</sup>			sI large	2335 <sup>†</sup>
	v3 asym C—O stretch				sI small	2347 <sup>†</sup>
	v3 asym C—O stretch				sII small	2345 <sup>†</sup>
	v2 bend CO <sub>2</sub>	667 <sup>†</sup>			sI large	660 <sup>†</sup>
	v2 bend CO <sub>2</sub>				sI small	655 <sup>†</sup>
	v2 bend CO <sub>2</sub>				sII small	655 <sup>†</sup>

(Continued)

**TABLE 6.7**  
Continued

Guest composition	Vibrational mode	Guest environment ( $\text{cm}^{-1}$ )			
		Gas	Dissolved in water	Liquid	Cage type
$\text{C}_2\text{H}_6$	v3 sym C—C stretch	994 <sup>†</sup>	1005 <sup>†</sup>	sI large	1001 <sup>†</sup>
	v3 sym C—C stretch				1020 <sup>†</sup>
	v3 sym C—C stretch				993 <sup>†</sup>
	v3 sym C—C stretch				1020 <sup>†</sup>
	v1 + 2v11 C—H	2900 <sup>†</sup>		sI large	2891 <sup>†</sup>
	v1 + 2v11 C—H	2956 <sup>†</sup>		sI large	2946 <sup>†</sup>
	v1 + 2v11 C—H			sII large	2887 <sup>†</sup>
	v1 + 2v11 C—H			sII large	2942 <sup>†</sup>
$\text{C}_2\text{H}_2$	v3 C—H stretch	3289 <sup>†</sup>		sI large	3261 <sup>†</sup>
				sI small	3280 <sup>†</sup>
				sII small	3274 <sup>†</sup>
$\text{C}_3\text{H}_8$	v8 sym C—C stretch	871 <sup>†</sup>		sII large	878 <sup>†</sup>
i-C <sub>4</sub> H <sub>10</sub>	v3 sym C—C stretch	799 <sup>†</sup>		sII large	812 <sup>†</sup>
$\text{CH}_4 + \text{N}_2$	v1 sym C—H stretch	2918*		sI large	2905*
	v1 sym C—H stretch			sI small	2915*
	v1 sym N—N stretch	2330*		sI small	2324*
CD <sub>4</sub> + C <sub>3</sub> H <sub>8</sub>	v1 sym C—D stretch	2110*		sII small	2103*
	v8 sym C—C (C <sub>3</sub> ) stretch	871*		sII large	878*
CH <sub>4</sub> + C <sub>7</sub> D <sub>14</sub>	v1 sym C—H stretch	2918*		sH small	2913*
$\text{C}_2\text{H}_6 + \text{C}_3\text{D}_8$	v3 sym C—C (C <sub>2</sub> ) stretch			sII large	993 <sup>†</sup>
	v1 + 2v11			sII large	2887 <sup>†</sup>
	v1 + 2v11			sII large	2942 <sup>†</sup>

<sup>a</sup> Raman spectra recorded at: CH<sub>4</sub> (g) at 298 K, 3.45 MPa, C<sub>2</sub>H<sub>6</sub> (g) at 298 K, 2.07 MPa, C<sub>2</sub>H<sub>6</sub> hydrate at 274 K, 1.03 MPa. sII hydrate from a C<sub>2</sub>H<sub>6</sub> (65 mol%) + C<sub>3</sub>D<sub>8</sub> (35 mol%) gas mixture at 274 K, 0.8 MPa. C<sub>3</sub>H<sub>8</sub> vapor and hydrate at 274 K, 0.61 MPa. i-C<sub>4</sub>H<sub>10</sub> hydrate at 274 K, 0.15 MPa.

<sup>b</sup> The symmetric C—C stretching mode of ethane hydrate shifts by 0.5  $\text{cm}^{-1}$  on increasing the pressure from 1.03 to 72.4 MPa (Subramanian, 2000).] Free gases when subjected to increasing pressure exhibit significant increases in the stretching mode frequencies, by 0.2–0.3  $\text{cm}^{-1}/\text{MPa}$ .

\* From Sum (1996).

<sup>†</sup> From Subramanian (2000).

<sup>§</sup> From Nakano et al. (1998b).

**TABLE 6.8**  
**List of Raman Peak Assignments for Nonnatural Gas Hydrates**

Guest composition	Vibrational mode	Guest environment ( $\text{cm}^{-1}$ )			
		Gas	Dissolved in water	Liquid	Cage type
$\text{C}_4\text{H}_8\text{O}$ (THF)	v12 predominantly sym C—C stretch		1036 <sup>†</sup>	1029 <sup>†</sup>	sI large
	v13 predominantly ring breathing		920 <sup>†</sup>	915 <sup>†</sup>	sI large
	v14 C—O—C sym stretch			892 <sup>†</sup>	
	v21 predominantly sym $\text{CH}_2$ stretch				sI large
	v4 predominantly sym $\text{CH}_2$ stretch				sI large
	v3 predominantly sym $\text{CH}_2$ stretch				sI large
	v19 predominantly asym $\text{CH}_2$ stretch				sI large
	v2 predominantly asym $\text{CH}_2$ stretch				sI large
	v18 asym $\text{CH}_2$ stretch				sI large
					2863 <sup>§</sup>
$\text{SO}_2$	v1 sym S—O stretch	1151.2 <sup>†</sup>			sI large
	v1 sym S—O stretch				sI small
	v3 asym S—O stretch	1361 <sup>†</sup>			sI large
	v3 asym S—O stretch				sI small
	v2 bending $\text{SO}_2$	519 <sup>†</sup>			sI large
	v2 bending $\text{SO}_2$				sI small
$(\text{SO}_4)^{2-}$	v1 sym S—O stretch		981		
$\text{O}_2$	v1 sym O—O stretch	1533 <sup>‡</sup>			sII small/ large
$\text{N}_2$	v1 sym N—N stretch	2329 <sup>‡</sup>			sII small/ large
$\text{H}_2$	H—H vibron(s) (pure molecular vibration)	4124 <sup>#</sup> 4141 <sup>#</sup> 4152 <sup>#</sup> 4158 <sup>#</sup>	4125 <sup>#</sup>		sII large sII small
					4135–4155 <sup>#</sup> 4115–4135 <sup>#</sup>

<sup>a</sup> Raman spectra were recorded under the following conditions:  $\text{H}_2$  (g) at 5 MPa, 298 K.  $\text{H}_2$  hydrate at 234 K and 200 MPa, THF hydrate at 10–170 K.

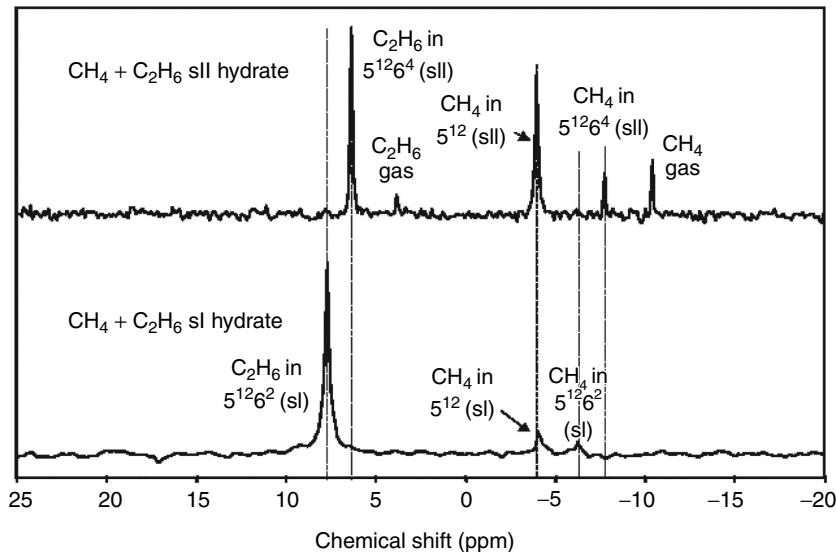
<sup>†</sup> From Subramanian (2000).

<sup>§</sup> From Tulk et al. (1998).

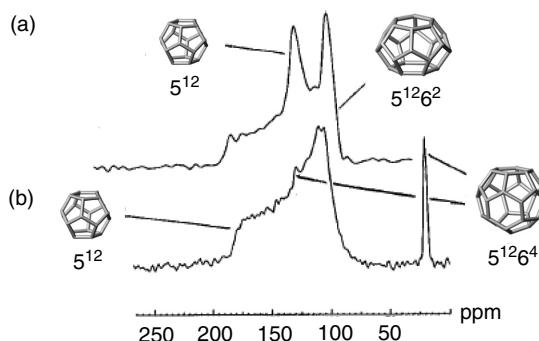
<sup>‡</sup> From Nakahara et al. (1988).

<sup>#</sup> From Florusse et al. (2004). THF assignments based on Cadioli et al. (1993).

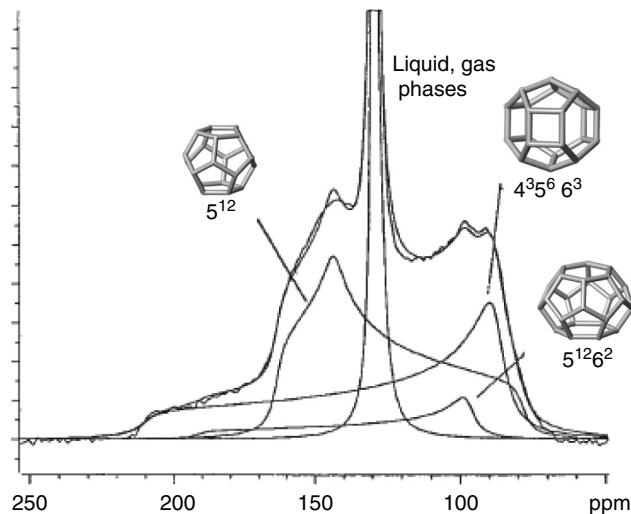
Kini (2002). The Raman data are based on the works by Sum (1996), Tulk et al. (1998), Subramanian (2000), and Hester (2007). To accompany these tables, select NMR and Raman spectra are given in Figures 6.13 through 6.19. These tables and sample spectra should serve as a useful reference to those embarking on spectroscopic measurements and analysis of clathrate hydrates.



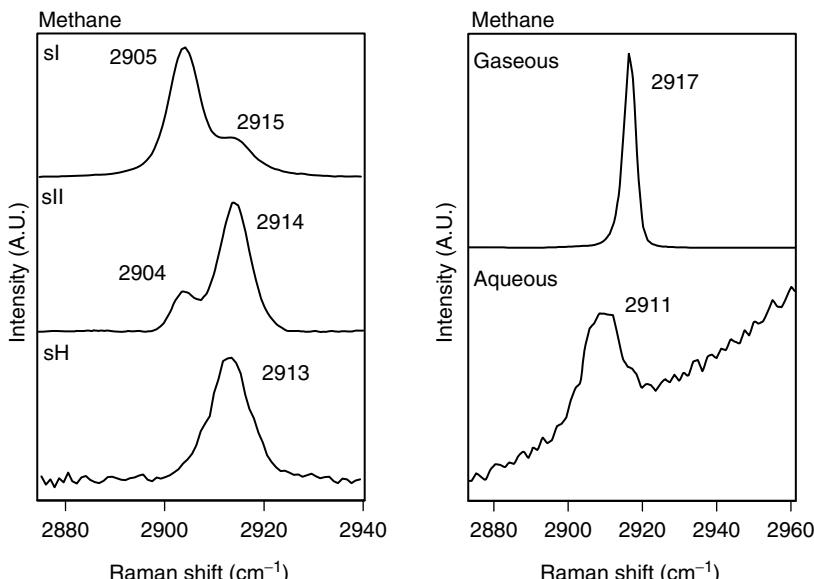
**FIGURE 6.13**  $^{13}\text{C}$  NMR spectra of sI and sII hydrates of methane + ethane. (From Kini, R.A., *NMR Studies of Methane, Ethane, and Propane Hydrates: Structure, Kinetics, and Thermodynamics*, Ph.D. Thesis, Colorado School of Mines, Golden, CO (2002). With permission.)



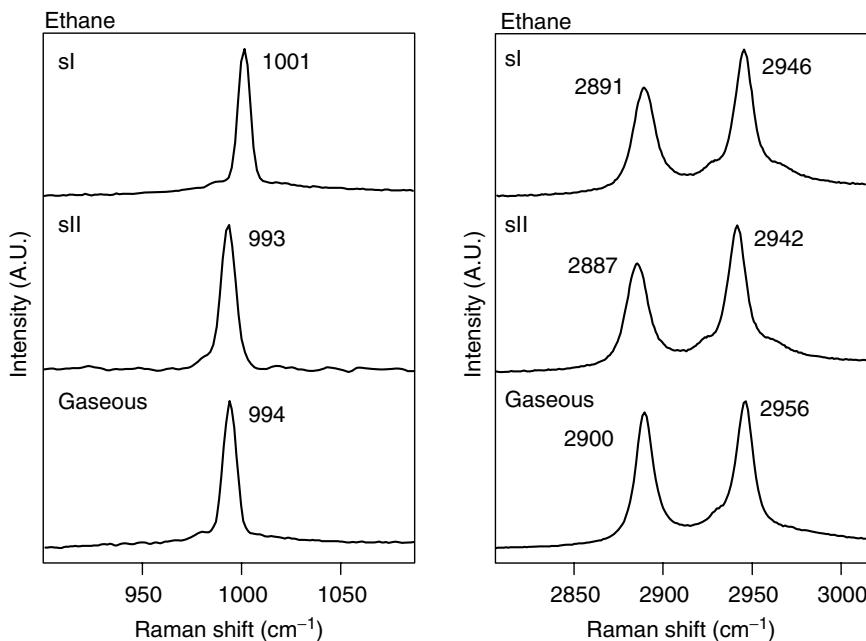
**FIGURE 6.14**  $^{13}\text{C}$  NMR spectra of (a)  $^{13}\text{CO}_2$  sI hydrate, (b)  $^{13}\text{CO}_2 + \text{C}_3\text{H}_8$  sII hydrate (isotropic line at 18 ppm is due to propane carbons). (From Ripmeester, J.A., and Ratcliffe, C.I., *Energy & Fuels*, **12**, 197 (1998). With permission.)



**FIGURE 6.15**  $^{13}\text{C}$  NMR spectra of  $^{13}\text{CO}_2 + \text{neohexane}$  sH hydrate. A small quantity of  $^{13}\text{CO}_2$  sI hydrate is also present; sH small cages occupied by  $\text{CO}_2$ . (From Ripmeester, J.A., and Ratcliffe, C.I., *Energy & Fuels*, **12**, 197 (1998). With permission.)



**FIGURE 6.16** Raman spectra of methane in the sI, sII (formed with  $\text{C}_2\text{D}_6$ ), sH (formed with  $\text{C}_7\text{D}_{14}$ ), gas and aqueous phases. (Collected by Hester; Subramanian.)



**FIGURE 6.17** Raman spectra of ethane in the sI, sII (formed with CD<sub>4</sub>), and gas phases. (Collected by Hester.)

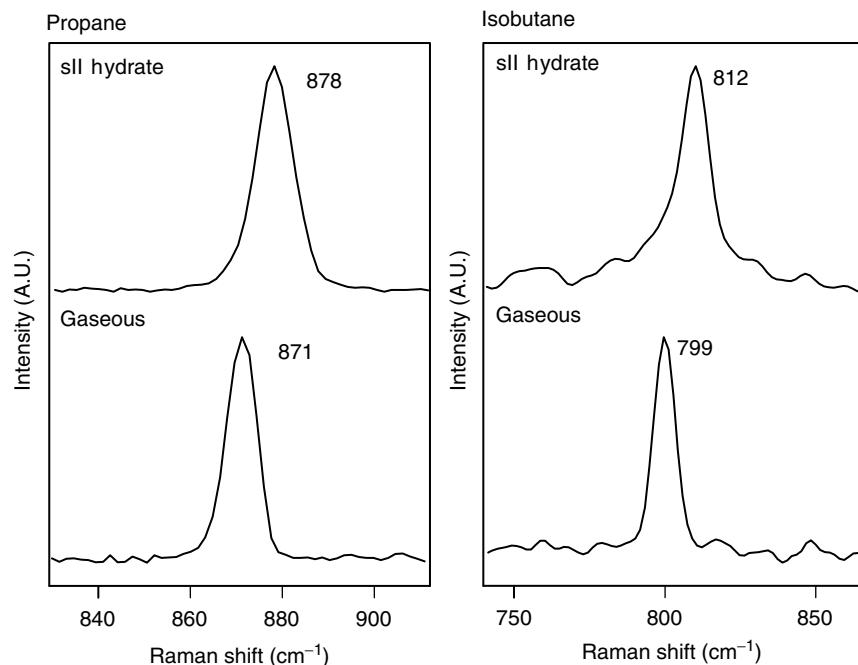
## 6.3 DATA FOR NATURAL GAS HYDRATE PHASE EQUILIBRIA AND THERMAL PROPERTIES

### 6.3.1 Phase Equilibria Data

#### 6.3.1.1 Equilibria of simple natural gas components

The accuracy of hydrate data has seldom been specified by experimentalists. In the following data, only a cursory effort has been made to exclude inaccurate data for simple hydrates. All three-phase data sets for simple hydrates were plotted (as logarithm pressure versus absolute temperature) to determine outliers.

In general, the data accuracy was surprisingly good. For example, while Deaton and Frost (1946, p. 13) specified that their “pure” ethane contained 2.1% propane and 0.8% methane, effects of those impurities may have counterbalanced each other; those impurities were insufficient to cause the data to fall outside the line formed by other ethane data sets. On the other hand, the simple hydrate data of Hammerschmidt (1934) for propane and isobutane all appear to be outliers on such semilogarithmic plots, because they are at temperatures much too far above the upper quadruple (Q<sub>2</sub>) point. Obvious outlying data were excluded from this work; less obvious outliers may be determined by inspection of the plots and subsequent numerical comparisons. The data, followed by the semilogarithmic plots



**FIGURE 6.18** Raman spectra of the hydrate and gas phases of propane and iso-butane. (Collected by Subramanian.)

for each simple hydrate, are listed chronologically by compound, in the following order: methane, ethane, propane, isobutane, carbon dioxide, nitrogen, and hydrogen sulfide.

While most of the simple hydrate data consist of the three-phase and quadruple point type, the available two-phase simple hydrate data are listed for methane, ethane, propane, and carbon dioxide. Plots of these data are not suitable for comparison between data sets and are therefore not provided.

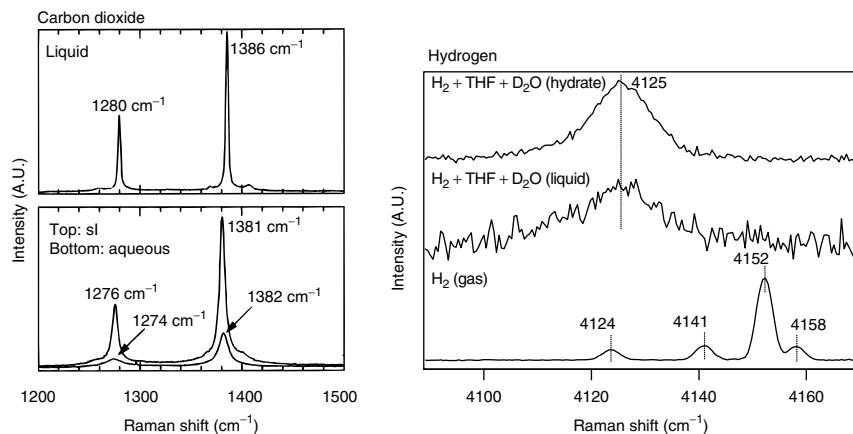
## METHANE

*Hydrate:* Methane

*Reference:* Roberts et al. (1940)

*Phases:* I-H-V and L<sub>W</sub>-H-V

T (K)	P (MPa)	Phases	T (K)	P (MPa)	Phases
259.1	1.648	I-H-V	286.5	10.63	L <sub>W</sub> -H-V
273.2	2.641	L <sub>W</sub> -I-H-V	286.7	10.80	L <sub>W</sub> -H-V
280.9	5.847	L <sub>W</sub> -H-V			



**FIGURE 6.19** Raman spectra of carbon dioxide in the liquid, hydrate, and aqueous phase. (Reproduced from Nakano, S., Moritoki, M., Ohgaki, K., *J. Chem. Eng. Data*, **43**, 807 (1998b). With permission from the American Chemical Society.) and hydrogen. (Reproduced from Florusse, L.J., Peters, C.J., Schoonman, J., Hester, K.C., Koh, C.A., Dec, S.F., Marsh, K.N., Sloan, E.D., *Science*, **306**, 469 (2004).)

*Hydrate:* Methane

*Reference:* Deaton and Frost (1946)

*Phases:* I–H–V and L<sub>W</sub>–H–V

### I–H–V

T (K)	P (MPa)						
262.4	1.79	266.5	2.08	268.6	2.22	270.9	2.39
264.2	1.90						

### L<sub>W</sub>–H–V

T (K)	P (MPa)						
273.7	2.77	275.9	3.43	280.4	5.35	282.6	6.77
274.3	2.90	277.1	3.81	280.9	5.71	284.3	8.12
275.4	3.24	279.3	4.77	281.5	6.06	285.9	9.78
275.9	3.42						

*Hydrate:* Methane

*Reference:* Kobayashi and Katz (1949)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (MPa)						
295.7	33.99	295.9	35.30	301.0	64.81	302.0	77.50

*Hydrate:* Methane

*Reference:* McLeod and Campbell (1961)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (MPa)						
285.7	9.62	285.7	9.62	295.9	34.75	300.9	62.40
286.3	10.31	289.0	13.96	298.7	48.68	301.6	68.09
286.1	10.10	292.1	21.13				

*Hydrate:* Methane

*Reference:* Marshall et al. (1964a)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (MPa)						
290.2	15.9	298.1	44.3	306.7	110.8	315.1	237.5
290.5	15.9	298.2	43.8	310.3	152.7	316.8	271.7
295.2	30.0	300.2	56.9	312.7	187.3	318.3	319.7
295.1	29.9	301.6	65.4	313.7	206.3	319.6	367.8
295.8	33.8	301.6	65.4	314.2	223.9	320.1	397.0

*Hydrate:* Methane

*Reference:* Jhaveri and Robinson (1965)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (MPa)						
273.2	2.65	280.4	5.58	287.3	11.65	291.7	20.11
277.6	4.17	284.7	8.67	288.9	14.05	294.3	28.57

*Hydrate:* Methane

*Reference:* Galloway et al. (1970)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (MPa)						
283.2	7.10	283.2	7.12	288.7	13.11	288.7	13.11

*Hydrate:* Methane

*Reference:* Verma (1974)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (MPa)						
275.2	3.02	278.6	4.385	285.4	9.191	291.2	18.55
276.7	3.69	288.5	13.04	290.7	16.96		

*Hydrate:* Methane

*Reference:* Falabella (1975)

*Phases:* I–H–V

T (K)	P (kPa)						
148.8	5.3	168.8	21.1	191.3	90.1	193.2	101.3
159.9	12.1	178.2	42.0				

*Hydrate:* Methane

*Reference:* Aoyagi et al. (1980)

*Phases:* V–H

T (K)	P (MPa)	H <sub>2</sub> O (ppm(mol))	T (K)	P (MPa)	H <sub>2</sub> O (ppm(mol))
		12.30			3.45
240.0	3.45	12.30	260.0	3.45	78.24
240.0	6.90	5.60	260.0	6.90	39.56
240.0	10.34	2.72	260.0	10.34	24.23
250.0	3.45	32.17	270.0	3.45	178.09
250.0	6.90	15.45	270.0	6.90	94.43
250.0	10.34	8.46	270.0	10.34	64.22

*Hydrate:* Methane

*Reference:* de Roo et al. (1983)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (MPa)						
273.3	2.69	279.5	5.04	282.8	7.04	285.0	9.04
275.4	3.34	281.3	6.04	284.0	8.05	286.0	10.04
276.0	3.34						

*Hydrate:* Methane

*Reference:* Thakore and Holder (1987)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (MPa)						
275.4	2.87	277.2	3.90	279.2	4.90	281.2	6.10
276.2	3.37	278.2	4.50				

*Hydrate:* Methane

*Reference:* Adisasmito et al. (1991)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (MPa)						
273.4	2.68	278.3	4.39	282.3	6.65	285.7	9.17
274.6	3.05	279.6	5.02	283.6	7.59	286.4	10.57
276.7	3.72	280.9	5.77	284.7	8.55		

*Hydrate:* Methane

*Reference:* Makogon and Sloan (1994)

*Phases:* I–H–V

T (K)	P (MPa)						
190.2	0.08251	208.2	0.222	243.2	0.9550	262.4	1.798
198.2	0.1314	218.2	0.3571				

*Hydrate:* Methane at high pressure

*Reference:* Dyadin and Aladko (1996)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
287.0	8	319.0	358	320.8	590	325.0	806
296.6	37	320.0	405	320.6	600	325.4	814
300.8	59	320.4	443	320.2	631	316.8m	816
303.6	84	320.4	450	321.8	642	325.2	840
307.2	117	320.8	467	320.0m	658	325.6	864
308.6	133	320.8	506	322.8	707	326.6	874
310.6	162	320.9	527	324.0	731	326.0	902
311.0	166	320.9	536	319.0m	734	326.4	956
313.8	216	320.9	548	318.6m	749	326.6	983
315.6	242	320.9	572	318.2m	784	326.8	1000
318.4	317	320.8	580	325.2	786		

m = metastable phase.

*Hydrate:* Methane at High Pressure

*Reference:* Nakano et al. (1999)

*Phases:* Lw–H–V

<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
305.08	98	315.74	258
307.13	119	316.50	277
308.74	138	317.20	299
310.29	158	318.29	335
311.64	178	319.17	376
312.92	199	319.80	414
313.88	217	320.33	455
314.83	237	320.54	493

*Hydrate:* Methane

*Reference:* Nakamura et al. (2003)

*Phases:* Lw–H–V

<b>T (K)</b>	<b>P (MPa)</b>	<b><math>\Delta H</math> (kJ/mol)</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b><math>\Delta H</math> (kJ/mol)</b>
274.25	2.92	57.1	282.23	6.53	54.2
275.25	3.22	57.2	282.73	6.88	53.7
276.22	3.55	57.1	283.25	7.25	53.3
277.24	3.92	57.1	283.74	7.65	52.6
278.24	4.33	56.9	284.26	8.10	51.8
279.23	4.79	56.4	284.76	8.55	51.1
280.24	5.31	55.9	285.25	9.03	50.3
281.24	5.89	55.1	285.78	9.54	49.7
281.73	6.20	54.6			

$\Delta H$ : Enthalpy of hydrate formation calculated from the above data using the Clapeyron equation assuming ideal hydration.

*Hydrate:* Methane

*Reference:* Mohammadi et al. (2005)

*Phases:* L<sub>W</sub>–H–V

Setup	T (K) ( $\pm 0.1$ )	P (MPa) ( $\pm 0.007$ )
1	280.5	5.426
	283.7	7.584
	285.7	9.584
	286.4	10.342
	289.9	15.837
2	274.6	3.060
	276.2	3.446
	290.6	17.257
	293.6	25.841
	295.8	34.584
	298.3	47.863

Setup 1: 75 cm<sup>3</sup> equilibrium cell.  
 Setup 2: 650 cm<sup>3</sup> equilibrium rocking cell.

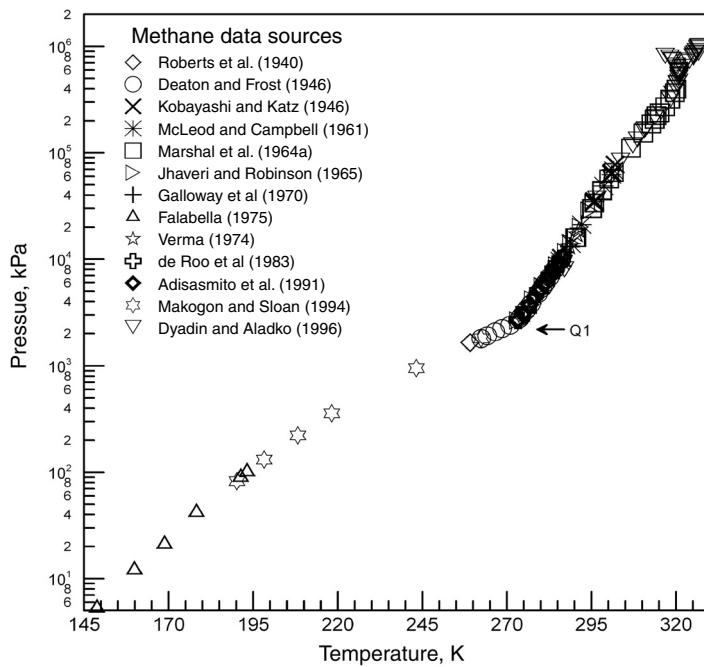
*Hydrate:* Methane

*Reference:* Yang et al. (2001)

*Phases:* L<sub>W</sub>–H

T (K)	P (MPa)	x <sub>CH<sub>4</sub></sub>	T (K)	P (MPa)	x <sub>CH<sub>4</sub></sub>
278.1	5.79	0.00114	278.1	19.35	0.000960
278.1	8.12	0.00103	273.1	4.98	0.000775
278.2	8.89	0.00104	273.1	5.20	0.000751
278.2	10.44	0.00113	273.1	7.85	0.000770
278.2	11.18	0.00101	273.1	8.42	0.000776
278.1	11.53	0.00106	273.1	11.63	0.000763
278.2	13.76	0.00106	273.1	12.28	0.000752
278.1	16.02	0.00100	273.1	13.50	0.000807
278.1	16.54	0.000953	273.1	14.81	0.000765
278.1	19.29	0.000954			

x<sub>CH<sub>4</sub></sub>: mole fraction of methane in water.



**FIGURE 6.20** Three-phase data for simple hydrates of methane.

*Hydrate:* Methane

*Reference:* Yang (2000)

*Phases:* L<sub>W</sub>-H

T (K)	P (MPa)	x <sub>CH<sub>4</sub></sub> in water
276.19	50.00	0.00125
277.85	50.81	0.00150
279.85	50.98	0.00165
280.47	51.26	0.00175
276.36	101.00	0.00125
278.71	101.73	0.00150
280.11	101.88	0.00165
280.65	102.43	0.00175
276.67	127.10	0.00125
278.90	127.22	0.00150
280.39	127.35	0.00165
281.08	127.45	0.00175
276.91	143.10	0.00125

**Continued**

<b>T (K)</b>	<b>P (MPa)</b>	<b>x<sub>CH<sub>4</sub></sub> in water</b>
279.20	143.62	0.00150
280.59	143.25	0.00165
281.65	143.24	0.00175

$x_{\text{CH}_4}$ : mole fraction of methane in water.

*Hydrate:* Methane

*Reference:* Seo and Lee (2002)

*Phases:* L<sub>W</sub>-H

<b>T (K)</b>	<b>P (MPa)</b>	<b>x<sub>CH<sub>4</sub></sub></b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>x<sub>CH<sub>4</sub></sub></b>
274.15	6.00	0.001264	282.15	15.00	0.001621
278.15	6.00	0.001452	286.15	15.00	0.001826
274.15	10.00	0.001202	274.15	20.00	0.001106
278.15	10.00	0.001414	278.15	20.00	0.001322
282.15	10.00	0.001687	282.15	20.00	0.001583
274.15	15.00	0.001157	286.15	20.00	0.001799
278.15	15.00	0.001362			

$x_{\text{CH}_4}$ : mole fraction of methane in water.

*Hydrate:* Methane

*Reference:* Servio and Englezos (2002)

*Phases:* L<sub>W</sub>-H, L<sub>W</sub>-H-V, L<sub>W</sub>-V

<b>T (K)</b>	<b>P (MPa)</b>	<b>x<sub>CH<sub>4</sub></sub></b>	<b>Phases</b>	<b>P</b>			<b>Phases</b>
				<b>T (K)</b>	<b>P (MPa)</b>	<b>x<sub>CH<sub>4</sub></sub></b>	
274.35	3.5	0.001170	L <sub>W</sub> -H	281.55	5.0	0.001524	L <sub>W</sub> -V
275.45	3.5	0.001203	L <sub>W</sub> -H	282.65	5.0	0.001357	L <sub>W</sub> -V
276.25	3.5	0.001240	L <sub>W</sub> -H-V	275.25	6.5	0.001201	L <sub>W</sub> -H
278.65	3.5	0.001190	L <sub>W</sub> -V	280.15	6.5	0.001567	L <sub>W</sub> -H
280.45	3.5	0.001102	L <sub>W</sub> -V	282.05	6.5	0.001850	L <sub>W</sub> -H-V
274.15	5.0	0.001190	L <sub>W</sub> -H	283.25	6.5	0.001720	L <sub>W</sub> -V
277.35	5.0	0.001360	L <sub>W</sub> -H	284.35	6.5	0.001681	L <sub>W</sub> -V
279.65	5.0	0.001600	L <sub>W</sub> -H-V				

$x_{\text{CH}_4}$ : mole fraction of methane in water.

*Hydrate:* Methane

*Reference:* Chou, I.M. and Burruss, R.C. (Personal Communication, December 18, 2006).

*Phases:* L<sub>W</sub>-H

T (K)	P (MPa)	x <sub>CH<sub>4</sub></sub>	T (K)	P (MPa)	x <sub>CH<sub>4</sub></sub>
278.1	5.79	0.00114	278.1	19.35	0.00096
278.1	8.12	0.00103	273.1	4.98	0.000775
278.2	8.89	0.00104	273.1	5.20	0.000751
278.2	10.44	0.00113	273.1	7.85	0.00077
278.2	11.18	0.00101	273.1	8.42	0.000776
278.1	11.53	0.00106	273.1	11.63	0.000763
278.2	13.76	0.00106	273.1	12.28	0.000752
278.1	16.02	0.00100	273.1	13.50	0.000807
278.1	16.54	0.000953	273.1	14.81	0.000765
278.1	19.29	0.000954			

x<sub>CH<sub>4</sub></sub>: mole fraction of methane in water in the absence of a vapor phase.

## ETHANE

*Hydrate:* Ethane

*Reference:* Roberts et al. (1940)

*Phases:* I-H-V, L<sub>W</sub>-H-V, L<sub>W</sub>-H-L<sub>C<sub>2</sub>H<sub>6</sub></sub>

T (K)	P (kPa)	Phases	T (K)	P (kPa)	Phases
260.8	294	I-H-V	285.8	2537	L <sub>W</sub> -H-V
260.9	290	I-H-V	287.0	3054	L <sub>W</sub> -H-V
269.3	441	I-H-V	287.7	4909	L <sub>W</sub> -H-L <sub>E</sub>
273.4	545	L <sub>W</sub> -H-V	287.8	3413	L <sub>W</sub> -H-L <sub>E</sub>
275.4	669	L <sub>W</sub> -H-V	287.8	4289	L <sub>W</sub> -H-L <sub>E</sub>
277.6	876	L <sub>W</sub> -H-V	288.1	3716	L <sub>W</sub> -H-L <sub>E</sub>
279.1	1048	L <sub>W</sub> -H-V	288.1	6840	L <sub>W</sub> -H-L <sub>E</sub>
219.7	1131	L <sub>W</sub> -H-V	288.2	4944	L <sub>W</sub> -H-L <sub>E</sub>
281.1	1317	L <sub>W</sub> -H-V	288.2	5082	L <sub>W</sub> -H-L <sub>E</sub>
282.8	1641	L <sub>W</sub> -H-V	288.3	4358	L <sub>W</sub> -H-L <sub>E</sub>
284.4	2137	L <sub>W</sub> -H-V	288.4	6840	L <sub>W</sub> -H-L <sub>E</sub>
284.6	2055	L <sub>W</sub> -H-V			

*Hydrate:* Ethane

*Reference:* Deaton and Frost (1946)

*Phases:* I–H–V and L<sub>W</sub>–H–V

### I–H–V

T (K)	P (kPa)						
263.6	313	266.5	357	269.3	405	272.0	457

### L<sub>W</sub>–H–V

T (K)	P (kPa)						
273.7	510	278.7	931	280.4	1165	283.2	1689
273.7	503	278.7	931	280.9	1255	284.3	1986
274.8	579	279.3	1007	281.5	1345	285.4	2303
275.9	662	279.8	1083	282.1	1448	285.4	2310
277.6	814	280.4	1165	282.6	1558	286.5	2730

*Hydrate:* Ethane

*Reference:* Reamer et al. (1952b)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (kPa)						
279.9	972	282.8	1666	284.7	2129	287.4	3298

*Hydrate:* Ethane

*Reference:* Galloway et al. (1970)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)
277.6	814	277.7	823	282.5	1551

*Hydrate:* Ethane

*Reference:* Falabella and Vanpee (1974)

*Phases:* I–H–V

T (K)	P (kPa)						
200.8	8.3	230.2	56.4	240.4	98.1	240.8	101.3
215.7	22.1						

*Hydrate:* Ethane

*Reference:* Holder and Grigoriou (1980)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (kPa)						
277.5	780	279.9	1040	283.3	1660	286.5	2620
278.1	840	281.5	1380	284.5	2100		

*Hydrate:* Ethane

*Reference:* Holder and Hand (1982)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (MPa)						
278.8	950	282.0	1450	286.0	2510	288.2	3360
280.2	1140	281.1	1280	286.5	2600		

*Hydrate:* Ethane

*Reference:* Ng and Robinson (1985)

*Phases:* L<sub>W</sub>–H–L<sub>C<sub>2</sub>H<sub>6</sub></sub>

T (K)	P (MPa)						
288.0	3.33	288.2	5.00	288.5	6.99	289.7	13.95
288.1	3.84	288.4	6.06	289.2	10.39	290.6	20.34

*Hydrate:* Ethane

*Reference:* Avlonitis (1988)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (MPa)						
277.8	0.848	280.4	1.200	282.3	1.551	285.9	2.461
278.6	0.945	281.5	1.365	284.0	1.889	287.2	3.082
279.4	1.055	282.1	1.510				

*Hydrate:* Ethane

*Reference:* Song and Kobayashi (1994)

*Phases:* H–V and H–L<sub>C<sub>2</sub>H<sub>6</sub></sub>

### H–V Isobar at 2.483 MPa

T (K)	$y_{\text{H}_2\text{O}} \times 10^3$	T (K)	$y_{\text{H}_2\text{O}} \times 10^3$	T (K)	$y_{\text{H}_2\text{O}} \times 10^3$
276.2	0.345	280.0	0.455	283.6	0.575

### H–L<sub>C<sub>2</sub>H<sub>6</sub></sub> Isobar at 3.45 MPa

T (K)	$x_{\text{H}_2\text{O}} \times 10^3$	T (K)	$x_{\text{H}_2\text{O}} \times 10^3$	T (K)	$x_{\text{H}_2\text{O}} \times 10^3$
281.2	0.135	271.2	0.058	240.0	0.004
276.2	0.090	260.0	0.024		

*Hydrate:* Ethane

*Reference:* Nakano et al. (1998a)

*Phases:* L<sub>w</sub>–H–L<sub>C<sub>2</sub>H<sub>6</sub></sub>

T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
290.42	19.48	293.01	39.15	295.91	61.60
290.85	23.00	293.24	40.62	296.51	67.52
291.16	25.02	293.35	41.57	297.12	71.89
291.36	26.21	293.56	42.49	297.57	77.30
291.66	28.73	293.61	43.32	297.65	77.43
291.90	30.56	293.95	45.37	297.73	78.09
292.12	31.67	294.76	51.92	298.01	82.19
292.36	33.63	295.60	59.83	298.36	83.75
292.56	34.39	295.80	60.86		

*Hydrate:* Ethane

*Reference:* Yang (2000)

*Phases:* L<sub>w</sub>–H

P (MPa)	T (K)	$x_{\text{C}_2\text{H}_6}$ in water
51.0	277.31	0.0004115
101.0	277.82	0.0004115
151.0	278.46	0.0004115

*Hydrate:* Ethane

*Reference:* Morita et al. (2000)

*Phases:* Lw–H– $\text{L}_{\text{C}_2\text{H}_6}$

<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)
298.01	89	314.20	298
299.15	99	315.26	318
300.82	119	316.39	336
302.56	139	317.49	355
304.15	158	318.67	374
305.65	178	319.65	393
307.26	198	320.72	413
308.57	217	322.11	436
301.07	237	322.83	454
311.44	257	323.93	479
312.86	279		

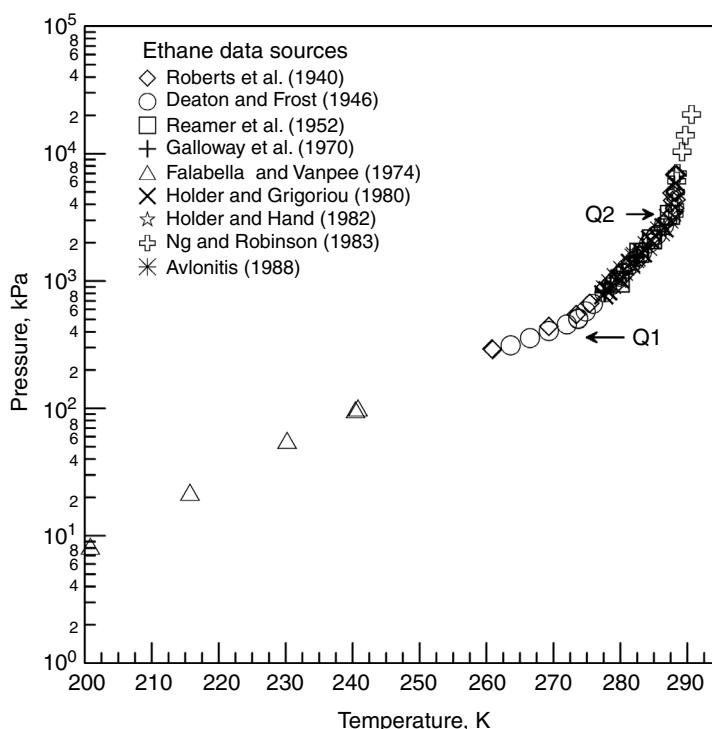


FIGURE 6.21 Three-phase data for simple hydrates of ethane.

**PROPANE***Hydrate:* Propane*Reference:* Wilcox et al. (1941)*Phases:* L<sub>W</sub>–H–L<sub>C<sub>3</sub>H<sub>8</sub></sub>

<b>T</b> (K)	<b>P</b> (kPa)						
278.9	807	278.6	1758	279.2	2902	278.9	6115
278.6	1296	278.8	2034	278.8	4247		

*Hydrate:* Propane*Reference:* Miller and Strong (1946)*Phases:* L<sub>W</sub>–H–V

<b>T</b> (K)	<b>P</b> (kPa)						
273.2	165	273.7	186	277.1	390	277.8	459
273.4	172	273.9	190	277.2	393	278.0	472
273.5	176	276.8	365				

*Hydrate:* Propane*Reference:* Deaton and Frost (1946)*Phases:* I–H–V and L<sub>W</sub>–H–V**I–H–V**

<b>T</b> (K)	<b>P</b> (kPa)						
261.2	100	267.4	132	269.8	149	272.9	172
264.2	115	267.6	135	272.2	167		

**L<sub>W</sub>–H–V**

<b>T</b> (K)	<b>P</b> (kPa)						
273.7	183	274.8	232	275.9	301	277.1	386
273.7	183	275.4	270				

*Hydrate:* Propane

*Reference:* Reamer et al. (1952)

*Phases:* L<sub>W</sub>-H-V and L<sub>W</sub>-H-L<sub>C<sub>3</sub>H<sub>8</sub></sub>

### L<sub>W</sub>-H-V

T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)
274.3	241	275.7	305	277.2	414

### L<sub>W</sub>-H-L<sub>C<sub>3</sub>H<sub>8</sub></sub>

T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)
278.6	684	278.7	1477	278.8	2046

*Hydrate:* Propane

*Reference:* Robinson and Mehta (1971)

*Phases:* L<sub>W</sub>-H-V

T (K)	P (kPa)						
274.3	207	276.4	331	277.8	455	278.9	552*
274.8	241						

\* = Q<sub>2</sub> Quadruple point (L<sub>W</sub>-H-V-L<sub>C<sub>3</sub></sub>).

*Hydrate:* Propane

*Reference:* Verma (1974)

*Phases:* L<sub>W</sub>-H-V, L<sub>W</sub>-H-L<sub>C<sub>3</sub>H<sub>8</sub></sub> and L<sub>W</sub>-H-V-L<sub>C<sub>3</sub>H<sub>8</sub></sub>

### L<sub>W</sub>-H-V, L<sub>W</sub>-H-L<sub>C<sub>3</sub>H<sub>8</sub></sub>

T (K)	P (kPa)						
273.9	188	275.7	288	276.7	361	278.0	512
274.6	219	276.2	322	277.4	425	278.4	562*
275.1	250						

\* = L<sub>W</sub>-H-V-L<sub>C<sub>3</sub></sub> Quadruple point.

### L<sub>W</sub>-H-V-L<sub>C<sub>3</sub>H<sub>8</sub></sub>

T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
278.42	3.87	278.5	7.03	278.6	11.3	278.5	16.8

*Hydrate:* Propane

*Reference:* Holder and Godbole (1982)

*Phases:* I–H–V

T (K)	P (kPa)						
247.9	48.2	251.6	58.3	258.2	81.1	260.9	94.5
251.4	58.3	255.4	69.6	260.8	90.5	262.1	99.4

*Hydrate:* Propane

*Reference:* Kubota et al. (1984)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (MPa)						
274.2	0.207	276.2	0.323	277.6	0.455	278.2	0.517
274.6	0.232	276.8	0.371	278.0	0.500	278.4	0.542
274.8	0.239						

*Hydrate:* Propane

*Reference:* Thakore and Holder (1987)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (kPa)						
274.2	217	276.2	310	277.2	450	278.2	510
275.2	248						

*Hydrate:* Propane

*Reference:* Patil (1987)

*Phase:* L<sub>W</sub>–H–V

T (K)	P (kPa)						
273.6	207	276.2	338	277.2	417	278.0	510
274.6	248						

*Hydrate:* Propane

*Reference:* Song and Kobayashi (1994)

*Phases:* H-L<sub>C<sub>3</sub></sub>

### Isobar at 1.1 MPa

T (K)	x <sub>H<sub>2</sub>O</sub> × 10 <sup>3</sup>	T (K)	x <sub>H<sub>2</sub>O</sub> × 10 <sup>3</sup>	T (K)	x <sub>H<sub>2</sub>O</sub> × 10 <sup>3</sup>
276.2	0.116	261.8	0.037	235.6	0.004
267.8	0.060	255.6	0.021		
264.4	0.046	246.6	0.011		

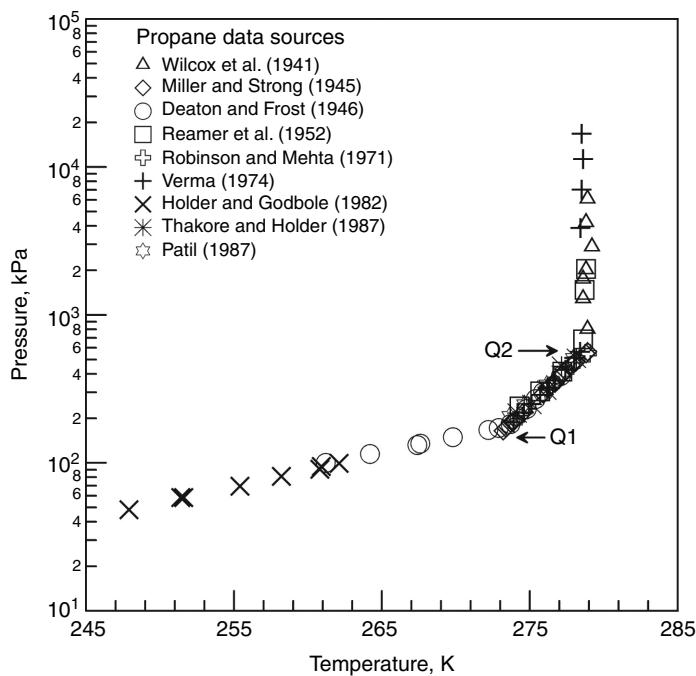
*Hydrate:* Propane

*Reference:* Mooijer-van den Heuvel et al. (2002)

*Phase:* L<sub>W</sub>-H-V, L<sub>W</sub>-H-L<sub>C<sub>3</sub>H<sub>8</sub></sub> and Q<sub>2</sub>

**Feed composition: x<sub>H<sub>2</sub>O</sub> = 0.9503, x<sub>C<sub>3</sub>H<sub>8</sub></sub> = 0.0407  
Q<sub>2</sub> at T = 278.62, P = 0.6 MPa**

L <sub>W</sub> -H-V		L <sub>W</sub> -H-L <sub>C<sub>3</sub>H<sub>8</sub></sub>	
T (K)	P (MPa)	T (K)	P (MPa)
276.77	0.368	278.71	0.643
277.01	0.377	278.75	0.893
277.22	0.405	278.75	1.393
277.36	0.425	278.75	1.891
277.44	0.433	278.78	1.893
277.87	0.473	278.80	2.391
278.01	0.527	278.80	2.891
278.22	0.483	278.79	2.893
278.55	0.547	278.75	3.891
		278.77	3.391
		278.81	4.391
		278.79	5.892
		278.86	6.392
		278.88	6.892
		278.80	8.393
		278.84	8.893
		278.89	9.893



**FIGURE 6.22** Three-phase data for simple hydrates of propane.

## ISOBUTANE

*Hydrate:* Isobutane

*Reference:* Schneider and Farrar (1968)

*Phases:* L<sub>W</sub>-H-V and I-H-V

### I-H-V

T (K)	P (kPa)						
273.1	109	272.8	109	272.3	105	271.2	95
275.1	109	272.8	102	272.2	103		

### L<sub>W</sub>-H-V

T (K)	P (kPa)						
275.1	167	274.4	141	273.6	124	273.2	109
275.0	165	274.2	137	273.4	117	273.2	110
274.9	163	273.9	130				

*Hydrate:* Isobutane

*Reference:* Rouher and Barduhn (1969)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (kPa)						
273.2	115	273.7	126	274.1	137	274.6	151
273.3	118	273.8	129	274.2	140	274.6	157
273.5	122	273.9	132	274.2	140	274.8	160
273.5	122	274.0	135	274.3	143	275.0	164
273.6	123	274.0	134	274.4	147	275.0	168
273.6	124	274.0	135	274.6	151	275.0	169

*Hydrate:* Isobutane

*Reference:* Wu et al. (1976)

*Phases:* L<sub>W</sub>–H–L<sub>i</sub>C<sub>4</sub>H<sub>10</sub>

T (K)	P (kPa)						
275.4	226	275.4	903	275.6	5650	275.8	14270
275.4	357	275.5	2410				

*Hydrate:* Isobutane

*Reference:* Holder and Godbole (1982)

*Phases:* I–H–V

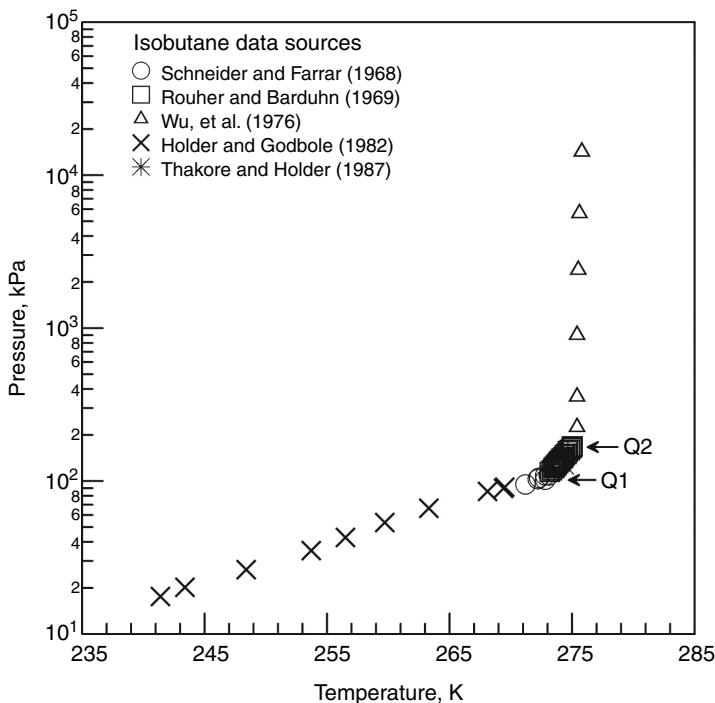
T (K)	P (kPa)						
241.4	17.6	253.7	35.1	263.3	66.4	269.4	89.7
243.4	20.2	256.5	42.8	268.1	85.5	269.5	91.3
248.4	26.4	259.7	53.5				

*Hydrate:* Isobutane

*Reference:* Thakore and Holder (1987)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (kPa)	T (K)	P (kPa)
274.4	128	274.6	155



**FIGURE 6.23** Three-phase data for simple hydrates of iso-butane.

## CARBON DIOXIDE

*Hydrate:* Carbon dioxide

*Reference:* Deaton and Frost (1946)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (kPa)						
273.7	1324	275.4	1613	278.7	2427	281.5	3530
273.7	1324	276.5	1848	278.7	2413	281.9	3709
274.3	1393	277.6	2075	279.8	2758	282.6	4130
274.3	1420	277.6	2082	279.8	2786	282.9	4323
274.3	1420	277.6	2103	280.9	3213		

*Hydrate:* Carbon dioxide

*Reference:* Unruh and Katz (1949)

*Phases:* L<sub>W</sub>-H-V

T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)
277.2	2041	280.9	3227	283.1	4502*
279.2	2586	281.9	3689		

\* = Q<sub>2</sub> Quadruple point (L<sub>W</sub>-H-V-L<sub>CO<sub>2</sub></sub>).

*Hydrate:* Carbon dioxide

*Reference:* Larson (1955)

*Phases:* I-H-V, L<sub>W</sub>-H-V, and H-V-L<sub>CO<sub>2</sub></sub>

### I-H-V

T (K)	P (kPa)						
256.8	545	268.9	924	270.7	1000	271.7	1041
264.0	752	270.0	972	271.4	1027	271.8	1048
267.4	869						

### L<sub>W</sub>-H-V

T (K)	P (kPa)						
271.8	1048	274.4	1386	277.8	2137	280.5	3020
271.9	1048	275.0	1510	278.0	2165	280.8	3158
272.2	1089	275.1	1496	278.6	2344	281.1	3282
272.5	1110	275.7	1634	278.8	2448	281.5	3475
273.1	1200	276.0	1682	279.1	2530	281.9	3634
273.4	1234	276.2	1717	279.2	2544	282.0	3689
273.5	1241	276.5	1806	279.8	2730	282.3	3868
273.9	1317	276.9	1889	280.1	2861	283.1	4468
274.1	1351	277.2	1951	280.2	2923	283.2	4502

### H-V-L<sub>CO<sub>2</sub></sub>

T (K)	P (kPa)						
258.8	2337	263.8	2696	272.1	3385	281.5	4316
256.5	2179	264.4	2744	273.1	3475	281.4	4302
260.2	2434	264.9	2779	274.4	3592	283.1	4489
258.5	2310	266.1	2875	275.1	3661	282.8	4454
261.2	2503	267.3	2972	276.3	3778	283.5	4523
260.1	2420	268.5	3068	277.0	3847	283.7	4558
262.5	2599	270.2	3220	278.9	4040	284.5	4640
262.5	2599	270.8	3268	279.1	4061	285.0	4695

*Hydrates:* Carbon dioxide

*Reference:* Takenouchi and Kennedy (1965)

*Phases:* L<sub>W</sub>–H–L<sub>CO<sub>2</sub></sub>

T (K)	P (MPa)						
2832	4.500	285.2	24.30	289.2	88.10	291.6	149.30
283.6	8.500	286.2	37.20	290.2	109.50	292.2	165.10
284.2	13.00	287.2	52.20	290.6	122.00	292.7	186.20
284.6	18.20	288.2	69.60	291.2	135.30		

*Hydrate:* Carbon dioxide

*Reference:* Miller and Smythe (1970)

*Phases:* I–H–V

T (K)	P (kPa)						
151.5	0.535	167.1	2.81	176.9	6.77	186.8	14.5
162.4	1.77	171.5	4.20	182.2	10.3	192.5	21.9

*Hydrate:* Carbon dioxide

*Reference:* Robinson and Mehta (1971)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (kPa)						
273.9	1379	276.1	1758	280.7	3130	283.3	4468*
275.2	1558	278.9	2420	282.0	3840		

\* = Quadruple point (L<sub>W</sub>–H–V–L<sub>CO<sub>2</sub></sub>).

*Hydrate:* Carbon dioxide

*Reference:* Ng and Robinson (1985)

*Phases:* L<sub>W</sub>–H–V, L<sub>W</sub>–H–L<sub>CO<sub>2</sub></sub>

### L<sub>W</sub>–H–V

T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
279.6	2.74	282.1	4.01	282.8	4.36

### L<sub>W</sub>–H–L<sub>CO<sub>2</sub></sub>

T (K)	P (MPa)						
282.9	5.03	283.1	6.47	283.6	11.98	283.9	14.36
282.9	5.62	283.2	9.01				

*Hydrates:* Carbon dioxide

*Reference:* Vlahakis et al. (1972)

*Phases:* L<sub>W</sub>–H–V, H–L<sub>CO<sub>2</sub></sub>–V

### H–L<sub>CO<sub>2</sub></sub>–V

T (K)	P (MPa)						
263.0	2.644	269.1	3.131	275.1	3.669	281.6	4.331
264.0	2.717	269.2	3.134	275.2	3.674	282.0	4.379
264.1	2.724	270.1	3.213	275.2	3.681	282.1	4.383
264.1	2.727	270.2	3.221	277.0	3.858	283.0	4.482
264.6	2.726	271.0	3.292	277.3	3.885	283.2	4.492
265.2	2.803	271.1	3.304	278.0	3.955	283.2	4.497
265.6	2.845	271.2	3.305	278.1	3.960	283.6	4.551
266.2	2.884	272.3	3.405	278.1	3.966	284.6	4.662
266.3	2.892	273.1	3.481	278.2	3.965	285.1	4.713
267.1	2.962	273.1	3.484	279.1	4.071	287.0	4.951
267.2	2.965	273.2	3.482	281.0	4.268	288.0	5.058
267.8	3.021	274.1	3.576	281.1	4.273	288.0	5.065
268.2	3.045	274.2	3.582	281.2	4.295	288.0	5.076
268.3	3.058	27.51	3.664				

### L<sub>W</sub>–H–V

T (K)	P (MPa)						
271.6	1.040	274.2	1.387	277.7	2.093	281.2	3.327
271.7	1.045	274.7	1.462	277.7	2.127	281.4	3.471
271.7	1.043	274.7	1.472	278.1	2.230	281.8	3.626
272.0	1.088	275.3	1.569	278.6	2.372	281.8	3.680
272.1	1.096	275.7	1.651	278.7	2.400	282.2	3.833
272.3	1.117	276.1	1.742	278.8	2.411	282.3	3.947
272.7	1.163	276.6	1.844	279.2	2.541	282.6	4.082
273.1	1.218	276.7	1.849	279.7	2.737	282.7	4.165
273.1	1.222	277.0	1.927	280.1	2.879	282.9	4.311
273.6	1.300	277.2	1.983	280.4	2.989	283.2	4.508
273.9	1.342	277.2	1.984	280.7	3.134	283.2	4.509

*Hydrate:* Carbon dioxide

*Reference:* Falabella (1975)

*Phases:* I–H–V

T (K)	P (kPa)						
194.5	24.8	213.8	81.6	218.2	104.3	217.8	101.3
203.2	43.3						

*Hydrate:* Carbon dioxide

*Reference:* Song and Kobayashi (1987)

*Phases:* As noted

<b>H<sub>2</sub>O Mol fraction</b>				<b>H<sub>2</sub>O Mol fraction</b>			
<b>T (K)</b>	<b>P (kPa)</b>	<b>x 10<sup>3</sup></b>	<b>Phases</b>	<b>T (K)</b>	<b>P (kPa)</b>	<b>x 10<sup>3</sup></b>	<b>Phases</b>
251.8	690	0.1800	V–H	290.2	4830	0.8229	V–L <sub>W</sub>
254.2	690	0.2190	V–H	298.2	4830	1.2787	V–L <sub>W</sub>
265.2	690	0.5570	V–I	288.7	5240	0.6400	V–L <sub>W</sub>
294.3	690	4.3276	V–L <sub>W</sub>	288.7	5240	1.1200	L <sub>CO<sub>2</sub></sub> –L <sub>W</sub>
255.2	1380	0.1142	V–H	293.4	5790	0.8999	V–L <sub>W</sub>
258.0	1380	0.1471	V–H	293.4	5790	1.5000	L <sub>CO<sub>2</sub></sub> –L <sub>W</sub>
262.2	1380	0.2201	V–H	257.2	6210	0.5170	L <sub>CO<sub>2</sub></sub> –H
271.2	1380	0.4885	V–H	263.7	6210	0.6647	L <sub>CO<sub>2</sub></sub> –H
275.2	1380	0.6836	V–L <sub>W</sub>	280.2	6210	1.0960	L <sub>CO<sub>2</sub></sub> –H
273.2	2070	0.2775	V–H	299.8	6690	1.2700	V–L <sub>W</sub>
275.7	2070	0.4368	V–H	299.8	6690	1.9541	L <sub>CO<sub>2</sub></sub> –L <sub>W</sub>
288.7	2070	1.0656	V–L <sub>W</sub>	302.7	7170	1.4981	V–L <sub>W</sub>
268.8	2070	0.2321	V–H	302.7	7170	2.1940	L <sub>CO<sub>2</sub></sub> –L <sub>W</sub>
260.7	2070	0.1194	V–H	304.2	7390	2.1079	3-ϕ endpt
257.2	2070	0.0890	V–H	256.2	8280	1.0890	L <sub>CO<sub>2</sub></sub> –H
252.7	2070	0.2013	L <sub>CO<sub>2</sub></sub> –H	265.9	8280	1.5741	L <sub>CO<sub>2</sub></sub> –H
245.2	2070	0.1361	L <sub>CO<sub>2</sub></sub> –H	270.2	8280	1.8695	L <sub>CO<sub>2</sub></sub> –H
255.4	3450	0.2616	L <sub>CO<sub>2</sub></sub> –H	286.9	8280	2.7852	L <sub>CO<sub>2</sub></sub> –L <sub>W</sub>
260.2	3450	0.3222	L <sub>CO<sub>2</sub></sub> –H	298.2	8280	3.0152	L <sub>CO<sub>2</sub></sub> –L <sub>W</sub>
269.7	3450	0.4585	L <sub>CO<sub>2</sub></sub> –H	256.2	10340	1.2738	L <sub>CO<sub>2</sub></sub> –H
274.2	3450	0.2410	V–H	264.2	10340	1.6509	L <sub>CO<sub>2</sub></sub> –H
278.7	3450	0.3794	V–H	276.2	10340	2.4687	L <sub>CO<sub>2</sub></sub> –H
285.2	3450	0.6030	V–L <sub>W</sub>	298.2	10340	3.3739	L <sub>CO<sub>2</sub></sub> –L <sub>W</sub>
293.2	3450	1.0010	V–L <sub>W</sub>	255.4	13790	1.5091	L <sub>CO<sub>2</sub></sub> –H
255.4	4830	0.3313	L <sub>CO<sub>2</sub></sub> –H	260.1	13790	1.8057	L <sub>CO<sub>2</sub></sub> –H
263.2	4830	0.4705	L <sub>CO<sub>2</sub></sub> –H	267.7	13790	2.2043	L <sub>CO<sub>2</sub></sub> –H
269.7	4830	0.5402	L <sub>CO<sub>2</sub></sub> –H	275.9	13790	2.7441	L <sub>CO<sub>2</sub></sub> –H
276.2	4830	0.7182	L <sub>CO<sub>2</sub></sub> –H	286.3	13790	3.3627	L <sub>CO<sub>2</sub></sub> –L <sub>W</sub>

*Hydrate:* Carbon dioxide

*Reference:* Adisasmito et al. (1991)

*Phases:* L<sub>W</sub>–H–V

<b>T (K)</b>	<b>P (MPa)</b>						
274.3	1.42	277.6	2.11	280.6	3.12	282.1	3.81
275.5	1.63	279.1	2.55	281.5	3.51	282.9	4.37
276.8	1.90						

*Hydrate:* Carbon dioxide + pure water

*Reference:* Ohgaki et al. (1993)

*Phases:* L<sub>w</sub>-H-V, H-L<sub>w</sub>-L<sub>CO<sub>2</sub></sub>, H-L<sub>CO<sub>2</sub></sub>-V, L<sub>w</sub>-L<sub>CO<sub>2</sub></sub>-V (no hydrate)

### L<sub>w</sub>-H-V

T (K)	P (MPa)	T (K)	P (MPa)
273.36	1.338	278.13	2.482
274.03	1.509	278.69	2.656
274.94	1.651	278.76	2.604
276.01	1.839	279.23	3.030
276.29	1.971	279.50	3.019
276.56	1.966	280.13	3.228
276.57	2.005	280.34	3.395
276.98	2.108	280.79	3.667
277.51	2.238	281.10	4.085
273.95	1.347	279.42	2.674
275.37	1.544	281.21	3.279
276.82	1.977	281.79	3.831
277.82	2.116		
275.97	1.740	278.75	2.499
276.54	1.881	279.16	2.614
277.45	2.126	280.33	3.076
278.66	2.497		

### H-L<sub>w</sub>-L<sub>CO<sub>2</sub></sub>

T (K)	P (MPa)	T (K)	P (MPa)
281.52	4.386	281.70	6.861
281.14	5.596	282.21	8.615
281.28	5.693		
283.23	4.541	283.59	8.930
283.25	6.306		

### H-L<sub>CO<sub>2</sub></sub>-V

T (K)	P (MPa)	T (K)	P (MPa)
274.92	3.637	278.80	4.012
275.90	3.730	279.82	4.115
276.85	3.823	280.82	4.222
277.84	3.910	281.27	4.281

**Continued****L<sub>W</sub>-L<sub>CO<sub>2</sub></sub>-V**

<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
283.07	4.485	285.43	4.748
283.15	4.495	286.38	4.860
283.46	4.524	287.39	4.977
283.95	4.578	288.40	5.089
284.47	4.636	289.37	5.216

*Hydrate:* Carbon dioxide*Reference:* Nakano et al. (1998b)*Phases:* L<sub>W</sub>-H-L<sub>CO<sub>2</sub></sub>

<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
289.73	104	293.97	316
290.32	117	294.00 <sup>a</sup>	328
290.95	138	293.99	338
291.64	158	293.92	358
292.14	177	293.77	377
292.64	197	293.57	397
293.04	218	293.35	422
293.34	237	293.13	441
293.58	257	292.82	460
293.73	276	292.45	479
293.84	296	292.14	494

<sup>a</sup> Maximum temperature point.*Hydrate:* Carbon dioxide*Reference:* Fan and Guo (1999)*Phases:* As noted**Q<sub>2</sub> at 283.1 K and 4.65 MPa**

<b>L<sub>W</sub>-H-V</b>			<b>L<sub>CO<sub>2</sub></sub>-H-V</b>		
<b>T (K)</b>	<b>P (MPa)</b>	<b>Phases</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>Phases</b>
273.6	1.31	L <sub>W</sub> -H-V	281.3	3.47	L <sub>W</sub> -H-V
274.2	1.39	L <sub>W</sub> -H-V	282.0	4.02	L <sub>W</sub> -H-V
275.2	1.57	L <sub>W</sub> -H-V	278.9	4.12	L <sub>CO<sub>2</sub></sub> -H-V
276.4	1.81	L <sub>W</sub> -H-V	280.7	4.23	L <sub>CO<sub>2</sub></sub> -H-V
278.5	2.25	L <sub>W</sub> -H-V	283.1	9.32	L <sub>CO<sub>2</sub></sub> -H-L <sub>W</sub>
279.2	2.52	L <sub>W</sub> -H-V	283.2	9.43	L <sub>CO<sub>2</sub></sub> -H-L <sub>W</sub>
280.3	3.04	L <sub>W</sub> -H-V	283.6	12.87	L <sub>CO<sub>2</sub></sub> -H-L <sub>W</sub>

*Hydrate:* Carbon dioxide

*Reference:* Fan et al. (2000)

*Phases:* L<sub>W</sub>-H-V

T (K)	P (MPa)	T (K)	P (MPa)
274.7	1.50	279.7	2.78
277.5	2.03		

*Hydrate:* Carbon dioxide

*Reference:* Mooijer-van den Heuvel et al. (2001)

*Phases:* L<sub>W</sub>-H-V, L<sub>W</sub>-H-L<sub>CO<sub>2</sub></sub> and Q<sub>2</sub>

**Overall feed composition:**  
 $x_{\text{H}_2\text{O}} = 0.8668$ ,  $x_{\text{CO}_2} = 0.1332$   
Q<sub>2</sub> at 283.27 K and 4.48 MPa

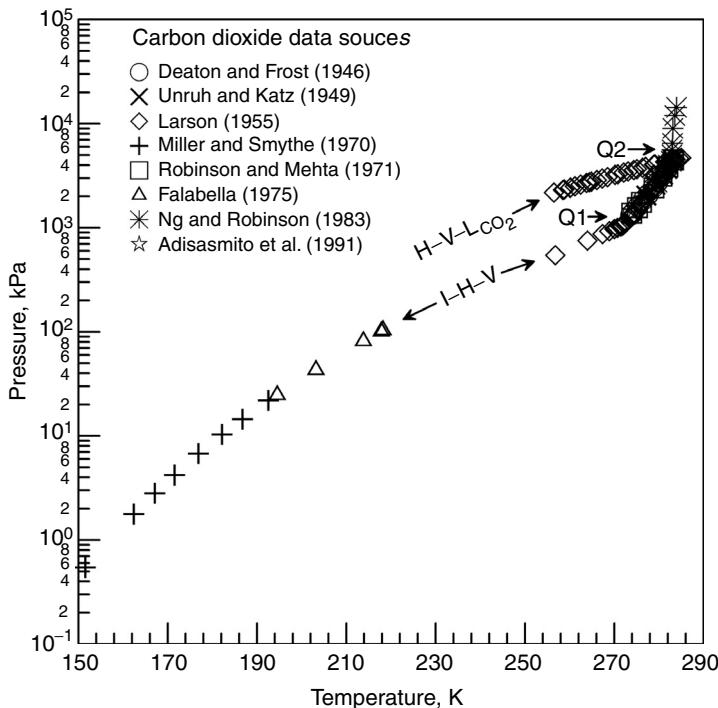
L <sub>W</sub> -H-V		L <sub>W</sub> -H-L <sub>CO<sub>2</sub></sub>	
T (K)	P (MPa)	T (K)	P (MPa)
276.52	1.82	283.33	5.97
277.85	1.95	283.36	7.35
278.52	2.21		
279.49	2.62		
280.44	2.88		
281.49	3.35		
281.97	3.68		
282.00	3.69		
282.45	3.85		
282.50	4.01		

*Hydrate:* Carbon dioxide

*Reference:* Zhang (2003)

*Phases:* L<sub>W</sub>-H

x <sub>CO<sub>2</sub></sub>	P (MPa)	T (K)	x <sub>CO<sub>2</sub></sub>	P (MPa)	T (K)	x <sub>CO<sub>2</sub></sub>	P (MPa)	T (K)
0.0199	50.582	279.3	0.0177	45.262	277.8	0.0160	50.012	276.8
0.0199	37.872	279.1	0.0177	18.002	277.2	0.0160	31.142	275.6
0.0199	23.582	277.9	0.0177	6.65	276.5	0.0160	16.472	274.0



**FIGURE 6.24** Three-phase data for simple hydrates of carbon dioxide.

*Hydrate:* Carbon dioxide

*Reference:* Mohammadi et al. (2005)

*Phases:* L<sub>W</sub>-H-V

<b>T (K)</b> <b>(±0.1)</b>	<b>P (MPa)</b> <b>(±0.007)</b>
295.8	34.584
298.3	47.863
277.5	2.048
282.2	3.840
282.5	4.020

**NITROGEN***Hydrate:* Nitrogen*Reference:* van Cleeff and Diepen (1960)*Phases:* L<sub>W</sub>–H–V

<b>T (K)</b>	<b>P (MPa)</b>						
272.0	14.48	274.8	19.25	279.2	29.89	285.2	55.43
272.6	15.30	275.2	19.66	279.2	30.30	286.2	61.40
272.8	15.91	275.6	20.67	280.2	33.94	287.2	67.79
273.0	15.91	275.8	21.58	281.2	37.49	287.8	71.23
273.2	16.01	276.2	22.39	281.6	38.61	288.4	74.58
273.2	16.31	276.6	23.10	282.2	41.44	289.2	81.47
273.4	16.62	277.2	24.83	283.2	45.90	290.2	89.37
274.0	17.53	278.2	27.36	284.2	50.66	290.6	92.21
274.2	17.73	278.2	27.97	284.6	52.29	291.0	95.86
274.8	19.15	278.6	28.27				

*Hydrate:* Nitrogen*Reference:* Marshall et al. (1964a)*Phases:* L<sub>W</sub>–H–V

<b>T (K)</b>	<b>P (MPa)</b>						
277.6	24.93	293.0	115.49	298.8	192.37	302.6	268.32
281.2	36.82	294.3	128.80	299.7	207.78	304.7	317.65
286.7	63.71	296.6	153.48	300.6	219.60	305.5	328.89
291.6	101.98	297.7	169.27				

*Hydrate:* Nitrogen*Reference:* Jhaveri and Robinson (1965)*Phases:* L<sub>W</sub>–H–V

<b>T (K)</b>	<b>P (MPa)</b>						
273.2	16.27	274.9	19.13	277.4	25.20	279.3	30.27
273.7	17.13	276.5	23.69	278.6	28.61	281.1	35.16

*Hydrate:* Nitrogen

*Reference:* Sugahara et al. (2002)

*Phases:* L<sub>W</sub>-H-V

<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)
285.63	55	298.47	180	305.46	324
287.87	69	299.31	195	305.85	331
289.47	78	299.92	206	306.26	342
290.80	88	300.49	219	306.74	354
291.96	101	301.86	240	307.21	373
292.90	113	302.64	256	307.50	383
294.60	127	303.08	265	308.09	398
295.61	139	303.82	280	308.57	412
296.62	152	304.23	294	308.82	420
297.32	162	304.43	304	309.21	431
297.86	169	304.56	306	309.43	439

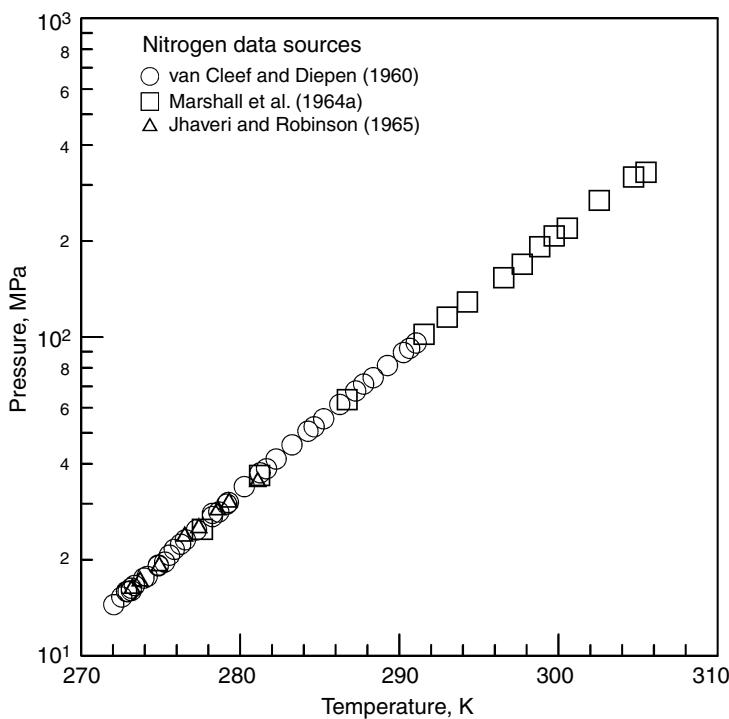


FIGURE 6.25 Three-phase data for simple hydrates of nitrogen.

*Hydrate:* Nitrogen

*Reference:* Mohammadi et al. (2003)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (kPa)
274.55	19,093
277.55	25,380
283.05	45,355

## HYDROGEN SULFIDE

*Hydrate:* Hydrogen sulfide

*Reference:* Bond and Russell (1949)

*Phases:* L<sub>W</sub>–H–V

T (K)	P (kPa)						
283.2	310	291.2	710	299.7	1496	302.7	2241

*Hydrate:* Hydrogen sulfide

*Reference:* Selleck et al. (1952)

*Phases:* L<sub>W</sub>–H–V, I–H–V, H–V–L<sub>H<sub>2</sub>S</sub>, L<sub>W</sub>–H–L<sub>H<sub>2</sub>S</sub>

## L<sub>W</sub>–H–V

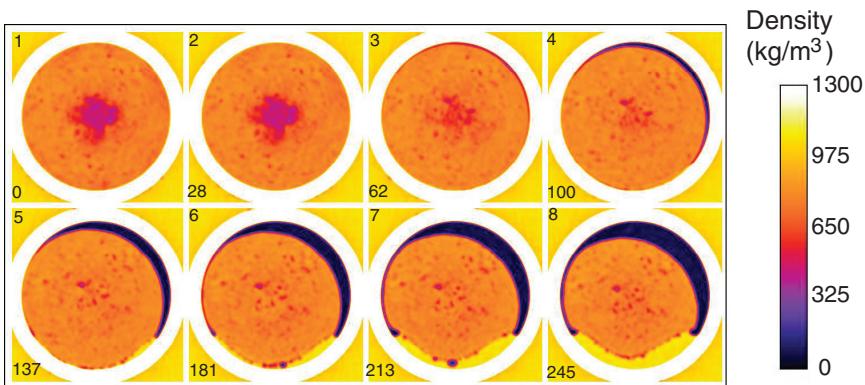
T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)
272.8	93 Q <sub>1</sub>	285.2	345	295.7	1034	302.1	2068
272.8	93	288.7	499	298.5	1379	302.7	2239 Q <sub>2</sub>
277.6	157	291.8	689	299.8	1596	302.7	2239 Q <sub>2</sub>
283.2	280	294.3	690	300.5	1724		

Q<sub>1</sub> = lower Quadruple point (I–L<sub>W</sub>–H–V).

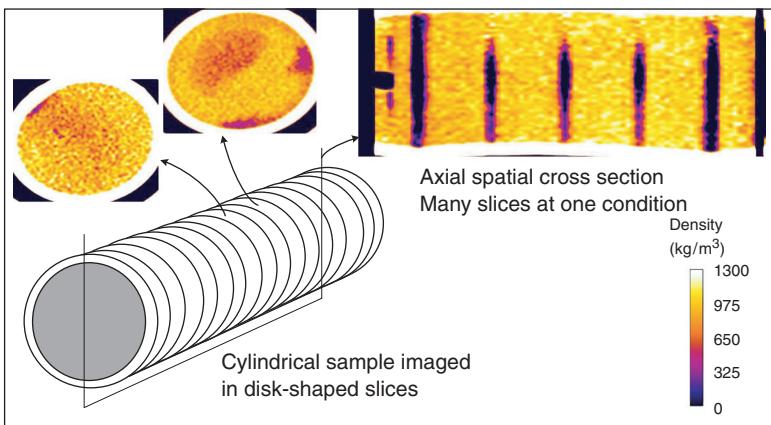
Q<sub>2</sub> = upper Quadruple point (L<sub>W</sub>–H–V–L<sub>H<sub>2</sub>S</sub>).

## I–H–V

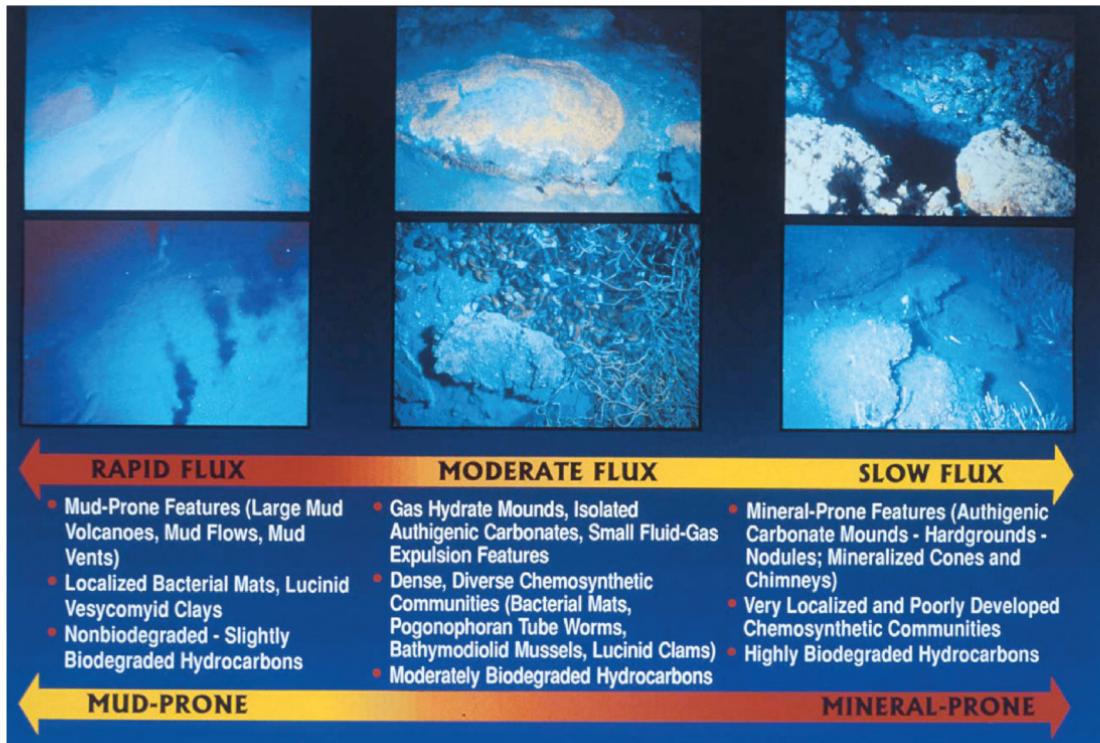
T (K)	P (kPa)						
250.5	34	260.9	57	266.5	72	272.1	90
255.4	44	263.7	64	269.3	81	272.8	93 Q <sub>1</sub>
258.2	50	265.3	69				



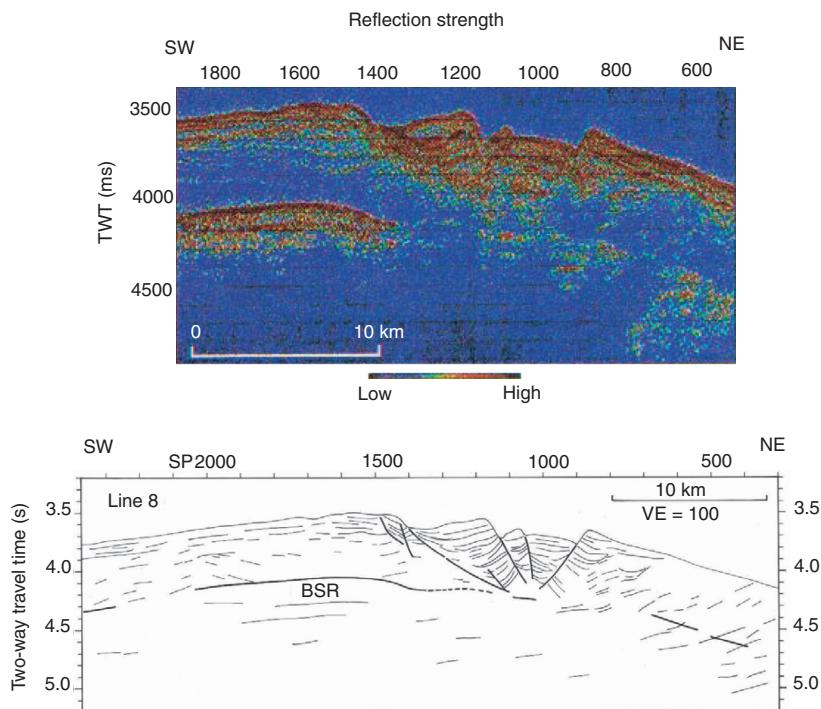
**COLOR FIGURE 3.35** X-ray CT imaging shows radial dissociation of a hydrate core. Image number 1–8 (top number on each image) recorded over 0–245 min (bottom number on each image). The cell pressure was decreased from 4.65 to 3.0 MPa over 248 min. The hydrate core temperature decreased from 277 to 274 K with time, following the three-phase methane hydrate equilibrium line. (From Gupta, A., *Methane Hydrate Dissociation Measurements and Modeling: The Role of Heat Transfer and Reaction Kinetics*, Ph.D. Thesis Colorado School of Mines, Golden, CO (2007). With permission.)



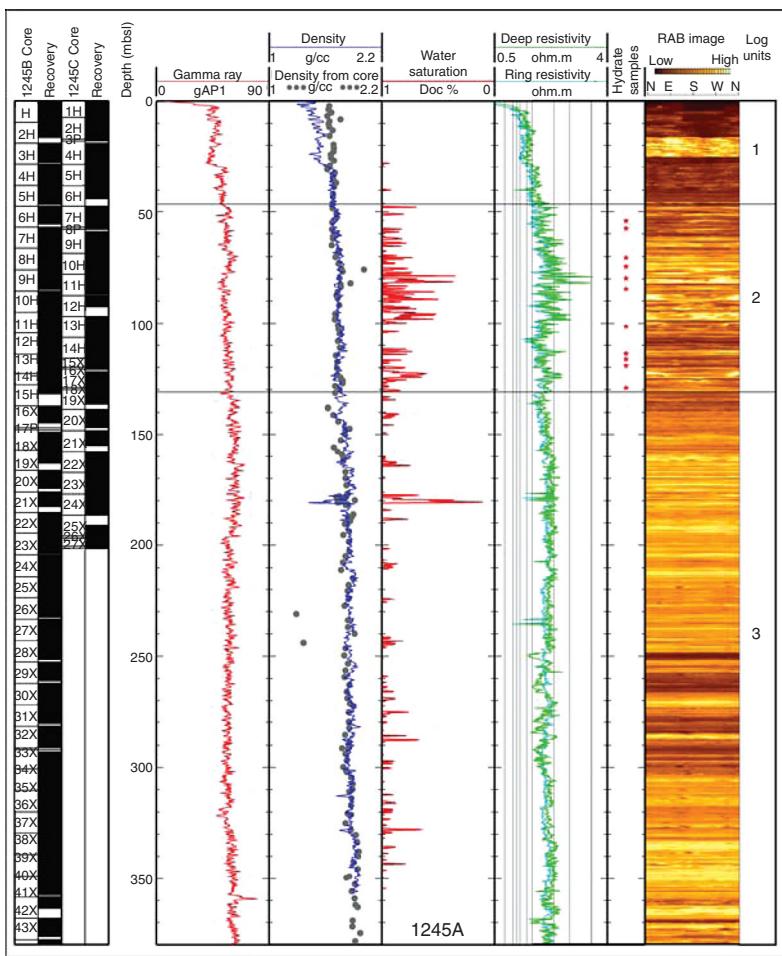
**COLOR FIGURE 6.11** Schematic of the application of x-ray CT analysis to provide density profile images of different sections of a hydrate core contained in a cylindrical high pressure aluminum cell. (From Gupta, A., *Methane Hydrate Dissociation Measurements and Modeling: The Role of Heat Transfer and Reaction Kinetics*, Ph.D. Thesis, Colorado School of Mines, Golden, CO (2007). With permission.)



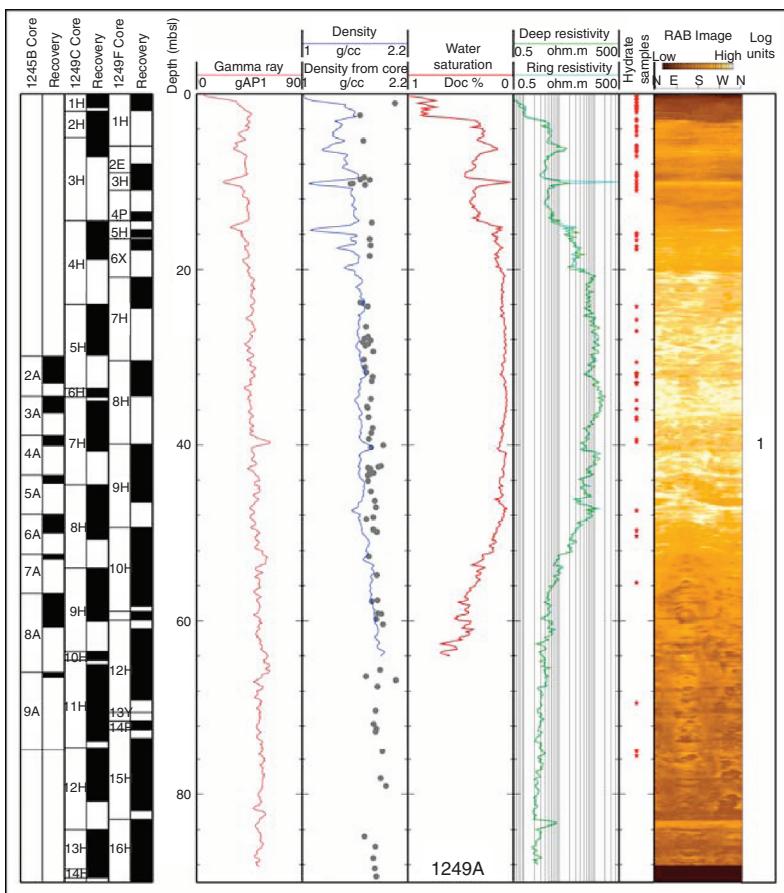
**COLOR FIGURE 7.9** Qualitative relationships between fluid fluxes and geologic–biologic response. Each picture has a field of view 3–4 m across. (From Roberts, H.H., in *Natural Gas Hydrates: Occurrence, Distribution and Detection*, (Paull, C.K., Dillon, W.P., eds.) p. 145. American Geophysical Union, Washington, DC (2001). With permission.)



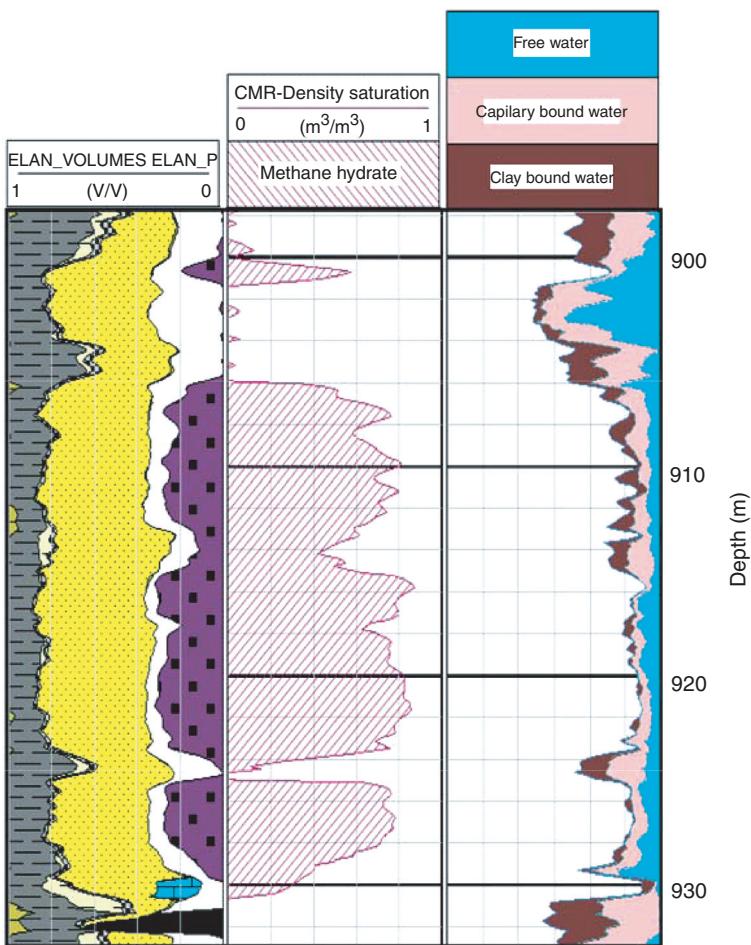
**COLOR FIGURE 7.20** Seafloor slump in the Blake-Bahama Ridge shown in both seismic (top) and cartoon (bottom) relief. (From Dillon, W.P., Nealon, J.W., Taylor, M.H., Lee, M.W., Drury, R.M., Anton, C.H., *Natural Gas Hydrates: Occurrence, Distribution, and Detection*, (Paull, C.K., Dillon, W.P., eds.) American Geophysical Union Monograph, 124, p. 41, Washington DC (2001). With permission.) Note the bottom simulating reflector parallel to the ocean bottom, except in the middle section where it appears a seafloor eruption has occurred.



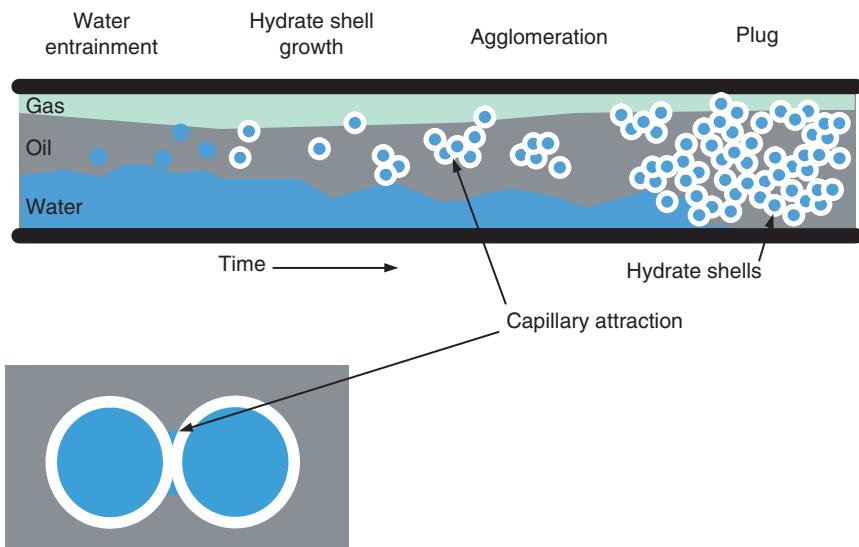
**COLOR FIGURE 7.26** Site 1245A southern Hydrate Ridge Flank logs (gamma ray, density, Resistivity at Bit, and Archie water saturation). (T.S. Collett, Personal Communication, November 18, 2005, Leg 204, Scientific Party, 2005.)



**COLOR FIGURE 7.27** Site 1249A southern Hydrate Ridge crest remote sensing logs (gamma ray, density, RAB, and Archie water saturation). (T.S. Collett, Personal Communication, November 18, 2005, Leg 204 Scientific Party, 2005.)



**COLOR FIGURE 7.37** 5L-38 CMR logs showing hydrate extent at depths between 900 and 930 m. Note that hydrates are obtained by the difference (middle column) between the total porosity as determined by density (not shown), and the capillary, clay-bound and free water determined by NMR.



**COLOR FIGURE 8.8** Plug formation via aggregation in an oil-dominated system. (From Turner, D.J., *Clathrate Hydrate Formation in Water-in-Oil Dispersions*, Ph.D. Thesis, Colorado School of Mines, Golden, CO (2004). With permission.)

**Continued****H–V–L<sub>H<sub>2</sub>S</sub>**

<b>T (K)</b>	<b>P (kPa)</b>						
259.2	689	272.3	1034	288.7	1605	299.8	2097
260.9	731	277.6	1202	291.6	1724	302.7	2239 Q <sub>2</sub>
266.5	870	282.7	1379	294.3	1839	302.7	2239 Q <sub>2</sub>
272.1	1027	283.2	1393	299.2	2068		

**L<sub>W</sub>–H–L<sub>H<sub>2</sub>S</sub>**

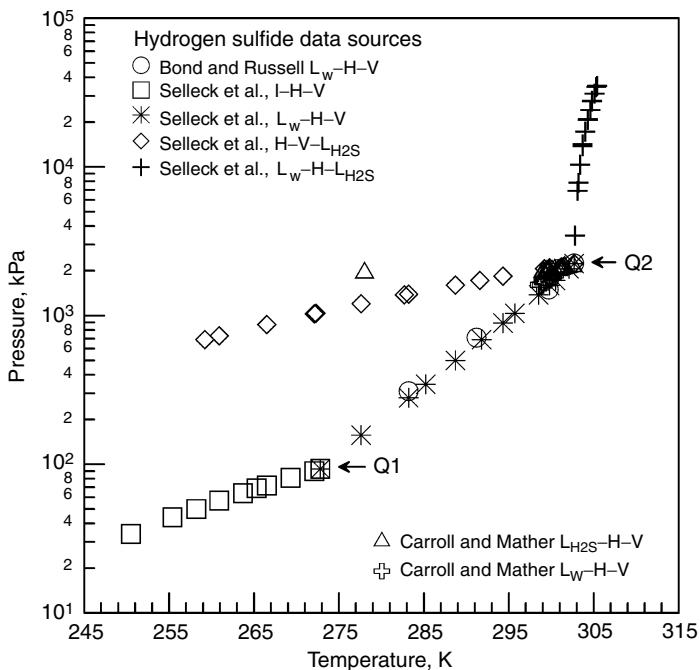
<b>T (K)</b>	<b>P (kPa)</b>	<b>T (K)</b>	<b>P (kPa)</b>	<b>T (K)</b>	<b>P (kPa)</b>	<b>T (K)</b>	<b>P (kPa)</b>
302.7	2239 Q <sub>2</sub>	303.4	10342	304.3	20685	304.8	27842
302.7	2239 Q <sub>2</sub>	303.7	13790	304.3	20954	305.1	31027
302.8	3447	303.7	14190	304.6	24132	305.3	34475
303.1	6895	304.0	17237	304.8	27580	305.4	35068
303.2	7826						

*Hydrates:* Hydrogen sulfide*Reference:* Carroll and Mather (1991)*Phases:* L<sub>H<sub>2</sub>S</sub>–H–V and L<sub>W</sub>–H–V**L<sub>H<sub>2</sub>S</sub>–H–V**

<b>T (K)</b>	<b>P (MPa)</b>						
278.0	2.03	299.7	2.09	301.0	2.13	301.4	2.18
299.0	2.05	299.8	2.09	301.1	2.15	301.6	2.20
299.1	2.06	300.1	2.09	301.2	2.17	301.6	2.22
299.4	2.08	300.4	2.12	301.2	2.15	302.6	2.24
299.6	2.08	300.8	2.11	301.4	2.17		

**L<sub>W</sub>–H–V**

<b>T (K)</b>	<b>P (MPa)</b>						
298.6	1.61	299.2	1.70	299.8	1.77	300.4	1.87
298.8	1.62	299.4	1.70	300.1	1.81	300.7	1.97
299.0	1.71	299.8	1.75	300.2	1.85	300.8	2.07
299.1	1.68						



**FIGURE 6.26** Three-phase data for simple hydrates of hydrogen sulfide.

### 6.3.1.2 Equilibria of binary guest mixtures

#### 6.3.1.2.1 Structure I and II hydrate binary data

The phase equilibria data for binary guest mixtures are listed under the lighter component. For example, under the heading of binary guest mixtures of methane will be found data for methane + ethane, methane + propane, methane + isobutane, methane + *n*-butane, methane + nitrogen, methane + carbon dioxide, and methane + hydrogen sulfide. Concentrations are in mole percent or mole fraction in the gas phase, unless otherwise indicated.

The subsection for binary guest mixtures of ethane will thus contain no methane, only mixtures of ethane and heavier (or noncombustible) components. As an indication of consistency the data tabulations for each binary pair are followed by a semilogarithmic plot of pressure versus temperature, where there is more than one data set.

As a second means to examine binary (and higher) hydrate data, one should determine the consistency of the simple gas hydrates that compose the mixed hydrate. For example, the data for binary hydrates of methane and carbon dioxide by Berecz and Balla-Achs (1983, pp. 221ff.) show interesting new retrograde phenomena. However, a nitrogen impurity in their carbon dioxide (p. 185) may have caused a systematic deviation from the other CO<sub>2</sub> data sets shown in Figure 6.24, and their methane purity was only 98%, providing a simple methane hydrate data

deviation (p. 221). Because the simple hydrate data appeared quantitatively deviant they were excluded, and the resulting binary hydrate data are also suspect.

Gas impurities may have caused the systematic deviation of the Berecz and Balla-Achs CH<sub>4</sub> + CO<sub>2</sub> hydrate data from those of Unruh and Katz (1949) and Adisasmto et al. (1991) and for those reasons the former data are excluded.

### BINARY-GUEST MIXTURES CONTAINING METHANE AND HEAVIER (OR NONCOMBUSTIBLE) COMPOUNDS

*Hydrate:* Methane + ethane

*Reference:* Deaton and Frost (1946)

*Phases:* L<sub>W</sub>-H-V

%CH <sub>4</sub>	T (K)	P (kPa)	%CH <sub>4</sub>	T (K)	P (kPa)
56.4	214.8	945	95.0	283.2	4771
56.4	277.6	1289	97.1	274.8	2158
56.4	280.4	1758	97.1	277.6	2958
56.4	283.2	2434	97.1	280.4	4034
90.4	274.8	1524	97.8	274.8	2365
90.4	277.6	2096	97.8	277.6	3227
90.4	280.4	2889	97.8	280.4	4413
90.4	283.2	3965	97.8	282.6	5668
95.0	274.8	1841	97.8	283.2	6088
95.0	274.8	1841	98.8	274.8	2861
95.0	277.6	2530	98.8	277.6	3806
95.0	280.4	3447	98.8	280.4	5088

*Hydrate:* Methane + ethane

*Reference:* McLeod and Campbell (1961)

*Phases:* L<sub>W</sub>-H-V

%CH <sub>4</sub>	T (K)	P (MPa)	%CH <sub>4</sub>	T (K)	P (MPa)
94.6	302.0	68.43	80.9	304.1	68.57
94.6	301.2	62.23	80.9	303.1	61.95
94.6	299.1	48.23	80.9	301.3	48.64
94.6	296.6	34.44	80.9	299.0	35.61
94.6	293.6	24.24	80.9	296.4	23.48
94.6	289.7	13.89	80.9	293.3	13.89
94.6	287.9	10.45	80.9	291.7	10.45
94.6	284.9	6.93	80.9	288.8	7.00

*Hydrate:* Methane + ethane

*Reference:* Holder and Grigoriou (1980)

*Phases:* L<sub>W</sub>-H-V

%CH <sub>4</sub>	T (K)	P (kPa)	%CH <sub>4</sub>	T (K)	P (kPa)
1.6	283.9	1810	4.7	286.4	2510
1.6	285.7	2310	4.7	287.6	2990
1.6	286.6	2710	17.7	281.6	1420
1.6	287.8	3080	17.7	283.3	1770
4.7	279.4	990	17.7	284.8	2140
4.7	281.5	1340	17.7	286.2	2660
4.7	283.3	1710	17.7	287.0	3000
4.7	285.3	2170			

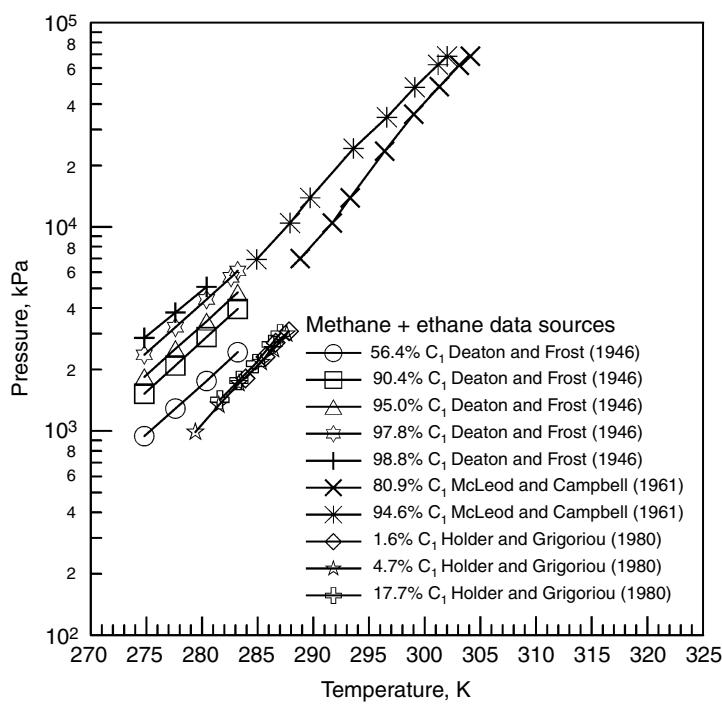


FIGURE 6.27 Methane + ethane mixture (L<sub>W</sub>-H-V) data.

*Hydrate:* Methane + propane

*Reference:* Deaton and Frost (1946)

*Phases:* L<sub>W</sub>-H-V

%CH <sub>4</sub>	T (K)	P (kPa)	%CH <sub>4</sub>	T (K)	P (kPa)
36.2	274.8	272	95.2	277.6	1138
36.2	277.6	436	95.2	280.4	1586
36.2	280.4	687	95.2	283.2	2227
71.2	274.8	365	97.4	274.8	1151
71.2	277.6	538	97.4	277.6	1593
71.2	280.4	800	97.4	280.4	2193
71.2	280.4	800	97.4	283.2	3013
71.2	283.2	1151	99.0	274.8	1627
88.3	274.8	552	99.0	277.6	2247
88.3	277.6	779	99.0	277.6	2255
88.3	280.4	1110	99.0	280.4	3123
88.3	283.2	1558	99.0	283.1	4358
95.2	274.8	814			

*Hydrate:* Methane + propane

*Reference:* McLeod and Campbell (1961)

*Phases:* L<sub>W</sub>-H-V

%CH <sub>4</sub>	T (K)	P (MPa)	%CH <sub>4</sub>	T (K)	P (MPa)
96.5	290.5	6.93	96.5	290.7	6.93
96.5	303.7	62.47	94.5	293.1	7.41
96.5	304.4	68.98	94.5	292.8	7.41
96.5	299.1	34.51	94.5	300.6	34.58
96.5	296.6	20.86	94.5	302.7	48.37
96.5	301.6	48.37	94.5	304.9	62.23
96.5	303.7	62.23	94.5	298.5	23.62
96.5	294.5	13.89	94.5	296.2	13.89
96.5	293.3	10.45			

*Hydrate:* Methane + propane

*Reference:* Verma et al. (1974)

*Phases:* L<sub>W</sub>-H-V and L<sub>W</sub>-H-V-L<sub>HC</sub>

**L<sub>W</sub>-H-V  
23.75% CH<sub>4</sub>**

T (K)	P (MPa)						
274.9	0.263	277.8	0.443	280.2	0.689	281.4	0.830
276.4	0.350	279.1	0.560				

**37.1% CH<sub>4</sub>**

T (K)	P (MPa)						
274.4	0.270	277.1	0.419	280.2	0.691	282.3	0.945
275.9	0.343	278.6	0.536				

**L<sub>W</sub>-H-V-L<sub>HC</sub>  
0.72% CH<sub>4</sub>**

T (K)	P (MPa)						
279.6	0.66*	279.9	6.70	280.0	10.3	280.2	15.3
279.8	3.03						

**0.92% CH<sub>4</sub>**

T (K)	P (MPa)						
280.4	0.74*	280.6	3.17	280.9	11.0	281.1	15.4
280.5	1.83	280.7	6.99				

**2.20% CH<sub>4</sub>**

T (K)	P (MPa)						
282.2	0.949*	282.4	1.76	282.6	3.17	282.9	6.00

**4.46% CH<sub>4</sub>**

T (K)	P (MPa)						
284.9	1.34*	285.3	3.61	286.2	10.14	286.7	14.33
285.1	2.06	285.7	6.59				

**Continued****7.80% CH<sub>4</sub>**

<b>T (K)</b>	<b>P (MPa)</b>						
288.0	2.03*	288.3	4.80	289.3	11.50	289.8	15.34
288.0	2.81	288.7	7.36				

**13.70% CH<sub>4</sub>**

<b>T (K)</b>	<b>P (MPa)</b>						
290.2	2.71*	290.7	5.51	291.6	9.38	292.1	13.13
290.4	3.36	290.9	6.36	291.7	10.39	292.7	16.94

**25.70 % CH<sub>4</sub>**

<b>T (K)</b>	<b>P (MPa)</b>						
294.2	4.96*	294.8	7.81	296.4	13.80	297.2	17.06
294.2	5.26	295.6	10.82				

**48.23% CH<sub>4</sub>**

<b>T (K)</b>	<b>P (MPa)</b>						
297.0	8.10*	297.9	11.08	298.7	13.99	299.7	17.49
297.1	8.43						

**56.35% CH<sub>4</sub>**

<b>T (K)</b>	<b>P (MPa)</b>						
297.6	9.16*	299.0	13.18	299.7	15.38	300.2	17.41
298.1	10.43						

**59.40% CH<sub>4</sub>**

<b>T (K)</b>	<b>P (MPa)</b>						
297.6	9.38*	298.9	12.62	299.4	14.53	300.2	17.29
298.2	10.71						

**65.10% CH<sub>4</sub>**

<b>T (K)</b>	<b>P (MPa)</b>						
297.7	9.56*	298.0	10.60	298.9	13.89	300.1	17.13

\* = Q<sub>2</sub> Quadruple point (L<sub>W</sub>-H-V-L<sub>HC</sub>).

*Hydrate:* Methane + propane

*Reference:* Song and Kobayashi (1982)

*Phases:* V–H

### 5.31 mol% propane in methane

<b>T (K)</b>	<b>P (MPa)</b>	<b>H<sub>2</sub>O mol fract (x10<sup>6</sup>)</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>H<sub>2</sub>O mol fract (x10<sup>6</sup>)</b>
234.2	2.07	6.86	246.2	6.89	7.03
246.2	2.07	24.28	252.1	6.89	12.25
251.7	2.07	41.54	260.0	6.89	25.42
260.1	2.07	85.20	263.2	6.89	35.78
266.5	2.07	161.99	276.2	6.89	103.70
277.2	2.07	427.28	234.2	10.34	1.15
234.2	3.45	3.47	246.2	10.34	3.75
246.2	3.45	13.85	252.1	10.34	7.33
252.1	3.45	27.50	260.1	10.34	14.67
263.2	3.45	78.76	266.5	10.34	26.75
274.7	3.45	187.89	277.6	10.34	81.15
234.2	6.89	1.92			

*Hydrate:* Methane + propane

*Reference:* Thakore and Holder (1987)

*Phases:* L<sub>W</sub>–H–V

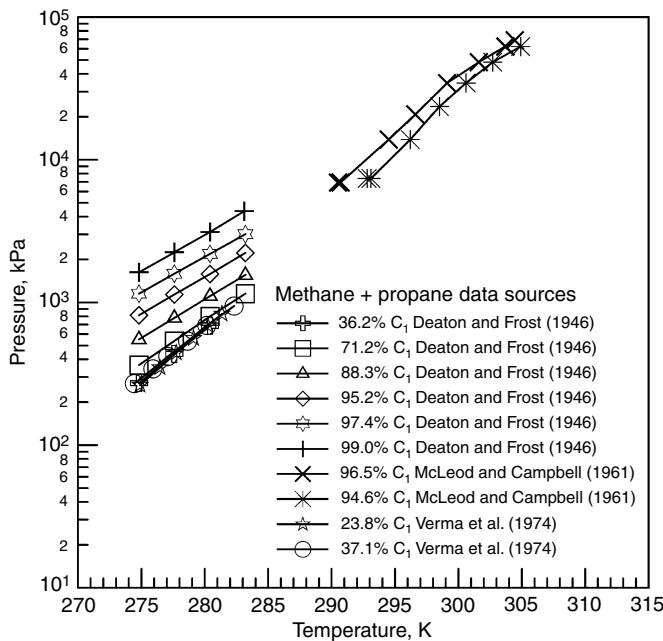
### T = 275.15 K

<b>%CH<sub>4</sub></b>	<b>P (kPa)</b>	<b>%CH<sub>4</sub></b>	<b>P (kPa)</b>	<b>%CH<sub>4</sub></b>	<b>P (kPa)</b>
1.000	3370	0.420	279	0.054	245
0.903	672	0.366	279	0.046	245
0.765	424	0.352	269	0.037	245
0.727	393	0.190	245*	0.021	245
0.700	365	0.083	245	0.000	278
0.516	303	0.081	245		

### T = 278.15 K

<b>%CH<sub>4</sub></b>	<b>P (kPa)</b>	<b>%CH<sub>4</sub></b>	<b>P (kPa)</b>	<b>%CH<sub>4</sub></b>	<b>P (kPa)</b>
1.000	4495	0.530	496	0.394	458
0.956	1306	0.510	489	0.390	458*
0.947	1144	0.502	479	0.030	479
0.894	848	0.468	475	0.026	480
0.768	630	0.412	479	0.000	509

\* = Azeotrope point.

**FIGURE 6.28** Methane + propane mixture (L<sub>W</sub>-H-V) data.*Hydrate:* Methane + isobutane*Reference:* Deaton and Frost (1946)*Phases:* L<sub>W</sub>-H-V

%CH <sub>4</sub>	T (K)	P (kPa)	%CH <sub>4</sub>	T (K)	P (kPa)
98.9	274.8	1324	98.9	277.6	1841

*Hydrate:* Methane + isobutane*Reference:* McLeod and Campbell (1961)*Phases:* L<sub>W</sub>-H-V

%CH <sub>4</sub>	T (K)	P (MPa)	%CH <sub>4</sub>	T (K)	P (MPa)
98.6	300.0	47.68	95.4	297.1	13.96
98.6	297.8	34.51	95.4	298.2	23.27
98.6	297.6	33.61	95.4	300.5	34.58
98.6	295.2	21.06	95.4	302.6	48.37
98.6	299.9	49.13	95.4	305.0	63.33
98.6	288.6	6.79	95.4	303.1	49.06
98.6	302.1	62.23	95.4	298.3	23.82
95.4	294.3	6.72	95.4	296.7	13.96
95.4	293.8	6.72	95.4	295.3	10.58
95.4	296.5	13.89	95.4	294.6	7.69

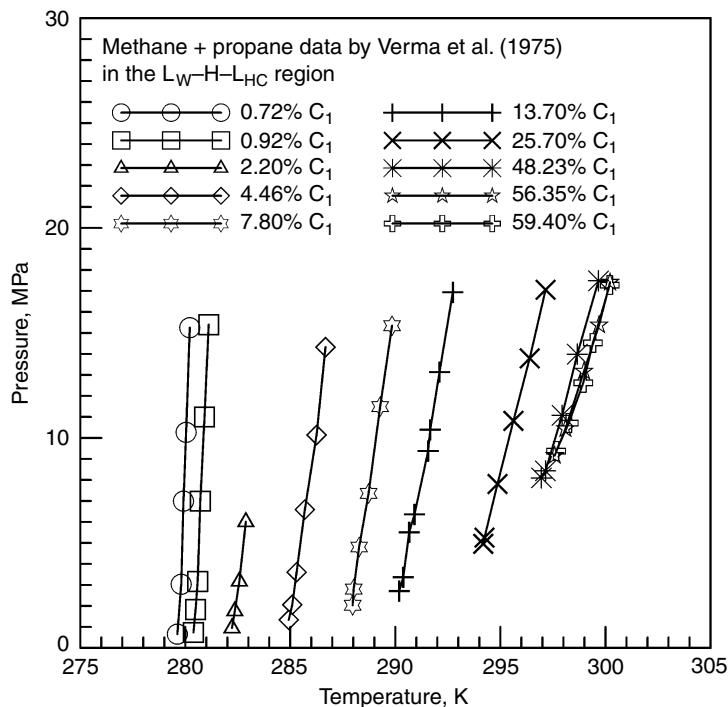


FIGURE 6.29 Methane + propane mixture ( $L_w$ -H- $L_p$ ) data.

*Hydrate:* Methane + isobutane

*Reference:* Wu et al. (1976)

*Phases:*  $L_w$ -H-V and  $L_w$ -H-V- $L_{iC_4}$

### $L_w$ -H-V

$\% i-C_4H_{10}$	$T$ (K)	$P$ (kPa)	$\% i-C_4H_{10}$	$T$ (K)	$P$ (kPa)
0.23	275.2	2,080	2.50	277.8	1,080
0.23	279.7	3,440	2.50	279.8	1,390
0.27	284.6	6,010	2.50	283.3	2,150
0.36	285.4	6,190	2.50	285.2	2,740
0.37	288.0	9,690	2.50	287.2	3,450
0.40	276.2	1,810	2.50	289.3	4,560
0.43	285.3	5,590	2.50	293.6	10,070
0.45	282.0	3,500	6.00	274.8	505
0.46	280.9	3,150	6.00	280.4	1,010
0.54	286.2	5,480	6.00	284.5	1,690

**Continued**

%i-C <sub>4</sub> H <sub>10</sub>	T (K)	P (kPa)	%i-C <sub>4</sub> H <sub>10</sub>	T (K)	P (kPa)
0.82	275.4	1,270	6.00	288.5	2,820
0.82	280.0	2,190	15.20	274.0	304
0.82	283.5	3,340	15.20	278.9	564
0.82	287.4	5,900	15.20	283.4	1,030
0.82	290.9	10,040	15.20	288.9	2,030
1.20	274.4	950	28.60	273.9	208
1.20	277.7	1,390	28.60	277.2	356
1.20	279.9	1,800	28.60	279.2	477
1.20	283.2	2,700	28.60	280.8	602
1.20	284.9	3,470	28.60	282.7	786
1.20	287.5	4,880	63.60	273.8	159
1.20	290.0	6,950	63.60	275.5	221
2.50	274.4	703	63.60	276.9	284

**L<sub>W</sub>-H-V-L<sub>iC<sub>4</sub></sub>**  
**(%i-C<sub>4</sub>H<sub>10</sub> = vapor phase)**

%i-C <sub>4</sub> H <sub>10</sub>	T (K)	P (kPa)	%i-C <sub>4</sub> H <sub>10</sub>	T (K)	P (kPa)
65.1	277.0	254	12.2	293.2	3,990
44.5	279.6	427	12.0	293.3	4,100
31.3	282.3	703	11.2	294.8	5,560
23.8	284.7	1,030	11.0	295.3	5,760
18.2	287.5	1,540	15.0	298.0	9,990
13.8	290.8	2,700	19.8	298.6	11,570
13.5	291.5	2,970			

*Mixture:* Methane + isobutane

*Reference:* Ng and Robinson (1976a)

*Phases:* L<sub>W</sub>-H-L<sub>iC<sub>4</sub></sub>

%CH <sub>4</sub>	T (K)	P (kPa)	%CH <sub>4</sub>	T (K)	P (kPa)
0.1	275.4	179	15.2	288.9	1,931
0.1	275.4	226	15.2	289.0	2,441
0.1	275.4	357	15.2	289.4	3,785
0.1	275.4	903	15.2	289.9	7,129
0.1	275.6	2,406	15.2	290.5	10,577
0.1	275.7	5,653	15.2	291.2	14,073
0.1	275.8	14,251	28.4	292.9	3,792
4.3	282.2	682	28.4	293.0	4,268
4.3	282.3	1,048	28.4	293.7	6,957

(Continued)

**Continued**

%CH <sub>4</sub>	T (K)	P (kPa)	%CH <sub>4</sub>	T (K)	P (kPa)
4.3	282.7	2,179	28.4	294.8	10,439
4.3	282.9	4,474	28.4	295.0	13,866
4.3	283.3	8,233	42.5	295.9	6,619
4.3	283.9	14,024	42.5	296.4	8,784
8.7	286.4	1,338	42.5	297.2	11,321
8.7	266.5	1,744	42.5	297.9	14,093
8.7	286.8	3,958	64.7	298.1	10,204
8.7	287.2	6,902	64.7	298.4	11,232
8.7	287.8	11,197	64.7	298.7	12,528
8.7	288.4	14,231	64.7	299.3	14,548

*Hydrate:* Methane + isobutane

*Reference:* Thakore and Holder (1987)

*Phases:* L<sub>W</sub>-H-V

$$T = 274.35 \text{ K}$$

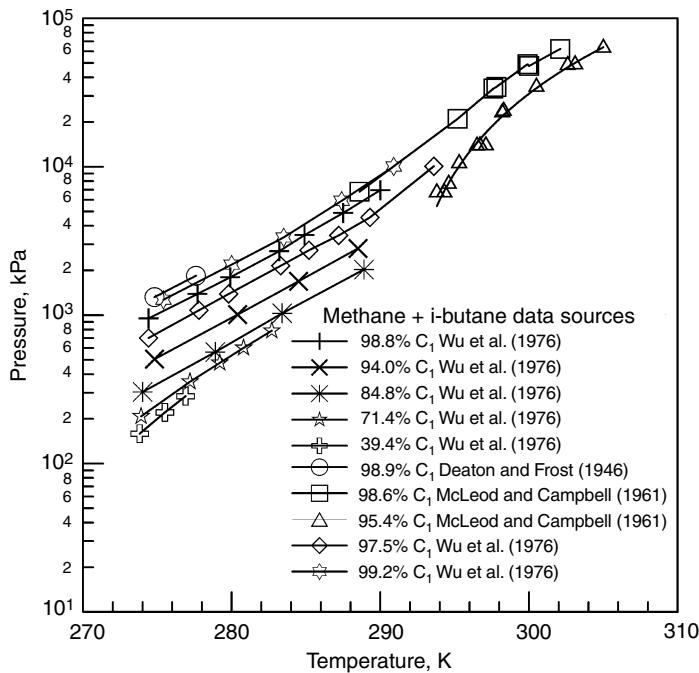
%CH <sub>4</sub>	P (kPa)	%CH <sub>4</sub>	P (kPa)	%CH <sub>4</sub>	P (kPa)
100.0	3099	31.3	156	7.3	131
94.9	841	17.2	136	6.6	129
91.9	461	15.0	134	5.6	129
79.2	268	12.4	133	5.1	129
72.5	234	9.1	132	4.8	127
63.2	210	8.6	131	3.6	129
50.0	180	7.6	131	0.0	128

*Hydrate:* Methane + *n*-butane

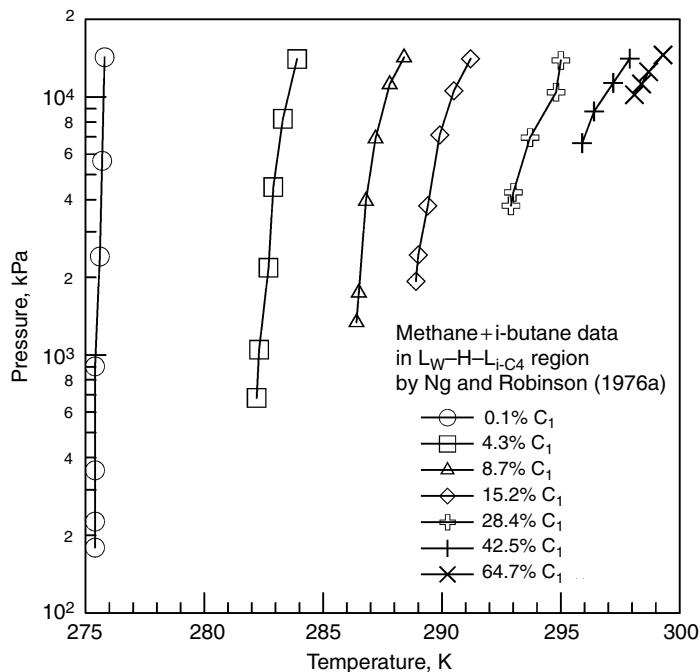
*Reference:* Deaton and Frost (1946)

*Phases:* L<sub>W</sub>-H-V

%CH <sub>4</sub>	T (K)	P (kPa)	%CH <sub>4</sub>	T (K)	P (kPa)
97.4	274.8	2048	97.5	274.8	2165
97.4	277.6	2875	99.2	274.8	3075
97.4	280.4	4061	99.2	277.6	4075



**FIGURE 6.30** Methane + iso-butane mixture ( $L_W$ -H-V) data.



**FIGURE 6.31** Methane + iso-butane mixture ( $L_W$ -H- $L_{iC_4}$ ) data.

*Hydrate:* Methane + *n*-butane

*Reference:* McLeod and Campbell (1961)

*Phases:* L<sub>W</sub>–H–V

%CH <sub>4</sub>	T (K)	P (MPa)	%CH <sub>4</sub>	T (K)	P (MPa)
97.4	285.0	7.69	94.7	295.1	34.16
97.4	287.7	12.45	94.7	297.9	48.23
97.4	295.7	34.58	94.7	300.1	61.61
97.4	301.1	65.95	94.7	301.1	68.43
97.4	286.3	10.45	94.7	290.3	17.96
97.4	285.7	9.07	94.7	288.8	13.89
97.4	282.5	5.76	94.7	287.6	10.65
94.7	287.5	10.65	94.7	286.6	8.69
94.7	292.4	23.89	94.7	285.3	7.00

*Hydrate:* Methane + *n*-butane

*Reference:* Ng and Robinson (1976b)

*Phases:* L<sub>W</sub>–H–V

%n-C <sub>4</sub> H <sub>10</sub>	T (K)	P (MPa)	%n-C <sub>4</sub> H <sub>10</sub>	T (K)	P (MPa)
1.64	276.0	2.48	2.48	284.75	7.47
1.64	279.4	3.82	2.48	286.40	10.40
1.64	283.4	6.65	3.91	276.91	2.15
1.64	286.1	10.08	3.91	279.74	3.14
1.64	287.4	12.06	3.91	283.12	5.09
1.64	288.5	13.72	3.91	285.95	8.16
2.48	276.4	2.30	3.91	287.55	11.05
2.48	279.7	3.59	5.82	277.99	2.05
2.48	282.4	5.13	5.82	281.43	3.29

*Hydrate:* Methane + *n*-butane

*Reference:* John and Holder (1982b)

*Phases:* L<sub>W</sub>–H–V, I–H–V–L<sub>n</sub>-C<sub>4</sub>H<sub>10</sub>, L<sub>W</sub>–H–V–L<sub>n</sub>-C<sub>4</sub>H<sub>10</sub>

### I–H–V

%n-C <sub>4</sub> H <sub>10</sub>	T (K)	P (kPa)	%n-C <sub>4</sub> H <sub>10</sub>	T (K)	P (kPa)
0.4	251.2	1267	4.2	262.2	846
0.7	251.2	1011	6.3	262.2	715
1.1	251.2	805	9.3	262.2	639
1.8	251.2	680	12.6	262.2	570*

**Continued****I-H-V**

% <i>n</i> -C <sub>4</sub> H <sub>10</sub>	<i>T</i> (K)	<i>P</i> (kPa)	% <i>n</i> -C <sub>4</sub> H <sub>10</sub>	<i>T</i> (K)	<i>P</i> (kPa)
3.8	251.2	522	0.55	268.2	2204
5.0	251.2	474	0.75	268.2	1963
5.9	251.2	446	1.15	268.2	1728
8.8	251.2	391	1.50	268.2	1563
13.3	251.2	336*	2.30	268.2	1342
0.5	256.2	1480	3.15	268.2	1232
0.6	256.2	1246	3.40	268.2	1177
1.0	256.2	1067	5.20	268.2	1011
1.5	256.2	901	6.80	268.2	915
2.0	256.2	818	7.80	268.2	880
3.2	256.2	680	11.00	268.2	784*
4.5	256.2	605	0.80	273.1	2611
6.5	256.2	536	0.95	273.1	2446
10.0	256.2	460	1.20	273.1	2335
11.4	256.2	446	1.40	273.1	2142
12.8	256.2	432*	1.95	273.1	1894
0.5	262.2	1784	2.75	273.1	1618
0.9	262.2	1529	4.10	273.1	1384
1.2	262.2	1356	6.60	273.1	1136
2.0	262.2	1108	10.10	273.1	1011*
2.9	262.2	970			

\* = Q<sub>1</sub> Quadruple point (I-H-V-L<sub>*n*-C<sub>4</sub>H<sub>10</sub></sub>).

**I-H-V-L<sub>*n*-C<sub>4</sub>H<sub>10</sub></sub>**

<i>T</i> (K)	<i>P</i> (kPa)						
255.3	417.1	259.9	524.0	264.5	661.9	270.3	875.6
256.1	430.9	260.8	544.7	255.1	682.6	271.0	903.2
257.2	458.5	261.9	575.7	265.9	710.2	271.7	937.7
258.0	479.2	263.6	620.5	269.1	813.6	272.5	979.0
259.0	499.9	263.9	634.0	269.2	827.4		

**L<sub>W</sub>-H-V-L<sub>*n*-C<sub>4</sub>H<sub>10</sub></sub>**

<i>T</i> (K)	<i>P</i> (kPa)						
273.3	1046.0	274.3	1177.0	275.9	1504.0	276.8	1722.0
273.8	1073.0	275.1	1342.0				

*Hydrate:* Methane + *n*-butane

*Reference:* Ng and Robinson (1977)

*Phases:* L<sub>W</sub>–H–L<sub>n</sub>–C<sub>4</sub>H<sub>10</sub>

### %CH<sub>4</sub> in L<sub>n</sub>–C<sub>4</sub>H<sub>10</sub>

%CH <sub>4</sub>	T (K)	P (MPa)	%CH <sub>4</sub>	T (K)	P (MPa)
8.7	275.0	1.24*	21.8	282.7	9.05
8.7	275.6	3.41	21.8	283.4	12.13
8.7	275.7	6.01	21.8	283.3	12.34
8.7	276.3	10.06	42.4	285.9	6.62*
8.7	276.7	12.82	42.4	286.1	7.78
15.7	279.4	2.39*	42.4	286.4	9.09
15.7	279.4	2.96	42.4	286.9	10.92
15.7	279.5	3.61	42.4	287.0	12.16
15.7	279.8	4.27	42.4	287.4	13.82
15.7	280.0	6.76	50.1	287.4	8.83*
15.7	280.6	9.09	50.1	287.5	9.85
15.7	281.1	12.44	50.1	287.8	10.75
21.8	281.8	3.45*	50.1	288.2	12.47
21.8	282.1	5.23	50.1	288.5	13.82
21.8	282.4	6.75			

\* = Q<sub>2</sub> Quadruple point (L<sub>W</sub>–H–V–L<sub>n</sub>–C<sub>4</sub>H<sub>10</sub>).

*Hydrate:* Methane + nitrogen

*Reference:* Jhaveri and Robinson (1965)

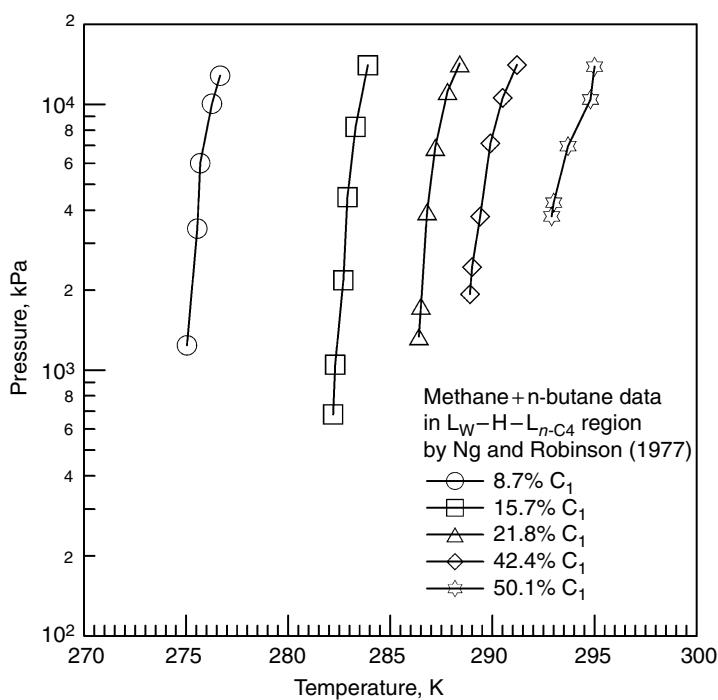
*Phases:* L<sub>W</sub>–H–V

%CH <sub>4</sub>	T (K)	P (MPa)	%CH <sub>4</sub>	T (K)	P (MPa)
87.3	282.8	7.40	50.25	291.8	33.19
87.3	284.6	9.31	27.2	273.2	7.96
87.3	287.7	14.52	27.2	277.1	10.16
87.3	289.5	17.11	27.2	280.0	12.64
87.3	290.4	17.49	27.2	282.9	17.04
87.3	291.0	19.53	27.2	283.2	17.50
87.3	291.5	19.99	27.2	285.1	20.72
87.3	292.9	22.94	27.2	286.8	25.15
87.3	293.4	24.66	27.2	288.0	28.49

**Continued**

%CH <sub>4</sub>	T (K)	P (MPa)	%CH <sub>4</sub>	T (K)	P (MPa)
87.3	295.2	31.31	24.0	273.2	8.62
73.1	273.2	3.90	24.0	274.6	9.15
73.1	283.3	8.95	24.0	278.8	12.96
73.1	286.8	13.22	24.0	282.1	17.44
73.1	289.9	19.55	24.0	285.1	24.34
73.1	292.3	25.99	24.0	287.6	31.99
73.1	294.4	34.33	24.0	289.1	35.96
50.25	273.2	4.96	10.8	273.2	12.55
50.25	277.2	6.13	10.8	277.2	15.86
50.25	279.7	7.77	10.8	279.1	19.39
50.25	282.3	10.49	10.8	280.9	22.52
50.25	287.3	17.90	10.8	282.1	25.82
50.25	289.8	24.99	10.8	283.2	28.79

(Continued)

**FIGURE 6.32** Methane + n-butane mixture (L<sub>w</sub>-H-L<sub>n-C<sub>4</sub>H<sub>10</sub></sub>) data.

**Continued****Isothermal  $P$ - $z$ - $y$  Data ( $z$  = hydrate mol fraction)**

273.2 K			277.4 K			279.8 K		
$P$ (MPa)	$y_{N_2}$	$z_{N_2}$	$P$ (MPa)	$y_{N_2}$	$z_{N_2}$	$P$ (MPa)	$y_{N_2}$	$z_{N_2}$
2.64	0.00	0.00	13.32	0.925	0.81	25.18	1.00	1.00
3.62	0.16	0.065	14.59	0.94	0.86	5.14	0.00	0.00
4.31	0.31	0.098	16.21	1.00	1.00	7.14	0.35	0.091
5.35	0.53	0.20	3.86	0.00	0.00	8.37	0.46	0.224
6.55	0.645	0.35	5.20	0.44	0.18	15.55	0.75	0.55
7.75	0.725	0.425	8.11	0.63	0.31	20.67	0.84	0.68
10.64	0.815	0.62	10.34	0.74	0.47	25.23	0.914	0.802
11.65	0.88	0.71	12.06	0.78	0.56	32.42	1.00	1.00
12.77	0.90	0.765						

 $z_{N_2}$  = Mol fraction nitrogen in hydrate phase. $y_{N_2}$  = Mol fraction nitrogen in vapor phase.*Hydrate:* Methane + nitrogen*Reference:* Mei et al. (1996a)*Phases:* L<sub>W</sub>-H-V**89.26 mol% CH<sub>4</sub>**

$T$ (K)	$P$ (MPa)	$T$ (K)	$P$ (MPa)
273.7	2.99	279.2	5.24
274.8	3.31	281.2	6.58
275.6	3.73	283.2	8.12
277.1	4.36	285.3	10.1

*Hydrate:* Methane + carbon dioxide*Reference:* Unruh and Katz (1949)*Phases:* L<sub>W</sub>-H-V

%CH <sub>4</sub> *	$T$ (K)	$P$ (MPa)	%CH <sub>4</sub> *	$T$ (K)	$P$ (MPa)
66.0	277.0	2.84	91.5	278.4	3.95
70.0	278.9	3.46	93.0	281.0	5.10
64.0	278.9	3.43	94.5	283.8	6.89
68.0	280.9	4.24	29.0	279.6	3.00
72.0	282.9	5.17	39.0	282.2	4.27
77.0	284.7	6.47	48.0	283.8	5.27
40.0	275.5	1.99	59.0	285.5	6.89
56.0	279.2	3.08	59.0	285.7	7.00
87.5	276.4	3.20			

\* = Vapor composition calculated in reference.

*Hydrate:* Methane + carbon dioxide

*Reference:* Adisasmito et al. (1991)

*Phases:* L<sub>w</sub>-H-V

%CO <sub>2</sub>	T (K)	P (MPa)	%CO <sub>2</sub>	T (K)	P (MPa)
10.0	273.7	2.52	40.0	280.7	4.03
9.0	275.8	3.10	39.0	283.1	5.43
8.0	277.8	3.83	39.0	285.1	6.94
8.0	280.2	4.91	39.0	287.4	9.78
8.0	283.2	6.80	50.0	275.6	1.99
8.0	285.1	8.40	47.0	278.5	2.98
9.0	287.2	10.76	40.0	280.9	4.14
14.0	274.6	2.59	41.0	281.8	4.47
13.0	276.9	3.24	44.0	285.1	6.84
13.0	279.1	4.18	45.0	287.4	9.59
13.0	281.6	5.38	73.0	274.6	1.66
13.0	284.0	7.17	70.0	276.4	2.08
12.0	286.1	9.24	68.0	278.2	2.58
13.0	287.4	10.95	68.0	280.2	3.28
25.0	273.8	2.12	67.0	282.0	4.12
22.0	279.4	3.96	79.0	273.7	1.45
22.0	283.4	6.23	78.0	275.9	1.88
21.0	285.2	7.75	76.0	277.8	2.37
25.0	287.6	10.44	75.0	279.6	2.97
44.0	273.7	1.81	74.0	281.6	3.79
42.0	276.9	2.63	85.0	282.7	4.37

*Hydrate:* Methane + carbon dioxide

*Reference:* Ohgaki et al. (1996)

*Phases:* L<sub>w</sub>-H-V

**T = 280.3 K**

P (MPa)	z <sub>CO<sub>2</sub></sub>	y <sub>CO<sub>2</sub></sub>	P (MPa)	z <sub>CO<sub>2</sub></sub>	y <sub>CO<sub>2</sub></sub>
3.04	1.00	1.000	4.22	0.44	0.241
3.24	0.84	0.683	4.31	0.39	0.215
3.38	0.80	0.585	4.32	0.36	0.217
3.60	0.67	0.488	4.34	0.37	0.203
3.64	0.69	0.450	4.37	0.35	0.203
3.67	0.68	0.448	4.37	0.36	0.183
3.71	0.61	0.429	4.44	0.36	0.179
3.77	0.60	0.384	4.50	0.35	0.169
3.86	0.59	0.357	4.57	0.32	0.144

(Continued)

**Continued**

<b>P (MPa)</b>	<b><math>z_{\text{CO}_2}</math></b>	<b><math>y_{\text{CO}_2}</math></b>	<b>P (MPa)</b>	<b><math>z_{\text{CO}_2}</math></b>	<b><math>y_{\text{CO}_2}</math></b>
3.98	0.53	0.302	4.58	0.32	0.141
4.00	0.52	0.310	4.63	0.29	0.143
4.01	0.55	0.311	4.75	0.24	0.104
4.06	0.51	0.288	4.85	0.23	0.090
4.07	0.52	0.293	4.99	0.16	0.065
4.15	0.47	0.268	5.46	0.00	0.000
4.20	0.45	0.245			

Mole fraction of CO<sub>2</sub> in vapor,  $y_{\text{CO}_2}$  measured directly;  
calculated mole fraction of CO<sub>2</sub> in hydrate phase,  $z_{\text{CO}_2}$

*Hydrate:* Methane + carbon dioxide

*Reference:* Fan and Guo (1999)

*Phases:* L<sub>W</sub>-H-V

**3.46% CH<sub>4</sub>**

<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
273.5	1.10	277.9	2.05
273.6	1.16	280.4	3.00
273.7	1.20	281.7	3.73
277.2	1.95	282.3	4.80
277.6	1.94		

*Hydrate:* Methane + carbon dioxide

*Reference:* Seo et al. (2001a) and Seo and Lee (2001b)

*Phases:* H-V, L<sub>W</sub>-H-V, L<sub>W</sub>-H-V-L<sub>CO<sub>2</sub></sub>

**H-V**

<b>%CO<sub>2</sub> (in vapor)</b>	<b>%CO<sub>2</sub> (in hydrate)</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>%CO<sub>2</sub> (in vapor)</b>	<b>%CO<sub>2</sub> (in hydrate)</b>	<b>T (K)</b>	<b>P (MPa)</b>
28.44	91.51	273.06	2.0	64.11	98.08	277.46	2.6
40.25	93.63	274.06	2.0	83.39	99.35	278.06	2.6
60.76	98.15	275.36	2.0	13.25	64.72	276.56	3.5
79.44	99.65	276.26	2.0	25.23	73.34	277.56	3.5
12.93	66.18	273.76	2.6	41.91	88.99	278.96	3.5
23.44	84.68	274.86	2.6	61.13	95.23	279.86	3.5
41.46	92.72	276.26	2.6	83.44	99.3	280.46	3.5

**Continued****L<sub>W</sub>-H-V**

%CO <sub>2</sub> (in vapor)		P (MPa)		%CO <sub>2</sub> (in vapor)		P (MPa)	
%CO <sub>2</sub> (loading)	T (K)	P (MPa)	%CO <sub>2</sub> (loading)	T (K)	P (MPa)		
	40.67	272.66	1.5		78.43	278.26	2.6
60.0	61.69	273.56	1.5	100.0	100.00	279.16	2.6
	90.41	274.36	1.5	0.0	0.00	276.16	3.5
100.0	100.00	274.76	1.5	20.0	20.09	278.06	3.5
20.0	26.34	273.56	2.0		42.65	279.26	3.5
	33.75	274.36	2.0	60.0	60.87	280.16	3.5
60.0	56.48	275.86	2.0		76.17	280.76	3.5
	79.54	276.56	2.0	100.0	100.00	281.46	3.5
100.0	100.00	277.16	2.0	0.0	0.00	279.60	5.0
0.0	0.00	273.16	2.6	20.0	19.71	281.46	5.0
20.0	18.54	275.36	2.6		40.89	282.56	5.0
	39.72	276.76	2.6	100.0	59.89	283.26	5.0
60.0	61.95	277.96	2.6		80.52	283.56	5.0

%CO <sub>2</sub> (in vapor)	T (K)	P (MPa)	%CO <sub>2</sub> (in vapor)	T (K)	P (MPa)
Q <sub>2</sub> : L <sub>W</sub> -H-V-L <sub>CO<sub>2</sub></sub> (Seo et al., 2001a)					
82.50	285.56	6.72	94.83	283.86	4.93
89.93	284.56	5.56	100.00	283.32	4.53
Q <sub>2</sub> : L <sub>W</sub> -H-V-L <sub>CO<sub>2</sub></sub> (Seo and Lee 2001b)					
100.00	283.32	4.12	83.56	285.03	6.22
94.04	283.86	4.93	79.74	285.76	7.251
89.13	284.39	5.50			

*Hydrate:* Methane + carbon dioxide*Reference:* Hachikubo et al. (2002)*Phases:* L<sub>W</sub>-H-V

%CO <sub>2</sub>	T (K)	P (MPa)
100	273.93	1.349
100	276.80	1.806
100	278.05	2.204
100	263.17	0.774
100	268.11	0.921
100	271.23	1.029
100	277.78	2.187
0	268.4	2.324
0	271.28	2.527

(Continued)

**Continued**

<b>%CO<sub>2</sub></b>	<b>T (K)</b>	<b>P (MPa)</b>
77	271.25	1.271
50	271.41	1.434
25	271.37	2.022

*Hydrate:* Methane + hydrogen sulfide

*Reference:* Noaker and Katz (1954)

*Phases:* L<sub>W</sub>-H-V

<b>%CH<sub>4</sub>*</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>%CH<sub>4</sub>*</b>	<b>T (K)</b>	<b>P (MPa)</b>
91.77/93.0	288.7	4.83	96.22/96.10	276.5	2.03
90.49/91.0	284.3	2.59	99.0	278.4	3.24
93.7	282.3	3.03	98.96	282.3	4.62
93.5	287.1	4.79	98.89/98.94	284.8	6.69
93.0	290.1	6.79	78.0	287.6	2.10
94.27/93.5	279.3	2.21	80.20/79.0	295.4	5.07
93.40/93.0	290.1	6.38	78.60/78.0	279.8	1.03
97.0	278.7	2.83	90.5	281.5	2.07
96.9	282.9	4.27	89.0	287.3	3.59
97.08/97.05	287.6	6.65	88.50/88.50	292.1	6.00

\* If two values of vapor composition are provided the first was measured and the second calculated; if only one value of vapor composition is given, it was calculated in the reference.

### BINARY GUEST MIXTURE CONTAINING ETHANE AND HEAVIER (OR NONCOMBUSTIBLE) COMPOUNDS

*Hydrate:* Ethane + propane

*Reference:* Holder and Hand (1982)

*Phases:* L<sub>W</sub>-H-V and L<sub>W</sub>-H-L<sub>HC</sub>

### L<sub>W</sub>-H-L<sub>HC</sub>

<b>%C<sub>3</sub>H<sub>8</sub></b>	<b>T (K)</b>	<b>P (kPa)</b>	<b>%C<sub>3</sub>H<sub>8</sub></b>	<b>T (K)</b>	<b>P (kPa)</b>
16.8	278.1	910*	43.5	280.2	5180
16.8	278.1	1440	43.5	280.6	6550
16.8	278.2	1550	68.9	284.3	2230*
16.8	278.3	2560	68.9	284.3	2900
16.8	278.6	2790	68.9	284.4	5580
43.5	279.9	1470*	68.9	284.5	7280
43.5	279.9	2300			

\* = Q<sub>2</sub> Quadruple point (L<sub>W</sub>-H-V-L<sub>HC</sub>).

**Continued****L<sub>W</sub>-H-V**

%C <sub>3</sub> H <sub>8</sub>	T (K)	P (kPa)	%C <sub>3</sub> H <sub>8</sub>	T (K)	P (kPa)
72.0	277.9	660	32.2	281.1	1630
72.0	276.9	530	27.1	273.4	490
72.0	276.5	460	27.1	273.9	540
55.7	275.9	50	27.1	274.3	610
55.7	276.4	570	27.1	274.6	600
55.7	276.7	610	27.1	275.3	770
55.7	277.0	650	27.1	275.6	870
55.7	277.4	720	27.1	275.8	920
54.1	275.8	500	26.0	274.5	630
54.1	276.4	590	26.0	274.7	690
54.1	277.0	660	26.0	275.2	790
54.1	277.6	770	26.0	276.4	940
54.1	278.0	850	26.0	277.1	1020
34.2	273.9	440	26.0	277.7	1120
34.2	274.2	470	18.6	273.1	540
34.2	275.1	590	18.6	273.8	640
34.2	275.8	690	18.6	273.8	640
34.2	276.2	830	18.6	274.3	660
34.2	276.3	850	18.6	274.7	710
34.2	276.5	870	18.6	276.8	940
34.2	277.6	1060	18.6	278.9	1210
32.2	275.6	750	18.6	279.6	1300
32.2	276.1	870	15.0	275.7	740
32.2	277.1	1140	15.0	277.2	900
32.2	277.2	1160	15.0	280.6	1370
32.2	277.9	1220	14.3	279.7	1190
32.2	278.6	1300	14.3	280.2	1300
32.2	279.4	1430	14.3	282.1	1670
32.2	280.4	1560	14.3	283.2	2030
32.2	280.6	1610	14.3	283.3	2020

*Hydrates:* Ethane + propane*Reference:* Song and Kobayashi (1994)*Phases:* L<sub>HC</sub>-H**Isobaric Data at 3.447 MPa**

Liquid phase %C <sub>2</sub> H <sub>6</sub>	H <sub>2</sub> O mol fract (x 10 <sup>4</sup> )	Liquid phase %C <sub>2</sub> H <sub>6</sub>	H <sub>2</sub> O mol fract (x 10 <sup>4</sup> )
0.5	276.8	1.13	0.75
0.5	267.0	0.532	0.75

(Continued)

**Continued**

Liquid phase %C <sub>2</sub> H <sub>6</sub>	H <sub>2</sub> O mol fract (x10 <sup>4</sup> )	Liquid phase %C <sub>2</sub> H <sub>6</sub>	H <sub>2</sub> O mol fract (x10 <sup>4</sup> )
T (K)		T (K)	
0.5	0.296	0.75	0.311
0.5	0.214	0.895	1.076
0.75	1.101	0.895	0.465
0.75	0.980	0.895	0.346
0.75	0.611	0.895	0.226

*Hydrates:* Ethane + carbon dioxide

*Reference:* Adisasmito and Sloan (1992)

*Phases:* L<sub>W</sub>-H-V

%CO <sub>2</sub>	T (K)	P (kPa)	%CO <sub>2</sub>	T (K)	P (kPa)
22.0	273.7	565.4	60.2	284.4	2833.7
20.2	275.6	696.4	80.7	274.2	1041.1
18.9	277.5	868.7	83.6	276.0	1344.5
19.3	279.3	1089.4	83.3	277.5	1613.4
24.6	281.1	1406.5	82.1	279.4	1958.1
25.6	282.9	1751.3	81.7	281.0	2406.3
31.7	285.1	2392.5	81.9	283.0	3150.9
42.8	276.5	854.9	81.4	284.6	3785.2
41.7	278.4	1075.6	93.4	273.9	1199.7
40.6	280.2	1351.4	93.2	275.6	1482.4
40.0	282.0	1716.8	92.6	277.6	1847.8
40.2	283.8	2185.6	92.4	279.2	2220.1
38.9	285.8	2826.8	92.3	281.2	2833.7
39.8	287.8	3826.6	96.5	273.7	1241.1
63.9	273.5	779.1	96.2	275.2	1482.4
62.8	274.8	889.4	96.1	276.7	1758.2
63.0	276.8	1123.8	95.5	278.6	2220.1
62.9	278.7	1420.3	95.7	280.6	2854.4
62.1	280.7	1806.4	96.6	281.8	3357.7
59.9	282.6	2240.8	96.7	283.1	4081.7

*Hydrate:* Ethane + carbon dioxide

*Reference:* Fan and Guo (1999)

*Phases:* L<sub>W</sub>-H-V

### 5.31 mol% Ethane

T (K)	P (MPa)	T (K)	P (MPa)
276.0	1.58	281.6	3.31
278.2	2.07	282.7	3.90
280.4	2.84		

## BINARY GUEST MIXTURES CONTAINING PROPANE AND HEAVIER (OR NONCOMBUSTIBLE) COMPONENTS

*Hydrate:* Propane + isobutane

*Reference:* Kamath and Holder (1984)

*Phases:* I–H–V

%C <sub>3</sub> H <sub>8</sub>	T (K)	P (kPa)	%C <sub>3</sub> H <sub>8</sub>	T (K)	P (kPa)
0.0	272.1	101.3	90.7	272.2	149.43
12.5	272.2	108.2	90.9	272.2	149.24
12.6	272.2	108.5	95.8	272.1	152.04
50.7	272.2	124.0	95.8	272.1	152.13
50.5	272.2	124.6	95.9	272.2	153.70
49.8	272.2	130.0	100.0	272.1	171.32
81.0	272.1	137.1			

*Hydrate:* Propane + isobutane

*Reference:* Paranjpe et al. (1987)

*Phases:* L<sub>W</sub>–H–V–L<sub>HC</sub>

**%C<sub>3</sub>H<sub>8</sub> = vapor composition**

%C <sub>3</sub> H <sub>8</sub>	T (K)	P (kPa)	%C <sub>3</sub> H <sub>8</sub>	T (K)	P (kPa)
11.2	275.25	213.0	48.8	276.65	365.4
27.1	275.85	282.7	65.3	277.15	426.1
47.5	276.55	355.1	79.4	277.85	490.0

*Hydrate:* Propane + *n*-butane

*Reference:* Kamath and Holder (1984)

*Phases:* I–H–V

%C <sub>3</sub> H <sub>8</sub>	T (K)	P (kPa)	%C <sub>3</sub> H <sub>8</sub>	T (K)	P (kPa)
90.3	260.15	110.10	83.5	248.15	69.03
90.3	257.85	99.26	83.5	245.85	66.76
90.3	254.35	83.86	83.5	242.45	59.59
90.3	248.65	67.09	70.0	253.75	97.16
90.3	245.05	61.23	70.0	250.95	85.86
90.3	242.05	49.20	70.0	245.65	70.07
83.5	250.55	76.36	70.0	241.85	55.38
83.5	249.55	73.37	70.0	238.25	46.90

*Hydrate:* Propane + *n*-butane

*Reference:* Paranjpe et al. (1987)

*Phases:* I–H–V, L<sub>W</sub>–H–V, L<sub>W</sub>–H–V–L<sub>n</sub>–C<sub>4</sub>, I–H–V–L<sub>n</sub>–C<sub>4</sub>

### I–H–V (%C<sub>3</sub>H<sub>8</sub> = vapor composition)

%C <sub>3</sub> H <sub>8</sub>	T (K)	P (kPa)	%C <sub>3</sub> H <sub>8</sub>	T (K)	P (kPa)
86.4	271.2	153.1	80.3	271.2	191.7
87.9	271.2	170.9	76.0	271.2	204.1
86.1	271.2	177.9	67.6	271.2	217.9

### L<sub>W</sub>–H–V

%C <sub>3</sub> H <sub>8</sub>	T (K)	P (kPa)	%C <sub>3</sub> H <sub>8</sub>	T (K)	P (kPa)
99.6	275.2	269.6	81.7	274.2	269.6
92.4	275.2	281.3	100.0	273.2	169.6
89.4	275.2	302.0	96.9	273.2	171.7
87.3	275.2	308.9	95.3	273.2	177.9
88.0	275.2	317.2	93.8	273.2	183.4
86.3	275.2	339.2	89.5	273.2	193.1
100.0	274.2	219.3	86.4	273.2	208.2
96.1	274.2	228.2	82.8	273.2	220.6
93.3	274.2	240.6	78.8	273.2	227.5
90.6	274.2	244.8	72.5	273.2	244.1

### I–H–V–L<sub>n</sub>–C<sub>4</sub>

%C <sub>3</sub> H <sub>8</sub>	T (K)	P (kPa)	%C <sub>3</sub> H <sub>8</sub>	T (K)	P (kPa)
64.9	273.0	215.1	64.9	267.4	174.4
67.4	271.0	211.7	63.9	266.8	168.2
67.3	270.0	201.3	64.8	264.0	157.9
62.1	269.6	184.8	66.5	262.0	146.2
66.5	269.0	192.4	65.1	260.6	133.8

### L<sub>W</sub>–H–V–L<sub>n</sub>–C<sub>4</sub>

%C <sub>3</sub> H <sub>8</sub>	T (K)	P (kPa)	C <sub>3</sub> H <sub>8</sub>	T (K)	P (kPa)
92.6	277.85	511.6	81.6	275.2	324.1
84.6	276.65	399.2	71.0	273.6	242.7

*Mixture:* Propane + nitrogen

*Reference:* Ng et al. (1977, 1978)

*Phases:* L<sub>W</sub>-H-V, L<sub>W</sub>-H-V-L<sub>C<sub>3</sub></sub>, L<sub>W</sub>-H-L<sub>C<sub>3</sub></sub>

**L<sub>W</sub>-H-V (%C<sub>3</sub>H<sub>8</sub> = vapor composition)**

%C <sub>3</sub> H <sub>8</sub>	T (K)	P (MPa)	%C <sub>3</sub> H <sub>8</sub>	T (K)	P (MPa)
0.94	275.3	4.59	13.00	281.5	2.74
0.94	279.6	8.16	13.00	283.2	3.54
0.94	283.0	13.68	13.00	286.2	5.54
0.94	284.3	18.09	28.30	274.6	0.569
2.51	276.3	3.03	28.30	277.0	0.889
2.51	279.3	4.51	28.30	279.2	1.31
2.51	282.7	7.35	28.30	280.8	1.72
2.51	287.1	13.64	54.20	274.2	0.332
6.18	274.5	1.72	54.20	276.8	0.570
6.18	278.3	2.85	54.20	280.3	1.19
6.18	283.0	5.50	75.00	274.5	0.256
6.18	287.0	9.47	75.00	275.9	0.359
6.18	289.2	13.71	75.00	277.4	0.517
13.00	275.1	1.10	75.00	278.7	0.676
13.00	278.4	1.72			

**L<sub>W</sub>-H-V-L<sub>C<sub>3</sub></sub> (%C<sub>3</sub>H<sub>8</sub> = vapor composition)**

%C <sub>3</sub> H <sub>8</sub>	T (K)	P (MPa)	%C <sub>3</sub> H <sub>8</sub>	T (K)	P (MPa)
71.1	279.0	0.76	18.8	289.6	8.58
47.7	281.2	1.54	21.3	292.3	13.37
26.5	283.2	2.88	21.6	292.3	13.51
22.9	284.6	3.68	23.0	293.0	14.92
18.8	288.0	6.37	23.7	293.8	16.99

**L<sub>W</sub>-H-L<sub>C<sub>3</sub></sub> (%C<sub>3</sub>H<sub>8</sub> = liquid composition)**

%C <sub>3</sub> H <sub>8</sub>	T (K)	P (MPa)	%C <sub>3</sub> H <sub>8</sub>	T (K)	P (MPa)
99.0	280.1	1.17	89.6	287.4	5.83
99.0	280.1	1.98	89.6	287.9	8.14
99.0	280.3	5.65	89.6	288.5	11.06
99.0	280.6	9.39	89.6	288.8	12.82

(Continued)

**Continued**

%C <sub>3</sub> H <sub>8</sub>	T (K)	P (MPa)	%C <sub>3</sub> H <sub>8</sub>	T (K)	P (MPa)
99.0	280.9	13.89	88.6	287.7	6.17
96.8	282.7	2.34	88.6	288.0	7.34
96.8	282.8	2.85	88.6	288.2	8.20
96.8	283.2	7.10	88.6	288.4	9.11
96.8	283.7	10.44	83.1	289.8	8.86
93.5	285.2	4.08	83.1	290.0	9.82
93.5	285.5	5.16	83.1	290.5	11.25
93.5	286.1	8.41	83.1	290.9	13.29
93.5	286.3	11.55	83.1	291.3	15.31
93.5	286.7	13.33			

*Hydrate:* Propane + carbon dioxide

*Reference:* Robinson and Mehta (1971)

*Phases:* L<sub>W</sub>-H-V

**%C<sub>3</sub>H<sub>8</sub> = vapor composition**

%C <sub>3</sub> H <sub>8</sub>	T (K)	P (kPa)	%C <sub>3</sub> H <sub>8</sub>	T (K)	P (kPa)
5.5	284.83	4268	25.0	283.8	1917
6.0	276.3	1151	25.0	280.2	979
7.0	273.8	814	26.0	281.8	1303
8.0	283.7	3179	42.0	283.7	1655
8.0	281.7	2186	42.2	275.7	414
8.0	273.9	676	47.5	278.6	689
9.0	283.5	3034	48.0	281.1	1069
9.0	280.4	1772	60.0	279.7	793
9.0	278.9	1455	60.0	274.8	324
10.0	278.3	1255	61.0	276.4	434
13.0	280.9	1572	63.0	279.6	752
13.0	273.8	517	65.0	278.3	579
14.0	279.4	1207	72.0	275.2	303
15.0	275.4	827	82.0	279.1	593
15.0	276.5	758	83.0	278.2	503
16.0	286.2	3378	83.0	279.1	641
21.0	274.0	359	84.0	277.8	476
23.0	278.1	710	86.0	276.0	338
24.0	277.4	655			

*Hydrate:* Propane + carbon dioxide

*Reference:* Adisasmito and Sloan (1992)

*Phases:* L<sub>w</sub>-H-V

%CO <sub>2</sub>	T (K)	P (kPa)	%CO <sub>2</sub>	T (K)	P (kPa)
9.9	273.7	220.6	91.2	278.2	1337.6
43.5	273.7	262.0	92.9	278.2	1537.5
60.2	273.7	337.8	94.7	278.2	2164.9
71.0	273.7	406.8	95.4	278.2	2440.7
84.2	273.7	489.5	97.0	278.2	2344.2
88.5	273.7	592.9	98.7	278.2	2227.0
90.8	273.7	655.0	30.0	280.4	930.8
93.3	273.7	717.1	49.7	280.4	965.3
94.4	273.7	848.1	74.0	280.4	1020.4
95.3	273.7	985.9	80.1	280.4	1123.8
96.3	273.7	1261.7	89.1	280.4	1640.9
97.1	273.7	1406.5	91.1	280.4	1999.5
98.5	273.7	1358.3	92.4	280.4	2316.6
32.7	275.9	351.6	94.0	280.4	2999.2
65.0	275.9	448.2	95.4	280.4	3109.5
74.8	275.9	551.6	96.5	280.4	3033.7
86.0	275.9	737.7	98.7	280.4	2909.6
92.2	275.9	917.0	35.0	282.0	1248.3
93.7	275.9	999.7	57.7	282.0	1317.2
95.1	275.9	1268.6	79.4	282.0	1510.3
95.8	275.9	1634.1	85.2	282.0	1800.0
96.8	275.9	1799.5	88.5	282.0	2206.9
97.1	275.9	1771.9	90.8	282.0	2779.3
99.0	275.9	1682.3	92.0	282.0	3186.2
35.7	278.2	551.6	92.8	282.0	3800.0
63.4	278.2	717.1	95.2	282.0	3820.7
81.1	278.2	965.3	97.0	282.0	3724.1
			98.7	282.0	3641.4

## BINARY GUEST MIXTURES CONTAINING

### ISOBUTANE AND/OR *n*-BUTANE

*Hydrates:* Isobutane + *n*-butane

*Reference:* Godbole (1981)

*Phases:* L<sub>w</sub>-H-V

%i-C <sub>4</sub> H <sub>10</sub>	T (K)	P (kPa)	%i-C <sub>4</sub> H <sub>10</sub>	T (K)	P (kPa)
0.77	267.3	68.8	0.748	265.3	80.8
0.77	261.1	56.2	0.748	263.4	73.2
0.835	264.3	63.2			

*Hydrates:* Isobutane + carbon dioxide

*Reference:* Adisasmito and Sloan (1992)

*Phases:* L<sub>W</sub>-H-V

%CO <sub>2</sub>	T (K)	P (kPa)	%CO <sub>2</sub>	T (K)	P (kPa)
20.7	273.7	144.8	79.0	277.6	537.8
52.8	273.7	165.5	85.2	277.6	641.2
66.6	273.7	206.8	94.2	277.6	958.4
77.5	273.7	275.8	96.6	277.6	1337.6
84.3	273.7	344.7	97.5	277.6	1792.6
89.3	273.7	427.5	98.2	277.6	2123.6
94.2	273.7	565.4	99.0	277.6	2082.2
96.7	273.7	744.6	62.5	279.3	517.1
97.7	273.7	937.7	71.9	279.3	551.6
98.3	273.7	1137.6	82.4	279.3	696.4
98.6	273.7	1358.3	88.0	279.3	841.2
99.3	273.7	1323.8	93.5	279.3	1151.4
30.8	275.9	262.0	95.4	279.3	1468.6
42.3	275.9	275.8	96.5	279.3	1840.9
58.8	275.9	303.4	97.1	279.3	2137.4
72.8	275.9	358.3	97.6	279.3	2564.8
85.4	275.9	496.4	98.4	279.3	2606.2
91.9	275.9	634.3	99.6	279.3	2558.0
94.4	275.9	744.6	79.1	280.9	875.6
95.4	275.9	827.4	85.2	280.9	1054.9
96.6	275.9	999.7	91.8	280.9	1523.7
97.4	275.9	1234.2	94.1	280.9	1799.5
98.3	275.9	1723.7	95.3	280.9	2033.9
99.0	275.9	1703.0	96.1	280.9	2316.6
54.0	277.6	413.7	97.3	280.9	3178.5
66.1	277.6	441.3	97.9	280.9	3171.6

*Hydrates:* n-Butane + carbon dioxide

*Reference:* Adisasmito and Sloan (1992)

*Phases:* L<sub>W</sub>-H-V

%CO <sub>2</sub>	T (K)	P (kPa)	%CO <sub>2</sub>	T (K)	P (kPa)
92.3	273.7	1137.9	94.4	277.0	1917.2
93.9	273.7	1206.9	95.2	277.0	1993.1
95.5	273.7	1317.2	96.8	277.0	2082.8
97.7	273.7	1351.7	98.0	277.0	2041.4
98.4	273.7	1337.9	98.8	277.0	2013.8
99.2	273.7	1324.1	99.4	277.0	1993.1
93.0	275.4	1462.1	96.2	278.2	2400.0
94.8	275.4	1586.2	97.5	278.2	2372.4
97.3	275.4	1675.9	98.5	278.2	2331.0
98.0	275.4	1655.2	99.1	278.2	2303.4
99.2	275.4	1620.7			

## BINARY GUEST MIXTURES CONTAINING NITROGEN AND CARBON DIOXIDE

*Hydrate:* Nitrogen + carbon dioxide

*Reference:* Fan and Guo (1999)

*Phases:* L<sub>W</sub>-H-V

mol% N <sub>2</sub>	T (K)	P (MPa)
3.48	273.1	1.22
3.48	274.6	1.54
3.48	278.3	2.42
3.48	279.4	2.89
3.48	280.2	2.95
9.01	273.4	1.37
9.01	274.1	1.53
9.01	276.7	1.89
9.01	279.1	3.09

*Hydrate:* Nitrogen + carbon dioxide

*Reference:* Kang et al. (2001)

*Phases:* L<sub>W</sub>-H-V

x <sub>CO<sub>2</sub></sub> (loading)	T (K)	P (MPa)	x <sub>CO<sub>2</sub></sub> (loading)	T (K)	P (MPa)
0.9659	274.95	1.565	0.1761	272.85	7.240
	277.45	2.060		274.05	8.120
	280.25	2.900		277.45	10.650
	282.55	4.000		278.65	11.748
	283.55	5.115		280.55	14.220
0.7780	274.00	2.000	0.1159	274.25	11.020
	276.15	2.600		275.65	13.870
	280.65	4.225		277.60	18.100
	283.45	6.450		278.95	22.230
	284.25	7.445			
0.4815	273.75	3.195	0.0063	273.95	14.085
	276.00	4.257		274.55	15.400
	279.00	5.867		277.00	20.680
	281.00	7.449		278.25	24.120
	282.00	8.975			

*Hydrate:* Nitrogen + carbon dioxide

*Reference:* Kang et al. (2001)

*Phases:* H–V

T (K)	P (MPa)	x <sub>CO<sub>2</sub></sub> (vapor)	x <sub>CO<sub>2</sub></sub> (hydrate)
274	1.394	1.0000	1.0000
	1.769	0.8205	0.9850
	2.354	0.5999	0.9517
	2.835	0.5048	0.9301
	3.560	0.3994	0.9001
	7.235	0.2057	0.5836
	11.200	0.1159	0.3426
	14.928	0.0498	0.1793
	17.926	0.0000	0.0000
277	1.953	1.0000	1.0000
	2.600	0.8491	0.9782
	3.377	0.5867	0.9455
	5.233	0.3899	0.8867
	11.980	0.1761	0.5400
	15.500	0.1159	0.3526
	19.174	0.0663	0.1928
	24.041	0.0000	0.0000
	280	1.0000	1.0000
280	2.801	1.0000	1.0000
	3.600	0.8520	0.9765
	4.233	0.6999	0.9612
	5.068	0.5917	0.9432
	8.275	0.3924	0.8641
	14.974	0.2510	0.6400
	20.753	0.1709	0.4500
	26.690	0.0905	0.2217
	32.308	0.0000	0.0000

### 6.3.1.2.2 Structure H hydrate data (binary, multicomponent, inhibited)

With few exceptions (as indicated in the table), all structure H equilibria data were obtained with methane as the small component. Also because there were always four phases present (L<sub>W</sub>–H–V–L<sub>HC</sub>) with three components (including water) the Gibbs Phase Rule provides for only one composition of each phase which satisfies the equilibrium conditions. Consequently all data were taken without measurement of any phase composition, and only the equilibrium temperature and pressure of the four phases are reported. Due to the paucity of structure H data, included here are one binary including nitrogen and three structure H systems with inhibitor. Such systems clearly illustrate the need for more structure H data.

*Hydrates:* Methane + large hydrocarbon component

*References:* Given in table

*Phases:* L<sub>W</sub>-H(sH)-V-L<sub>HC</sub>

<b>Large component</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>Reference</b>
Isopentane	275.2	2.654	Mehta and Sloan (1993)
	276.2	2.978	
	277.8	3.640	
	279.0	4.150	
Isopentane	274.0	2.241	Hütz and Englezos (1995)
	276.2	2.955	
	277.4	3.501	
Neopentane	276.6	0.400	Tohidi et al. (1997a)
	282.9	1.014	
	286.0	1.593	
	289.9	2.944	
	292.8	4.861	
Neohexane	276.0	1.598	Mehta and Sloan (1993)
	278.0	2.028	
	279.2	2.391	
	282.2	3.339	
Neohexane	285.4	5.22	Thomas and Behar (1994)
	288.2	7.51	
Neohexane	275.0	1.415	Hütz and Englezos (1995)
	276.8	1.805	
	279.9	2.601	
	282.8	3.750	
Neohexane	244.8	0.332	T. Makogon et al. (1996)
	251.4	0.447	
	258.8	0.626	
	274.0	1.241	
Neohexane	254.40	0.509	Ohmura et al. (2005)
	255.90	0.548	
	257.85	0.597	
	258.85	0.623	
	260.85	0.678	
	263.35	0.751	
	267.35	0.882	
	269.65	0.966	
	271.35	1.025	
	272.85	1.095	

(Continued)

**Continued**

<b>Large component</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>Reference</b>
2,3-Dimethylbutane	275.9	2.078	Mehta and Sloan (1994a)
	277.4	2.482	
	279.2	3.088	
	280.8	3.795	
2,3-Dimethylbutane	282.6	4.95	Thomas and Behar (1994)
	286.4	8.19	
2,2,3-Trimethylbutane	275.6	1.475	Mehta and Sloan (1994a)
	277.4	1.840	
	279.5	2.247	
	280.9	2.702	
2,2,3-Trimethylbutane	288.0	5.94	Thomas and Behar (1994)
	289.4	7.55	
2,2-Dimethylpentane	275.9	3.287	Mehta and Sloan (1994a)
	277.4	3.819	
	279.2	4.556	
	280.31	5.140	
	281.34	5.832	
	282.2	6.195	
2,2-Dimethylpentane	282.8	6.691	
	286.6	3.79	Thomas and Behar (1994)
	288.2	5.70	
	290.0	7.15	
3,3-Dimethylpentane	274.8	1.734	Mehta and Sloan (1994a)
	277.0	2.264	
	279.2	3.009	
	281.3	3.930	
3,3-Dimethylpentane	280.6	3.62	Thomas and Behar (1994)
	283.6	5.42	
	286.4	7.28	
Methylcyclopentane	276.5	2.199	Mehta and Sloan (1994a)
	277.8	2.578	
	279.5	3.195	
	280.8	3.812	

**Continued**

<b>Large component</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>Reference</b>
Methylcyclopentane	279.2	3.22	Thomas and Behar (1994)
	281.3	3.94	
	282.6	4.70	
	284.8	6.14	
	286.0	7.44	
	287.2	8.69	
	287.8	10.01	
Methylcyclopentane	278.2	2.635	Danesh et al. (1994)
	278.6	2.937	
	279.0	2.965	
	279.7	3.289	
	280.35	3.737	
	282.2	4.606	
	283.0	4.999	
	283.2	5.295	
	285.2	6.653	
	287.0	8.625	
Methylcyclopentane	274.28	1.75	Makino et al. (2004)
	275.25	1.98	
	276.20	2.22	
	277.08	2.48	
	277.99	2.77	
	278.88	3.08	
	279.78	3.47	
	280.67	3.88	
	281.48	4.29	
	282.27	4.75	
	283.06	5.25	
	283.86	5.79	
	284.66	6.44	
	285.43	7.12	
	286.21	7.92	
	286.77	8.57	
	287.40	9.34	
Methylcyclohexane	275.6	1.599	Mehta and Sloan (1994b)
	277.6	2.137	
	279.4	2.688	
	281.2	3.357	

(Continued)

**Continued**

<b>Large component</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>Reference</b>
Methylcyclohexane	280.2	3.0	Becke et al. (1992)
	280.6	3.2	
	285.6	6.0	
	289.6	10.2	
	290.4	11.2	
Methylcyclohexane	282.6	3.99	Thomas and Behar (1994)
	284.2	4.62	
	286.45	6.47	
	287.4	7.61	
	289.2	8.82	
	290.25	10.5	
Methylcyclohexane	277.1	2.041	Tohidi et al. (1996a)
	279.9	2.951	
	282.2	3.937	
	283.4	4.606	
	287.1	7.391	
Methylcyclohexane	279.48	2.65	Mooijer-van den Heuvel et al. (2000)
	280.49	2.93	
	281.43	3.17	
	282.42	3.87	
	283.39	4.37	
	284.44	4.81	
	284.95	5.20	
	285.44	5.50	
	285.95	5.96	
	286.49	6.34	
	286.96	6.75	
	287.46	7.34	
	288.40	8.33	
	288.97	9.13	
Methylcyclohexane	274.09	1.42	Nakamura et al. (2003)
	274.78	1.54	
	275.28	1.66	
	275.79	1.75	
	276.26	1.87	
	276.79	1.99	
	277.26	2.11	
	277.80	2.25	
	278.30	2.39	
	279.25	2.70	
	280.26	3.05	
	281.27	3.45	

**Continued**

<b>Large component</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>Reference</b>
Methylcyclohexane	282.28	3.90	Nakamura et al. (2003)
	283.29	4.43	
	284.30	5.03	
	285.29	5.72	
	286.28	6.50	
	287.25	7.42	
	288.29	8.48	
Methylcyclohexane	251.50	0.519	Ohmura et al. (2005)
	253.15	0.559	
	255.70	0.619	
	258.10	0.686	
	261.00	0.774	
	264.00	0.873	
	267.00	0.984	
	269.05	1.063	
	271.00	1.145	
	272.60	1.213	
cis-1,2-Dimethylcyclohexane	275.8	1.871	Mehta and Sloan (1994a)
	277.4	2.237	
	279.4	2.816	
	281.0	3.433	
cis-1,2-Dimethylcyclohexane	282.0	4.00	Thomas and Behar (1995)
	284.4	5.29	
	286.2	6.81	
	287.4	7.63	
	288.8	9.67	
	290.0	11.32	
cis-1,2-Dimethylcyclohexane	274.18	1.57	Nakamura et al. (2003)
	274.65	1.67	
	275.25	1.80	
	276.22	2.03	
	277.18	2.29	
	278.14	2.57	
	279.10	2.89	
	280.10	3.28	
	281.58	3.93	
	283.04	4.71	
	284.53	5.66	
	285.99	6.83	
	286.93	7.75	
	287.96	8.89	

(Continued)

**Continued**

<b>Large component</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>Reference</b>
2,3-Dimethyl-1-butene	275.7	2.530	Mehta and Sloan (1994a)
	277.8	3.275	
	279.53	4.088	
	280.78	4.805	
3,3-Dimethyl-1-butane	276.2	2.016	Mehta and Sloan (1994a)
	277.6	2.423	
	279.2	2.933	
	281.42	3.871	
3,3-Dimethyl-1-butyne	275.8	2.851	Mehta (1996)
	276.9	3.216	
	278.4	3.878	
	278.9	4.133	
	279.6	4.567	
Cyclopentane*	282.8	0.157	Tohidi et al. (1997a)
	283.8	0.237	
	285.5	0.372	
	289.1	0.869	
	291.7	1.462	
	294.4	2.082	
Cyclohexane*	283.5	2.68	Mooijer-van den Heuvel et al. (2000)
	285.51	3.61	
	287.48	4.82	
	289.49	6.49	
	291.48	8.70	
	293.46	11.66	
Cycloheptene	275.1	2.106	Mehta and Sloan (1994a)
	277.7	2.671	
	279.2	3.051	
	281.0	3.809	
cis-Cyclooctene	276.9	2.082	Mehta and Sloan (1994a)
	278.5	2.562	
	280.0	3.009	
	281.3	3.561	
Adamantane	275.1	1.779	Lederhos et al. (1992)
	276.9	2.165	
	278.4	2.510	
	280.2	3.001	

\* sII not sH

**Continued**

<b>Large component</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>Reference</b>
Adamantane	275.2	1.790	Hütz and Englezos (1995)
	275.9	1.941	
	277.6	2.300	
	279.1	2.709	
Ethylcyclopentane	280.2	3.59	Thomas and Behar (1995)
	281.2	4.02	
	283.2	5.16	
	284.8	6.39	
	286.4	7.93	
	287.4	9.13	
1,1-Dimethylcyclohexane	280.2	2.00	Thomas and Behar (1995)
	281.0	2.34	
	282.4	2.82	
	283.6	3.34	
	285.8	4.30	
	287.8	5.51	
	288.8	6.06	
	290.6	7.53	
	291.8	9.07	
	292.6	10.13	
	293.2	11.53	
1,1-Dimethylcyclohexane	274.67	1.07	Hara et al. (2005)
	276.67	1.37	
	278.65	1.76	
	280.63	2.19	
	282.61	2.90	
	284.57	3.74	
	286.53	4.75	
	288.51	6.08	
	289.31	6.77	
<i>cis</i> -1,4-Dimethylcyclohexane	274.13	1.62	Nakamura et al. (2004)
	274.75	1.76	
	275.30	1.88	
	275.98	2.03	
	276.79	2.24	
	277.55	2.46	
	278.57	2.79	
	279.53	3.14	

(Continued)

**Continued**

<b>Large component</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>Reference</b>
<i>cis</i> -1,4-Dimethylcyclohexane	280.50	3.53	Nakamura et al. (2004)
	281.44	3.93	
	281.97	4.22	
	282.45	4.45	
	283.43	5.01	
	284.30	5.62	
	285.30	6.32	
	285.72	6.78	
	286.15	7.16	
	286.97	8.04	
	287.49	8.53	
	287.95	9.13	
Ethylcyclohexane	283.6	6.3	Thomas and Behar (1995)
	286.0	8.9	
Cycloheptane	281.4	3.39	Thomas and Behar (1995)
	284.1	4.62	
	285.0	5.15	
	286.8	6.54	
	288.2	7.79	
	289.2	9.15	
	290.4	10.93	
Cyclooctane	282.4	4.21	Thomas and Behar (1995)
	284.4	5.36	
	285.8	6.29	
	286.4	6.63	
	287.4	7.55	
	289.0	9.65	
	290.4	11.65	
Cyclooctane	274.08	1.60	Makino et al. (2004)
	275.16	1.84	
	276.17	2.03	
	277.15	2.29	
	278.00	2.53	
	278.83	2.79	
	279.78	3.14	
	280.96	3.57	
	282.13	4.13	
	283.07	4.64	
	284.11	5.28	
	284.90	5.83	
	285.90	6.59	

**Continued**

<b>Large component</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>Reference</b>
Cyclooctane	286.91	7.50	Makino et al. (2004)
	287.87	8.53	
	288.13	8.84	
	288.57	9.33	
<i>tert</i> -Butyl methyl ether	274.6	1.85	Hütz and Englezos (1995)
	277.5	2.55	
	280.8	3.95	
	284.1	5.90	
<i>tert</i> -Butyl methyl ether	252.85	0.652	Ohmura et al. (2005)
	256.35	0.731	
	259.84	0.836	
	263.25	0.947	
	266.65	1.07	
	269.85	1.203	
	270.85	1.252	

*Hydrate:* Propane + methylcyclohexane

*Reference:* Mooijer-van den Heuvel et al. (2002)

*Phase:* L<sub>W</sub>-H\*-V-L<sub>HC</sub>, L<sub>W</sub>-H\*-L<sub>HC</sub>, and Q(L<sub>W</sub>-H\*-V-L<sub>HC</sub>)

Overall feed composition:  $x_{\text{H}_2\text{O}} = 0.9100$ ,  $x_{\text{C}_3\text{H}_8} = 0.0502$ ,  $x_{\text{MCH}} = 0.0398$

**Q(L<sub>W</sub>-H-V-L<sub>HC</sub>) at T = 276.50, P = 0.200 MPa**

<b>L<sub>W</sub>-H-V-L<sub>HC</sub></b>		<b>L<sub>W</sub>-H-L<sub>HC</sub></b>	
<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
274.52	0.139	276.71	0.647
275.04	0.158	276.91	0.897
275.46	0.163	277.13	1.147
275.51	0.164	277.19	1.396
275.76	0.167	277.33	1.896
276.05	0.185	277.12	2.396
		277.19	2.396
		277.05	2.893
		277.09	3.893
		277.05	4.893
		277.09	5.893
		277.07	6.893
		277.04	7.893

\* Probably sII (not sH), no structure confirmation done

*Hydrate:* Propane + cyclohexane

*Reference:* Mooijer-van den Heuvel et al. (2002)

*Phase:*  $L_W-H^*-V-L_{HC}$ ,  $L_W-H^*-L_{HC}$ , and  $Q(L_W-H^*-V-L_{HC})$

Overall feed composition:  $x_{H_2O} = 0.8987$ ,  $x_{C_3H_8} = 0.0503$ ,  $x_{CH} = 0.0510$

**$Q(L_W-H-V-L_{HC})$  at  $T = 276.05$ ,  $P = 0.172$  MPa**

$L_W-H-V-L_{HC}$		$L_W-H-L_{HC}$	
$T$ (K)	$P$ (MPa)	$T$ (K)	$P$ (MPa)
274.52	0.146	276.04	0.545
274.98	0.151	276.03	0.645
274.52	0.157	276.09	0.895
275.33	0.157	276.13	1.145
275.67	0.164	276.17	1.395
275.81	0.168	276.26	1.642
274.98	0.172	276.18	2.392
275.51	0.174	276.32	2.893
276.10	0.175	276.32	3.893
275.50	0.185	276.38	4.893
		276.43	5.893
		276.46	6.893
		276.53	7.893
		276.61	8.893
		276.61	9.893

\* Probably sII (not sH), no structure confirmation done

*Hydrate:* Carbon dioxide + methylcyclohexane

*Reference:* Mooijer-van den Heuvel et al. (2001)

*Phases:*  $L_W-H-V-L_{MCH}$ ,  $L_W-H-L_{CO_2}-L_{MCH}$ , and Quadruple point  $Q_2$

Overall feed composition:  $x_{H_2O} = 0.7488$ ,  $x_{CO_2} = 0.1257$ ,  $x_{MCH} = 0.1255$

**$Q_2$  at 280.22 K and 2.89 MPa**

$L_W-H-V-L_{MCH}$		$L_W-H-L_{CO_2}-L_{MCH}$	
$T$ (K)	$P$ (MPa)	$T$ (K)	$P$ (MPa)
277.06	1.86	280.24	2.90
277.22	1.89	280.24	3.39
277.29	1.91	280.25	3.89
277.33	1.94	280.30	4.89
277.36	1.91	280.31	4.39
277.59	2.00	280.43	5.40
277.77	2.05	280.46	6.39

**Continued**

<b>L<sub>W</sub>-H-V-L<sub>MCH</sub></b>		<b>L<sub>W</sub>-H-L<sub>CO<sub>2</sub></sub>-L<sub>MCH</sub></b>	
<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
277.99	2.10	280.47	6.39
278.18	2.15	280.50	5.89
278.35	2.22	280.53	6.89
278.63	2.26	280.63	8.39
278.85	2.32	280.68	7.39
279.07	2.44	280.70	7.89
279.37	2.53	280.76	8.89
279.49	2.59	280.81	9.39
279.61	2.58	280.84	10.39
279.74	2.64	280.84	9.89
279.79	2.69	280.89	10.39
279.84	2.71	280.94	11.39
279.99	2.76	280.99	10.89
280.15	2.78		

*Hydrates:* Natural gas + methylcyclohexane

*Reference:* Tohidi et al. (2001)

*Phases:* L<sub>W</sub>-H-V-L<sub>HC</sub>

Composition (mol%) of natural gas: 4.99% N<sub>2</sub>; 1.12% CO<sub>2</sub>; 86.36% CH<sub>4</sub>; 5.43% C<sub>2</sub>H<sub>6</sub>; 1.49% C<sub>3</sub>H<sub>8</sub>; 0.18% i-C<sub>4</sub>H<sub>10</sub>; 0.31% n-C<sub>4</sub>H<sub>10</sub>; 0.06% i-C<sub>5</sub>H<sub>12</sub>; 0.06% n-C<sub>5</sub>H<sub>12</sub>; <0.01% C<sub>6</sub><sup>+</sup>

### **L<sub>W</sub>-H-V-L<sub>HC</sub> Conditions of Gas Mixture with Methylcyclohexane (MCH)**

<b>Natural gas (NG)</b>		<b>NG + 21.9 mol% MCH</b>		<b>NG + 37.2% MCH</b>		<b>NG + 49.3% MCH</b>	
<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
276.15	1.269	278.75	2.103	279.75	3.089	280.6	3.468
283.35	3.054	280.85	2.875	282.05	4.089	284.0	5.357
284.15	3.337	283.75	4.316	284.95	6.109	286.5	7.543
285.65	4.075	287.65	7.377	287.95	9.308	290.8	13.79
286.25	4.688	290.05	11.04	289.65	12.34		
290.05	7.619						
291.05	8.705						

*Hydrates:* Nitrogen + methylcyclopentane (MCP) or methylcyclohexane (MCH)

*Reference:* Danesh et al. 1994 (MCP); Tohidi et al. 1996a (MCH)

*Phases:* L<sub>W</sub>–H(sH)–V–L<sub>HC</sub>

T (K)	P (MPa)	T (K)	P (MPa)
Methylcyclopentane			
274.2	7.770	281.0	18.216
276.2	9.997	282.0	20.422
278.2	12.769	285.8	30.709
Methylcyclohexane			
276.4	8.805	283.7	20.843
279.2	12.473		

*Hydrates:* Nitrogen + cyclopentane; nitrogen + neopentane

*Reference:* Tohidi et al. (1997a)

*Phases:* L<sub>W</sub>–H–V–L<sub>HC</sub>

Nitrogen + cyclopentane*		Nitrogen + neopentane	
T (K)	P (MPa)	T (K)	P (MPa)
282.9	0.647	278.9	2.303
284.3	1.282	282.5	4.337
286.6	2.117	287.8	9.708
289.1	3.496	281.3	15.775

\* sII not sH

*Hydrates:* Methane + nitrogen + (methylcyclohexane or methylcyclopentane)

*Reference:* Tohidi et al. (1996a)

*Phases:* L<sub>W</sub>–H(sH)–V–L<sub>HC</sub>

Feed compositions: methylcyclohexane = 16.05 mol% CH<sub>4</sub>, 23.17% N<sub>2</sub>, 3.79%

MCH, 56.99% H<sub>2</sub>O; methylcyclopentane = 9.65 mol% CH<sub>4</sub>, 12.38% N<sub>2</sub>, 7.21% MCP, 70.76% H<sub>2</sub>O

**Continued**

<b>Methylcyclohexane</b>		<b>Methylcyclopentane</b>	
<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
279.4	5.178	278.0	5.495
282.3	7.577	280.9	8.122
286.1	12.328	284.8	13.872

*Hydrates:* Methane + large component + NaCl

*References:* Hütz and Englezos (1995)

*Phases:* L<sub>W</sub>–H(sH)–V–L<sub>HC</sub>

<b>Large component</b>	<b>wt% NaCl</b>	<b>T (K)</b>	<b>P (MPa)</b>
Isopentane	10	271.2	2.61
		272.6	3.16
		275.8	4.90
2,2-Dimethylbutane	12	272.4	2.06
		273.0	2.31
		276.1	3.35
		279.0	4.95
		281.2	6.55
tert-Butyl methyl ether	12	270.4	2.325
		274.4	3.601
		277.0	4.925
		279.4	6.96

*Hydrates:* Carbon dioxide + cyclohexane

*Reference:* Mooijer-van den Heuvel et al. (2001)

*Phases:* L<sub>W</sub>–H\*–V–L<sub>CH</sub>, L<sub>W</sub>–H\*–L<sub>CO<sub>2</sub></sub>–L<sub>CH</sub>, and Quadruple point Q<sub>2</sub>

Overall feed composition: x<sub>H<sub>2</sub>O</sub> = 0.7122, x<sub>CO<sub>2</sub></sub> = 0.1095, x<sub>CH</sub> = 0.1783

**Q<sub>2</sub> at 280.03 K and 2.65 MPa**

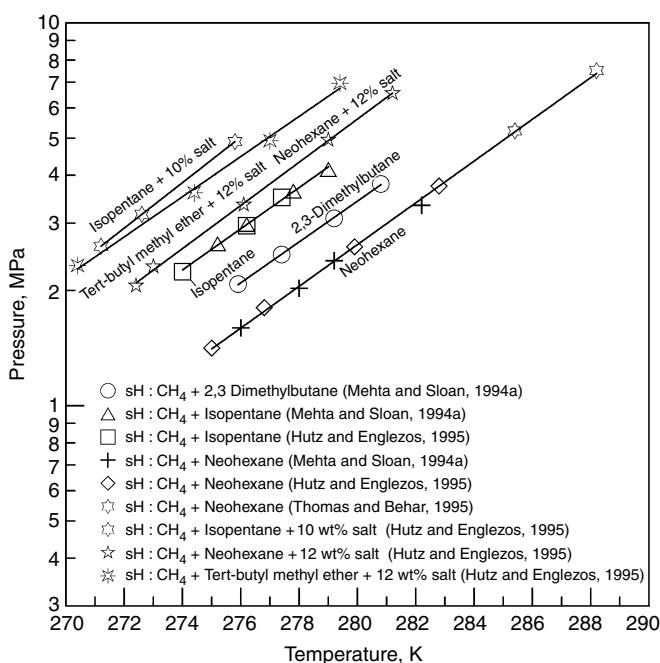
<b>L<sub>W</sub>–H–V–L<sub>CH</sub></b>		<b>L<sub>W</sub>–H–L<sub>CO<sub>2</sub></sub>–L<sub>CH</sub></b>	
<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
274.97	0.90	280.32	3.40
275.49	1.03	280.34	4.40

(Continued)

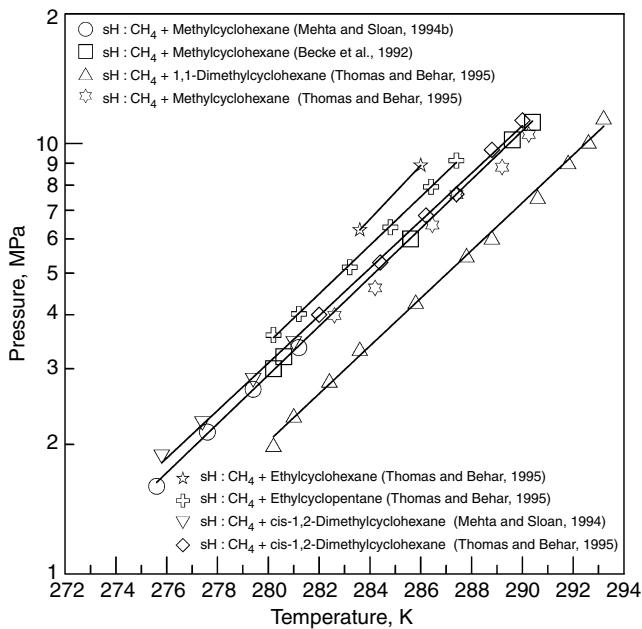
\* Probably sII (not sH), no structure confirmation done

## Continued

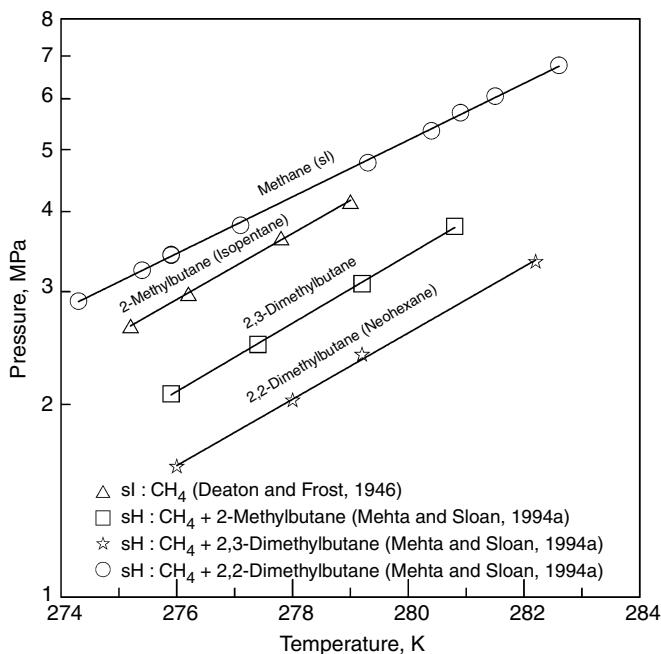
$L_W-H-V-L_{CH}$		$L_W-H-L_{CO_2}-L_{CH}$	
$T$ (K)	$P$ (MPa)	$T$ (K)	$P$ (MPa)
275.97	1.13	280.91	7.40
276.51	1.26	281.03	8.40
276.97	1.41	281.09	9.40
277.49	1.55	281.23	10.40
278.03	1.77		
278.94	2.41		
279.22	2.49		
279.44	2.53		
279.80	2.55		



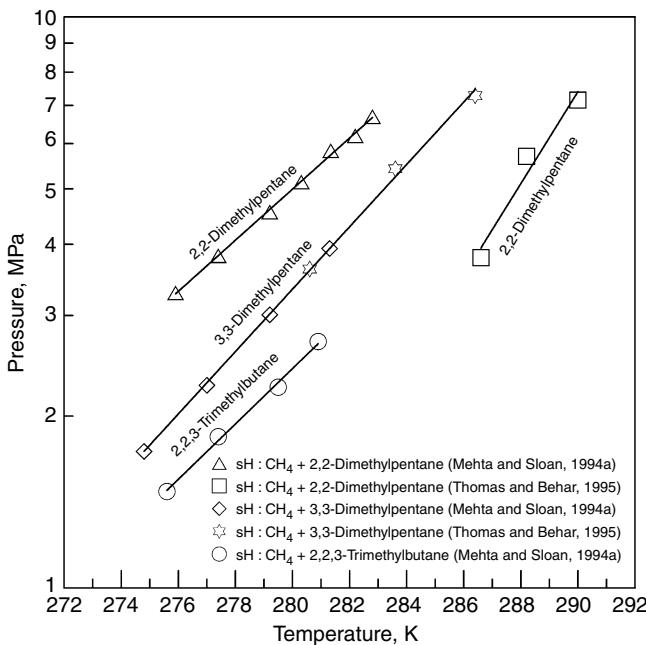
**FIGURE 6.33** Data for structure H hydrates of methane with isopentane, neohexane, 2,3-dimethylbutane, and sodium chloride inhibition of hydrates of methane with isopentane, neohexane, and tert-butyl methyl ether.



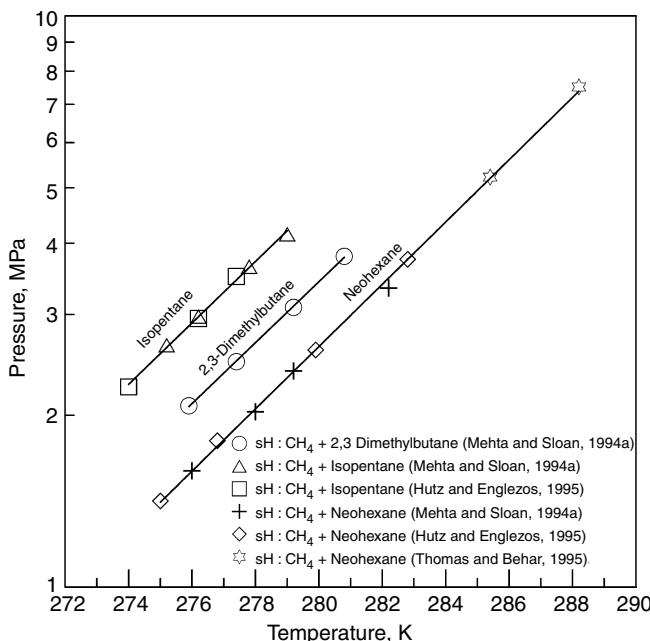
**FIGURE 6.34** Data for structure H hydrates of methane with methylcyclohexane, 1,1-dimethylcyclohexane, cis-1,2-dimethylcyclohexane, and ethylcyclohexane.



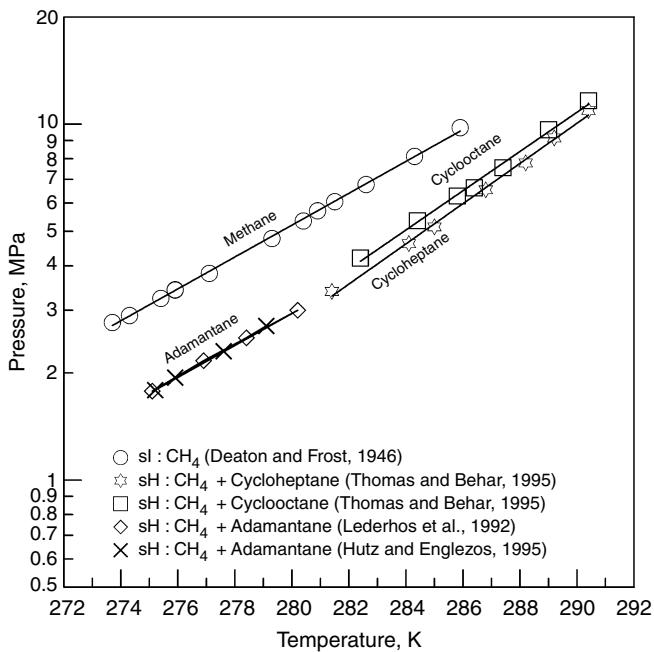
**FIGURE 6.35** Data for structure H hydrates of methane with 2-methylbutane, 2,2-dimethylbutane, and 2,3-dimethylbutane.



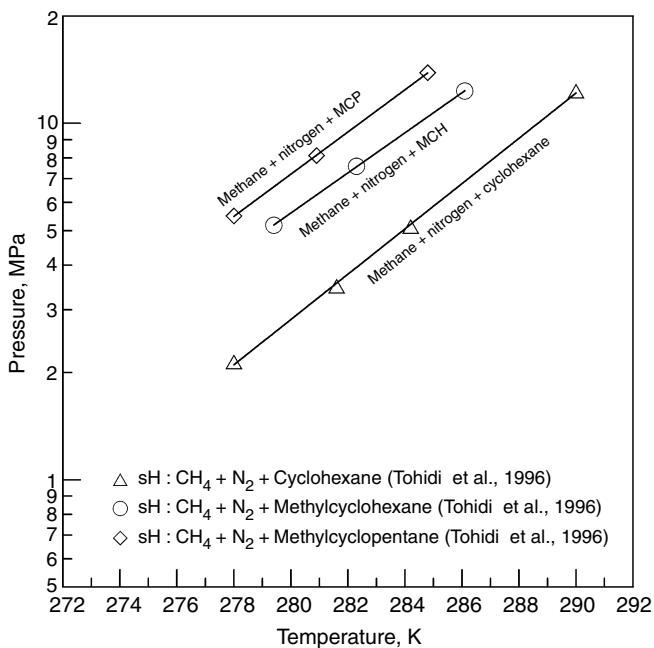
**FIGURE 6.36** Data for structure H hydrates of methane with 2,2-dimethylpentane, 3,3-dimethylpentane, and 2,2,3-trimethylbutane.



**FIGURE 6.37** Data for structure H hydrates of methane with 2,3-dimethylbutane, isopentane, and neohexane.



**FIGURE 6.38** Data for structure H hydrates of methane with cycloheptane, cyclooctane, and adamantanane.



**FIGURE 6.39** Data for structure H hydrates of methane + nitrogen with cyclohexane, methylcyclopentane, and methylcyclohexane.

### 6.3.1.3 Equilibria of ternary guest mixtures

Due to the diversity of gas compositions for ternary guest systems, duplicate data sets have not been obtained by various investigators. The variety of gas compositions make plots of the data meaningless, except for self-consistency within an individual investigation. Consequently plots of ternary (and higher) guest data sets are not provided. Frequently such plots are given in the original reference with the data set. Compositions are given in mol fractions or mol percent unless otherwise stated.

*Hydrate:* Methane + ethane + propane

*Reference:* Holder and Hand (1982)

*Phases:* L<sub>w</sub>-H-V-L<sub>HC</sub> (compositions are mol fractions in the L<sub>HC</sub> phase)

$$x_{C_1}/(x_{C_1} + x_{C_3}) = 0.0$$

$x_{C_2}$	$T$ (K)	$P$ (kPa)	$x_{C_2}$	$T$ (K)	$P$ (kPa)
0.168	278.1	900	NM	278.6	1300
NM	278.1	970	NM	279.4	1430
0.280	277.8	1080	NM	280.4	1560
NM	278.2	700	NM	280.6	1610
0.435	279.9	1480	NM	281.1	1630
0.523	281.8	1740	1.00	288.3	3330
0.689	284.3	2230			

NM = not measured.

$$x_{C_1}/(x_{C_1} + x_{C_3}) = 0.0255$$

$x_{C_2}$	$T$ (K)	$P$ (kPa)	$x_{C_2}$	$T$ (K)	$P$ (kPa)
0.000	282.8	1030	0.716	284.8	2320
0.189	281.7	1240	0.799	286.1	2730
0.314	280.1	1580	1.000	288.3	3330
0.517	282.8	2020			

**Continued**

$$x_{C1}/(x_{C1} + x_{C3}) = 0.051$$

$x_{C_2}$	$T$ (K)	$P$ (kPa)	$x_{C_2}$	$T$ (K)	$P$ (kPa)
0.082	284.9	1500	0.549	283.7	2180
0.181	284.2	1610	0.726	285.7	2730
0.231	283.5	1680	1.000	288.3	3330

$$x_{C1}/(x_{C1} + x_{C3}) = 0.092$$

$x_{C_2}$	$T$ (K)	$P$ (kPa)	$x_{C_2}$	$T$ (K)	$P$ (kPa)
0.054	287.4	2120	0.506	283.8	2380
0.148	286.9	2170	0.616	285.1	2570
0.212	285.7	2210	0.677	285.9	2820
0.365	284.9	2280	1.000	288.3	3330

*Hydrate:* Methane + ethane + propane

*Reference:* Mooijer-van den Heuvel (2004; pp. 91, 244–245)

*Phases:* L<sub>W</sub>–H(I + II)–V, L<sub>W</sub>–H–V–L<sub>HC</sub>, L<sub>W</sub>–H(II)–V, L<sub>W</sub>–H(I + II)–V, L<sub>W</sub>–H(I + II)–L<sub>HC</sub>, and L<sub>W</sub>–H(I)–L<sub>HC</sub> (Phase diagram is complex—see reference)

Overall composition:  $x_{H_2O} = 0.938$ ,  $y_{C_3H_6} = 0.501$

L <sub>W</sub> –H(I + II)–V		L <sub>W</sub> –H(II)–V–L <sub>HC</sub>		L <sub>W</sub> –H(II)–V	
$T$ (K)	$P$ (MPa)	$T$ (K)	$P$ (MPa)	$T$ (K)	$P$ (MPa)
277.59	1.13	277.91	1.15	277.06	0.81
277.78	1.09	277.93	1.15	277.90	0.81
277.80	1.17	277.98	1.01	277.96	0.86
277.86	1.00	278.05	1.05	278.03	0.86
		278.06	0.95	278.12	0.96
		278.06	1.01	278.18	0.91
		278.14	0.96		
		278.19	0.96		
		278.21	0.91		

(Continued)

**Continued**

<b>L<sub>W</sub>-H(I + II)-V</b>		<b>L<sub>W</sub>-H(I + II)-L<sub>HC</sub></b>		<b>L<sub>W</sub>-H(I)-L<sub>HC</sub></b>	
<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
276.66	1.12	277.70	3.40	281.64	1.90
276.99	1.11	277.43	5.40	281.68	2.40
277.34	1.17	277.61	5.40	281.71	2.90
				281.92	3.40
				281.94	3.90
				282.07	3.90
				282.18	4.40
				282.27	4.90
				282.30	5.40
				282.44	5.90
				282.47	6.90
				282.52	6.40
				282.73	7.40
				282.77	7.90
				283.05	8.40
				283.16	9.40
				283.17	8.40
				283.41	8.90
				283.47	9.90
				283.91	11.40
				283.98	10.40
				284.22	11.90

*Hydrate:* Methane + ethane + propane

*Reference:* Mooijer-van den Heuvel (2004; pp. 90, 244)

*Phases:* L<sub>W</sub>-H(II)-V-L<sub>HC</sub>, L<sub>W</sub>-H(II)-L<sub>HC</sub>, and L<sub>W</sub>-H(II)-V (Phase diagram is complex—see [reference](#))

Overall composition:  $x_{\text{H}_2\text{O}} = 0.938$ ,  $y_{\text{C}_2\text{H}_6} = 0.299$

<b>L<sub>W</sub>-H(II)-V-L<sub>HC</sub></b>		<b>L<sub>W</sub>-H(II)-L<sub>HC</sub></b>		<b>L<sub>W</sub>-H(II)-V</b>	
<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
277.96	0.97	277.88	1.39	277.03	0.54
277.97	0.93	277.89	1.74	277.43	0.58
278.01	0.86	277.89	2.14	277.78	0.63
278.13	0.72	277.91	2.54	277.99	0.66
278.15	0.80	277.91	1.19	278.17	0.67
		277.92	2.34		
		277.92	1.59		
		277.92	1.14		
		277.96	1.94		

*Hydrate:* Methane + propane + isobutane

*Reference:* Paranjpe et al. (1987)

*Phases:* L<sub>w</sub>-H-V-L<sub>HC</sub>

**Mol Fraction in Vapor**

T (K)	P (kPa)	CH <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	i-C <sub>4</sub> H <sub>10</sub>
276.2	220.6	0.261	0.000	0.739
276.2	248.2	0.155	0.106	0.739
276.2	262.0	0.123	0.194	0.683
276.2	303.4	0.000	0.369	0.631
279.2	398.0	0.511	0.000	0.489
279.2	458.5	0.201	0.085	0.714
279.2	495.0	0.092	0.279	0.629
279.2	543.3	0.128	0.542	0.330
279.2	576.4	0.128	0.737	0.135
279.2	606.7	0.102	0.851	0.047
279.2	674.0	0.010	0.990	0.000
281.2	585.1	0.620	0.000	0.380
281.2	621.9	0.242	0.071	0.687
281.2	668.8	0.187	0.393	0.420
281.2	723.9	0.150	0.569	0.281
281.2	773.6	0.126	0.814	0.060
281.2	832.0	0.030	0.970	0.000

*Hydrate:* Methane + propane + n-butane

*Reference:* Paranjpe et al. (1987)

*Phases:* I-H-V-L<sub>HC</sub> and L<sub>w</sub>-H-V-L<sub>HC</sub>

**Mol Fraction in Vapor**

T (K)	P (kPa)	CH <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	n-C <sub>4</sub> H <sub>10</sub>
268.2	181.4	0.000	0.660	0.340
268.2	216.5	0.349	0.407	0.244
268.2	270.3	0.736	0.082	0.182
268.2	362.7	0.840	0.027	0.127
268.2	784.0	0.890	0.000	0.110
275.2	315.8	0.000	0.834	0.166
275.2	478.5	0.327	0.258	0.415
275.2	523.4	0.922	0.051	0.027
275.2	551.6	0.935	0.012	0.053
275.2	1330.7	0.921	0.000	0.079
281.2	821.9	0.111	0.889	0.000
281.2	1048.0	0.686	0.206	0.108
281.2	1206.6	0.836	0.090	0.074
281.2	1834.0	0.942	0.018	0.040
281.2	2643.8	0.965	0.005	0.031
281.2	3441.0	0.985	0.000	0.015

*Hydrate:* Methane + propane + *n*-decane

*Reference:* Verma (1974)

*Phases:* L<sub>w</sub>–H–L<sub>HC</sub> and L<sub>w</sub>–H–V–L<sub>HC</sub> (compositions for hydrocarbon liquid phase)

### L<sub>w</sub>–H–L<sub>HC</sub>

T (K)	P (kPa)	%CH <sub>4</sub>	%C <sub>3</sub> H <sub>8</sub>	%C <sub>10</sub> H <sub>22</sub>
287.5	2,875	14.51	27.09	58.4
287.8	4,544	14.51	27.09	58.4
288.1	6,888	14.51	27.09	58.4
288.7	10,225	14.51	27.09	58.4
289.2	13,707	14.51	27.09	58.4

### L<sub>w</sub>–H–V–L<sub>HC</sub>

T (K)	P (kPa)	%CH <sub>4</sub>	%C <sub>3</sub> H <sub>8</sub>	%C <sub>10</sub> H <sub>22</sub>
278.3	539	0.00	96.55	3.45
278.2	525	0.00	94.88	5.12
277.9	501	0.00	91.81	8.19
277.4	443	0.00	80.71	19.29
277.5	465	0.00	80.32	19.68
276.7	391	0.00	72.16	27.84
276.1	343	0.00	63.45	36.55
275.0	269	0.00	49.90	50.10
288.5	2,241	10.32	74.47	15.21
286.2	1,806	8.26	59.76	31.97
283.9	1,338	6.41	46.40	47.19
281.4	1,014	5.01	32.55	59.44
278.8	758	3.92	27.91	68.17
296.0	7,122	33.64	57.19	9.17
295.1	6,585	29.38	51.10	19.52
293.8	5,702	25.78	45.55	28.68
292.2	4,826	22.39	39.91	37.70
290.6	3,951	19.32	34.87	45.81
289.2	3,427	17.01	31.06	51.93
287.5	2,875	14.51	27.09	58.40
297.8	11,597	44.66	38.46	16.88
296.3	11,370	42.74	24.93	32.33
294.0	8,763	34.95	20.48	44.58
291.7	6,764	29.09	17.08	53.83
289.5	5,426	24.68	14.51	60.82
287.4	4,344	20.75	12.23	67.02
297.9	15,031*	72.08	25.72	2.20

**Continued**

<b>T (K)</b>	<b>P (kPa)</b>	<b>%CH<sub>4</sub></b>	<b>%C<sub>3</sub>H<sub>8</sub></b>	<b>%C<sub>10</sub>H<sub>22</sub></b>
298.2	16,886	59.53	21.01	19.46
297.7	16,251	53.41	19.00	25.59
296.3	12,763	45.37	16.20	38.42
294.3	10,336	39.44	14.07	46.49
291.5	7,936	32.86	11.74	55.40
288.9	6,019	26.83	9.68	63.53
286.7	4,847	22.72	8.19	69.09
297.2	21,788*	86.60	8.60	4.80
292.9	13,121	55.42	5.62	38.96
288.7	8,019	41.00	4.02	54.98
285.9	5,868	32.12	3.16	64.71
282.2	4,302	25.36	2.50	72.14
279.2	3,151	19.36	1.90	78.74
295.4	31,027*	91.50	0.00	8.50
290.4	17,079	58.48	0.00	41.5
285.2	9,350	42.47	0.00	57.53
282.9	7,116	34.52	0.00	65.48
278.9	4,702	26.90	0.00	73.10

\* = Quadruple-cum-critical point.

*Hydrate:* Methane + carbon dioxide + hydrogen sulfide

*Reference:* Robinson and Hutton (1967)

*Phases:* L<sub>W</sub>-H-V

<b>T (K)</b>	<b>P (MPa)</b>	<b>%CH<sub>4</sub></b>	<b>%CO<sub>2</sub></b>	<b>%H<sub>2</sub>S</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>%CH<sub>4</sub></b>	<b>%CO<sub>2</sub></b>	<b>%H<sub>2</sub>S</b>
281.1	1.675	78.5	13.9	7.6	279.2	1.475	68.6	24.9	6.5
282.5	2.275	80.3	13.0	6.7	282.1	2.034	69.9	24.1	6.0
286.6	3.868	81.0	13.0	6.0	284.0	2.771	70.5	23.5	6.0
287.3	4.558	82.0	12.6	5.4	286.4	3.744	71.5	22.8	5.7
289.4	5.888	82.0	12.6	5.4	288.4	4.930	72.5	22.0	5.5
290.8	6.881	82.0	12.6	5.4	290.0	6.185	72.5	22.0	5.5
292.2	8.653	82.0	12.5	5.5	290.9	7.550	72.5	22.0	5.5
292.9	9.632	82.0	12.6	5.4	293.0	11.225	72.0	22.3	5.7
293.6	10.790	82.0	12.6	5.4	293.7	12.011	72.3	22.2	5.5
294.7	12.341	82.5	12.1	5.4	287.4	2.020	69.9	12.7	17.4
295.6	14.079	82.0	12.6	5.4	289.9	2.648	70.0	12.3	16.7
296.4	15.707	82.0	12.6	5.4	291.5	3.330	72.0	12.0	16.0
284.2	1.903	81.0	11.8	7.2	293.3	4.392	72.0	12.0	16.0
285.4	2.765	81.0	11.8	7.2	294.7	5.123	72.0	12.0	16.0
289.1	4.254	80.0	12.0	8.0	295.4	6.495	71.1	11.9	17.0
290.4	4.978	80.0	12.0	8.0	296.5	7.384	70.8	12.1	17.1
292.1	5.943	80.0	12.0	8.0	297.6	8.405	72.5	11.9	15.6
293.1	6.984	81.6	11.1	7.3	297.6	8.005	68.8	13.6	17.6
294.0	7.529	83.9	9.4	6.7					

*Hydrate:* Methane + carbon dioxide + hydrogen sulfide

*Reference:* Sun et al. (2003)

*Phases:* L<sub>W</sub>-H-V

Gas	%CO <sub>2</sub>	%H <sub>2</sub> S
I	7.40	4.95
II	10.77	6.78
III	7.16	9.93
IV	7.31	14.98
V	6.81	17.71
VI	7.00	26.62

### Gas I

T (K)	P (MPa)	T (K)	P (MPa)
274.2	1.044	286.2	5.121
277.2	1.58	288.2	6.358
280.2	2.352	289.2	7.212
282.2	3.126	290.2	8.220
284.2	3.964		

### Gas II

T (K)	P (MPa)	T (K)	P (MPa)
276.2	1.114	287.2	4.570
278.2	1.385	288.2	4.890
280.2	1.815	289.2	6.110
282.2	2.265	290.2	6.862
284.2	3.110	290.9	7.650
286.2	4.065	291.2	8.024

### Gas III

T (K)	P (MPa)	T (K)	P (MPa)
278.2	1.192	289.7	4.930
282.2	1.932	291.2	5.868
284.2	2.460	292.2	6.630
286.2	3.303	293.2	7.916
288.2	4.212		

**Continued****Gas IV**

<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
277.2	0.646	291.2	4.070
280.2	1.020	293.2	5.270
283.2	1.428	294.7	6.698
286.2	2.080	295.7	7.910
289.2	3.164		

**Gas V**

<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
282.2	0.950	294.2	5.314
284.2	1.244	295.2	6.310
286.2	1.670	295.8	6.880
288.2	2.368	296.6	7.825
290.2	3.080	297.2	8.680
292.2	4.008		

**Gas VI**

<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
281.2	0.582	295.2	3.910
284.2	0.786	296.7	5.030
287.2	1.160	298.2	6.562
290.2	1.788	299.7	8.080
293.2	2.688		

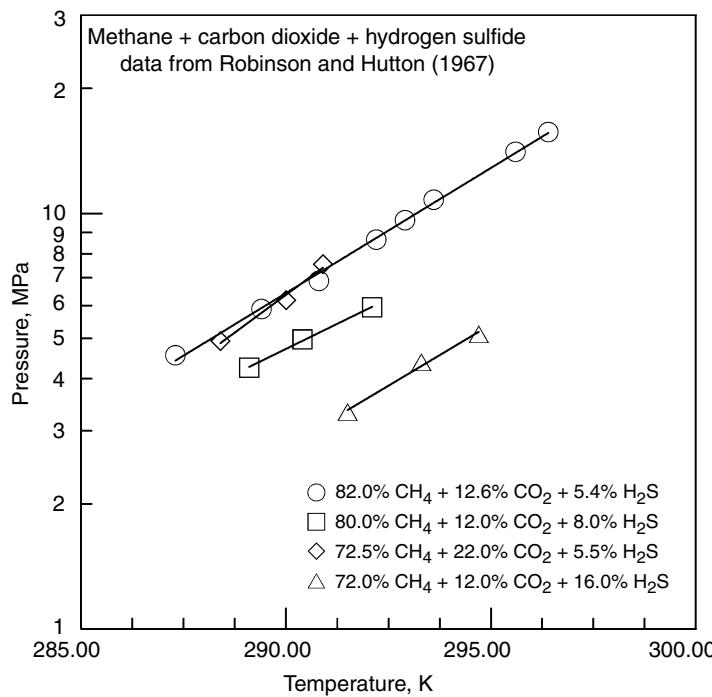
*Hydrates:* Methane + nitrogen + cyclohexane

*Reference:* Tohidi et al. (1996a)

*Phases:* L<sub>W</sub>-H-V

Feed composition (mol fraction): 0.1336 CH<sub>4</sub>; 0.1409 N<sub>2</sub>; 0.0464 c-C<sub>6</sub>H<sub>12</sub>; 0.6791 H<sub>2</sub>O

<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
278.0	2.144	284.2	5.137
281.6	3.496	290.0	12.321



**FIGURE 6.40** Methane + carbon dioxide + hydrogen sulfide mixture (L<sub>W</sub>-H-V) data.

#### 6.3.1.4 Equilibria of multicomponent guest mixtures

*Hydrate:* Methane + ethane + propane + 2-methylpropane

*Reference:* Mei et al. (1998)

*Phases:* L<sub>W</sub>-H-V

T (K)	P (MPa)	%CH <sub>4</sub> (mol%)	%C <sub>2</sub> H <sub>6</sub> (mol%)	%C <sub>3</sub> H <sub>8</sub> (mol%)	%2-Methylpropane (mol%)
273.5	0.92	97.25	1.42	1.08	0.25
275.0	1.15	97.25	1.42	1.08	0.25
276.6	1.36	97.25	1.42	1.08	0.25
277.7	1.50	97.25	1.42	1.08	0.25
278.8	1.63	97.25	1.42	1.08	0.25
279.7	1.87	97.25	1.42	1.08	0.25
280.9	2.24	97.25	1.42	1.08	0.25
281.9	2.67	97.25	1.42	1.08	0.25

*Hydrate:* Natural gases

*Reference:* Wilcox et al. (1941)

*Phases:* L<sub>W</sub>-H-V

### Compositions of Gases

Gas	%N <sub>2</sub>	%CO <sub>2</sub>	%CH <sub>4</sub>	%C <sub>2</sub> H <sub>6</sub>	%C <sub>3</sub> H <sub>8</sub>	%i-C <sub>4</sub> H <sub>10</sub>	%n-C <sub>4</sub> H <sub>10</sub>	%C <sub>5</sub> H <sub>12</sub>
B	0.64		86.41	6.47	3.57	0.99	1.14	0.78
C	0.43	0.51	93.20	4.25	1.61			
D			88.36*	6.82	2.54	0.38	0.89	1.01

\* = Includes nitrogen of unspecified amount.

### Phase Equilibrium Data Gas B

T (K)	P (MPa)						
278.8	1.255	292.2	6.964	295.1	12.27	297.1	20.68
282.9	1.924	294.1	9.680	296.1	16.84	298.3	27.32
288.7	4.123						

### Gas C

T (K)	P (MPa)						
277.7	1.600	289.2	6.964	292.1	10.501	293.3	14.13
283.9	3.392						

### Gas C (second series)

T (K)	P (MPa)						
279.1	1.924	290.3	8.136	295.0	20.264	296.7	27.50
281.8	2.648	291.2	9.481	294.3	17.16	295.6	22.99
286.7	4.820	293.3	13.780				

### Gas D

T (K)	P (MPa)						
276.8	1.207	284.9	3.516	291.2	8.205	293.2	12.00
281.6	2.186	288.7	5.447				

### Gas D (second series)

T (K)	P (MPa)						
289.2	6.171	293.9	14.07	296.9	26.55	295.9	22.55
292.1	9.308	295.0	18.20				

*Hydrate:* Natural gases

*Reference:* Deaton and Frost (1946)

*Phases:* Lw–H–V

### Compositions of Gases (mol%)

Gas	CO <sub>2</sub>	H <sub>2</sub> S	N <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>
A	0.20		7.7	65.4	12.7	10.3	3.7
B	0.20		1.1	87.9	4.4	4.9	1.5
C	0.20		9.4	78.4	6.0	3.6	2.4
D	0.30		9.5	79.4	5.8	3.6	1.4
E	3.25	0.25	1.1	87.8	4.0	2.1	1.5
F	0.40		0.3	91.0	3.2	2.0	3.1
G			1.0	90.8	3.0	2.1	3.2
H	0.20		14.3	75.2	5.9	3.3	1.1
I			3.4	88.5	4.3	2.0	1.7
J	0.9		1.2	90.6	3.8	1.5	2.0
K	0.8		25.0	67.4	3.7	1.9	1.2
L	0.6		0.2	96.5	0.9	1.8	

### Phase Equilibrium Data Gas A

T (K)	P (kPa)						
274.8	627	285.9	2571	290.1	4296	292.6	6302
280.3	1262	288.7	3592	291.5	5364	294.0	8536
283.2	1806						

### Gas B

T (K)	P (kPa)						
273.7	600	280.4	1338	283.7	2089	285.9	2668
275.4	738	282.6	1779	284.3	2248	286.5	2861
277.6	993						

### Gas C

T (K)	P (kPa)						
273.7	724	275.9	903	277.6	1172	279.8	1462
274.8	807	276.5	972	278.2	1241	283.2	2213

### Gas D

T (K)	P (kPa)						
273.7	752	276.5	1089	280.4	1675	282.1	2096
274.8	883	278.7	1400				

**Continued****Gas E**

<i>T</i> (K)	<i>P</i> (kPa)						
275.4	945	280.3	1717	285.9	3454	289.3	5254

**Gas F**

<i>T</i> (K)	<i>P</i> (kPa)						
273.7	765	280.4	1731	288.7	4909	292.1	8653
277.6	1241	285.9	3461	288.7	4895	292.7	9391
280.4	1731						

**Gas G**

<i>T</i> (K)	<i>P</i> (kPa)						
273.7	758	280.4	1723	288.7	5033	291.5	7729
277.6	1234	285.9	3468	288.7	5033		

**Gas H**

<i>T</i> (K)	<i>P</i> (kPa)						
274.2	758	277.6	1255	280.4	1758	282.1	2131
275.4	945						

**Gas I**

<i>T</i> (K)	<i>P</i> (kPa)						
273.7	793	275.3	972	277.6	1310	280.4	1813

**Gas J**

<i>T</i> (K)	<i>P</i> (kPa)						
273.7	883	277.6	1455	285.9	4034	287.6	5068
274.3	952	280.4	2027	285.9	4027	288.2	5433
274.8	1020	280.4	1993	285.9	4054	288.7	5812
274.8	1027	280.4	2006	286.5	4364	289.8	6985
275.9	1172	283.2	2841	287.1	4675	290.9	8384
277.6	1441	285.4	3765	287.1	4682		

**Gas K**

<i>T</i> (K)	<i>P</i> (kPa)						
274.3	1069	277.6	1607	283.2	3165	286.0	4592
275.4	1220	280.4	2248				

(Continued)

**Continued****Gas L**

<b>T (K)</b>	<b>P (kPa)</b>						
273.7	1,262	277.6	2,027	283.2	4,047	289.8	10,329
274.8	1,427	280.4	2,855	287.7	7,425	289.8	10,439
274.8	1,420						

*Hydrate:* Natural gases*Reference:* Kobayashi et al. (1951)*Phases:* L<sub>W</sub>-H-V**Compositions of Gases (mol%)**

<b>Gas</b>	<b>N<sub>2</sub></b>	<b>CH<sub>4</sub></b>	<b>C<sub>2</sub>H<sub>6</sub></b>	<b>C<sub>3</sub>H<sub>8</sub></b>	<b>i-C<sub>4</sub>H<sub>10</sub></b>	<b>n-C<sub>4</sub>H<sub>10</sub></b>	<b>C<sub>5</sub>H<sub>12</sub></b>	<b>C<sub>6</sub>H<sub>14</sub></b>
Hugoton	15.0	73.29	6.70	3.90	0.36	0.55	0.20	0.00
Michigan	6.8	79.64	9.38	3.22	0.18	0.58	0.15	0.05

**Phase Equilibrium Data  
Hugoton Gas**

<b>T (K)</b>	<b>P (MPa)</b>						
281.6	1.765	287.7	3.847	288.9	4.461	290.9	5.833
283.9	2.517						

**Michigan Gas**

<b>T (K)</b>	<b>P (MPa)</b>						
283.3	2.186	287.2	3.578	289.4	4.613	291.0	5.661
285.7	2.930						

*Hydrate:* Gas composition 90.6% CH<sub>4</sub>; 6.6% C<sub>2</sub>H<sub>6</sub>; 1.8% C<sub>3</sub>H<sub>8</sub>; 0.5% i-C<sub>4</sub>H<sub>10</sub>; 0.5% n-C<sub>4</sub>H<sub>10</sub>*Reference:* McLeod and Campbell (1961)*Phases:* L<sub>W</sub>-H-V

<b>T (K)</b>	<b>P (MPa)</b>						
293.6	13.55	300.0	41.34	303.1	62.85	298.6	33.75
297.5	27.68	301.7	52.16	295.8	20.24		

*Hydrates:* Three natural gases

*Reference:* Lapin and Cinnamon (1969)

*Phases:* L<sub>W</sub>–H–V

### Compositions of Gases

Gas	%N <sub>2</sub>	%CH <sub>4</sub>	%C <sub>2</sub> H <sub>6</sub>	%C <sub>3</sub> H <sub>8</sub>	%n-C <sub>4</sub> H <sub>10</sub>	%n-C <sub>5</sub> H <sub>12</sub>	%n-C <sub>6</sub> H <sub>14</sub>
1	1.70	72.78	14.50	7.63	2.65	0.63	0.11
2	1.58	67.69	13.50	14.10	2.45	0.58	0.10
3	1.47	62.49	12.47	20.62	2.26	0.58	0.11

### Formation Temperature at 4.207 MPa

Gas 1	Gas 2	Gas 3
288.75	289.85	289.85

*Hydrate:* Five natural gases with carbon dioxide

*Reference:* Adisasmito and Sloan (1992)

*Phases:* L<sub>W</sub>–H–V

### Composition (mol %)

Gas	%CO <sub>2</sub>	%CH <sub>4</sub>	%C <sub>2</sub> H <sub>6</sub>	%C <sub>3</sub> H <sub>8</sub>	%i-C <sub>4</sub> H <sub>10</sub>	%n-C <sub>4</sub> H <sub>10</sub>
A	0.00	76.62	11.99	6.91	1.82	2.66
B	31.40	52.55	8.12	4.74	1.31	1.88
C	66.85	24.42	3.99	3.07	0.75	0.92
D	83.15	12.38	1.96	1.66	0.37	0.48
E	89.62	7.86	1.13	0.86	0.20	0.33

### Hydrate Equilibria

Gas	T (K)	P (MPa)	Gas	T (K)	P (MPa)	Gas	T (K)	P (MPa)
A	273.7	496.6	B	282.0	1682.8	D	279.3	2565.5
A	276.5	703.4	C	273.7	758.6	D	282.0	3510.3
A	279.3	986.2	C	276.5	1089.7	E	273.7	1337.9
A	282.0	1413.8	C	279.3	1565.5	E	276.5	1841.4
B	273.7	593.1	C	282.0	2227.6	E	279.3	2531.0
B	276.5	841.4	D	273.7	1365.5	E	282.0	3469.0
B	279.3	1220.7	D	276.5	1869.0			

*Hydrate:* Natural gas (0.90% N<sub>2</sub>; 0.22% CO<sub>2</sub>; 85.24% CH<sub>4</sub>; 7.68% C<sub>2</sub>H<sub>6</sub>; 3.31% C<sub>3</sub>H<sub>8</sub>; 1.19% i-C<sub>4</sub>H<sub>10</sub>; 0.85% n-C<sub>4</sub>H<sub>10</sub>; 0.30% i-C<sub>5</sub>H<sub>12</sub>; 0.31% n-C<sub>5</sub>H<sub>12</sub>)

*References:* Tohidi et al. (1997b)

*Phases:* L<sub>W</sub>-H-V

T (K)	P (MPa)	T (K)	P (MPa)
279.1	1.317	288.1	3.930
281.9	1.772	290.1	4.881
283.3	2.062	291.5	6.088
283.5	2.110	292.9	7.619
285.3	2.606	294.8	11.769

*Hydrate:* Processed natural gas with hydrate structural transition

*Reference:* Jager and Sloan (2002)

*Phases:* L<sub>W</sub>-H-V

Gas composition: 97.53 mol% CH<sub>4</sub>; 0.8797% C<sub>2</sub>H<sub>6</sub>; 0.1397% C<sub>3</sub>H<sub>8</sub>; 0.0149% i-C<sub>4</sub>H<sub>10</sub>; 0.0248% n-C<sub>4</sub>H<sub>10</sub>; 0.0180% i-C<sub>5</sub>H<sub>12</sub>; 0.0203% n-C<sub>5</sub>H<sub>12</sub>; 0.0222% C<sub>6</sub>H<sub>14</sub>; 0.0126% C<sub>7</sub>H<sub>16</sub>; 0.9303% N<sub>2</sub>; 0.4100% CO<sub>2</sub>

Processed natural gas (PNG) + H <sub>2</sub> O			PNG + H <sub>2</sub> O+ 6 mol% NaCl		
T (K)	P (MPa)	Structure	T (K)	P (MPa)	Structure
278.8	3.83	II	268.0	3.68	II
283.6	6.71	II	274.4	7.21	II
285.8	8.43	II	279.1	13.95	II
287.2	11.16	II	282.1	22.38	II/I(?)
287.2	10.50	I	283.9	28.59	I(?)
287.5	11.81	II/I	284.3	31.12	I
287.9	12.29	II/I	284.7	32.33	I
288.7	13.51	I	285.2	34.70	I
290.4	16.67	I	286.5	42.25	I
292.8	23.48	I	288.0	50.71	I
294.6	29.83	I	289.2	57.28	I
295.8	34.25	I			
297.3	41.92	I			
298.5	48.51	I			
299.5	54.67	I			
300.4	60.87	I			
301.3	68.23	I			

*Hydrate:* Hydrate denuding of CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> from condensates or crudes

*Reference:* Verma et al. (1974)

*Phases:* L<sub>w</sub>-H-V-L<sub>HC</sub>

### Initial Properties of Condensates and Crude

Property	Prudhoe Bay condensate	Ray Field condensate	North slope crude
Molec Wt	136	110	260
Spec Grav	0.75	0.73	0.932

### Properties before and after Hydrate Formation

	Liquid composition			Hydrate composition		Quadruple	
	%CH <sub>4</sub>	%C <sub>3</sub> H <sub>8</sub>	%Cond	%CH <sub>4</sub>	%C <sub>3</sub> H <sub>8</sub>	T (K)	P (MPa)
<b>Prudhoe Bay condensate</b>							
Initial	32.2	18.2	49.6	N/A		293.9	6.825
Final	21.2	19.6	59.2	92.5	7.5	291.3	4.875
<b>Ray Field condensate<sup>a</sup></b>							
Initial	49.2	16.2	34.6	N/A		297.2	15.27
Final	46.1	13.1	40.8	64.8*	35.2*	295.4	13.66
<b>North slope crude oil</b>							
Initial	32.8	14.5	52.7	N/A		296.7	10.17
Final	17.0	14.2	68.8	85.9	14.1	290.5	6.41

\* Calculated by material balance.

*Hydrate:* Natural gases, hexane, decane, and crude oils

*Reference:* Holder (1976)

*Phases:* L<sub>w</sub>-H-V-L<sub>HC</sub>

### Overall mol% of Hydrocarbon Components

Expt	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	CO <sub>2</sub>	n-C <sub>6</sub> H <sub>14</sub>	c-C <sub>6</sub> H <sub>12</sub>	n-C <sub>10</sub> H <sub>22</sub>	MWcrude =
I	45.51	1.82	1.44			31.87		320
II	64.16	3.65	2.48	0.62	11.10		9.57	19.36
								8.42

(Continued)

**Continued**

<b>Experiment I</b>		<b>Experiment II</b>	
<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
285.9	8.412	289.0	8.688
286.3	8.826	289.2	8.908
288.1	9.998	289.4	9.412
288.4	10.204	289.9	10.025
288.7	10.342	290.6	10.770
288.8	10.928	290.8	10.722
289.2	11.308	291.5	10.963
289.9	11.997		
290.3	12.893		

*Hydrate:* Natural gas liquids

*Reference:* Ng and Robinson (1976a)

*Phases:* L<sub>W</sub>-H-L<sub>HC</sub> and L<sub>W</sub>-H-V-L<sub>HC</sub>

**Composition of Liquids in mol%**

<b>Gas composition</b>	<b>I</b>	<b>II</b>	<b>III</b>	<b>IV</b>	<b>V</b>	<b>VI</b>
Nitrogen	0.3	0.2	0.2			
Methane		2.2	21.9			
Ethane	31.3	30.6	24.7	23.4	21.5	17.0
Propane	51.5	50.8	40.8	30.4	48.9	38.6
Isobutane	16.9	16.2	12.4	19.6	23.8	18.9
<i>n</i> -Pentane				26.6		
Carbon dioxide					5.8	25.5

**Phase Equilibrium**

<b>Gas I</b>		<b>Gas II</b>		<b>Gas III</b>	
<b>T (K)</b>	<b>P (kPa)</b>	<b>T (K)</b>	<b>P (kPa)</b>	<b>T (K)</b>	<b>P (kPa)</b>
277.7	1,158*	281.2	1,565	291.7	4,799*
277.7	1,186	281.2	1,620	291.8	5,240
277.7	1,462	281.3	2,461	292.1	5,902
277.7	2,234	281.4	3,813	292.5	7,212
277.7	4,523	281.7	6,102	293.2	9,797
277.8	7,074	281.9	8,232	293.9	13,623
277.8	9,714	282.2	11,224		

**Continued****Gas IV****Gas V****Gas VI**

<b>T (K)</b>	<b>P (kPa)</b>	<b>T (K)</b>	<b>P (kPa)</b>	<b>T (K)</b>	<b>P (kPa)</b>
274.8	689*	280.1	1,207	283.9	2,344*
274.8	1,730	280.1	1,351	284.0	2,496
275.1	4,054	280.1	1,427	284.2	3,316
275.3	6,964	280.1	2,399	284.6	5,130
275.6	11,893	280.2	3,689	284.9	8,163
		280.4	6,129	285.7	14,700
		280.7	9,377		
		280.9	14,403		

\* = L<sub>W</sub>-H-V-L<sub>HC</sub>.

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*Hydrate:* Natural gases

*References:* Aoyagi and Kobayashi (1978)

*Phases:* V-H

**Compositions**

<b>Gas</b>	<b>%CH<sub>4</sub></b>	<b>%C<sub>2</sub>H<sub>6</sub></b>	<b>%C<sub>3</sub>H<sub>8</sub></b>	<b>%CO<sub>2</sub></b>
I	75.02	7.95	3.99	13.04
II	87.06	7.96	3.88	1.10

<b>T (K)</b>	<b>P (MPa)</b>	<b>H<sub>2</sub>O</b>		<b>T (K)</b>	<b>P (MPa)</b>	<b>H<sub>2</sub>O</b>	
		<b>ppm (mol)</b>	<b>(mol)</b>			<b>ppm (mol)</b>	<b>(mol)</b>
<b>Gas I</b>							
267.1	4.499	98.9		249.0	4.499	20.6	
267.1	5.857	87.1		249.8	12.078	18.4	
267.1	12.068	63.0		243.2	4.479	10.5	
260.9	4.458	58.8		243.7	5.847	10.3	
261.2	5.836	56.7		243.2	12.048	10.5	
260.9	12.048	41.6		237.2	12.088	4.52	
251.8	5.857	25.2		233.9	12.068	2.50	
<b>Gas II</b>							
277.6	0.345	18.0		260.9	3.445	63.0	
277.6	0.445	52.0		249.8	10.345	10.0	
260.9	0.345	8.4		249.8	3.445	19.7	

*Hydrate:* Gas liquids and condensate

*Reference:* Ng et al. (1987a)

*Phases:* As noted

### Composition of Hydrocarbon Liquids

	A	B	C	D
Concentration, mol%				
Nitrogen	0.00	0.04	0.16	0.64
Methane	2.49	12.48	26.19	73.03
Carbon dioxide	0.48	12.01	2.10	3.11
Ethane	4.22	8.88	8.27	8.04
Propane	8.63	10.57	7.50	4.28
Isobutane	2.85	2.14	1.83	0.73
n-Butane	7.02	5.63	4.05	1.50
Isopentane	3.39	1.74	1.85	0.54
n-Pentane	4.59	2.85	2.45	0.60
Hexanes plus	66.33	53.66	45.60	7.53
Mol.Wt.	123.0	113.0	90.2	32.4
Saturation pressure				
(MPa) at Ts	0.71*	4.34*	8.95*	43.94**
Ts (K)	281.15	310.95	310.95	416.15

\* = Bubble point temperature.

\*\* = Retrograde dew point pressure.

### Liquid A

T (K)	P (MPa)	Phases	T (K)	P (MPa)	Phases
273.8	0.64	L <sub>W</sub> -H-V-L <sub>HC</sub> (V = 0)	274.8	15.95	L <sub>W</sub> -H-L <sub>HC</sub>
274.0	5.27	L <sub>W</sub> -H-L <sub>HC</sub>	275.75	20.78	L <sub>W</sub> -H-L <sub>HC</sub>
274.4	10.34	L <sub>W</sub> -H-L <sub>HC</sub>			

### Liquid B

T (K)	P (MPa)	Phases	T (K)	P (MPa)	Phases
279.6	1.52	L <sub>W</sub> -H-V-L <sub>HC</sub>	286.8	12.00	L <sub>W</sub> -H-L <sub>HC</sub>
286.2	3.54	L <sub>W</sub> -H-V-L <sub>HC</sub> (V = 0)	288.4	20.00	L <sub>W</sub> -H-L <sub>HC</sub>

### Liquid C

T (K)	P (MPa)	Phases	T (K)	P (MPa)	Phases
287.0	4.00	L <sub>W</sub> -H-V-L <sub>HC</sub>	291.8	12.00	L <sub>W</sub> -H-L <sub>HC</sub>
291.4	7.74	L <sub>W</sub> -H-V-L <sub>HC</sub> (V = 0)	293.0	20.00	L <sub>W</sub> -H-L <sub>HC</sub>

**Continued****Liquid D**

<b>T (K)</b>	<b>P (MPa)</b>	<b>Phases</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>Phases</b>
290.8	6.01	L <sub>W</sub> -H-V-L <sub>HC</sub>	295.0	15.01	L <sub>W</sub> -H-V-L <sub>HC</sub>
293.8	11.07	L <sub>W</sub> -H-V-L <sub>HC</sub>	296.2	9.99	L <sub>W</sub> -H-V-L <sub>HC</sub>

*Hydrate:* Alaskan West Sak Crude

*Reference:* Paranjpe et al. (1988)

*Phases:* L<sub>W</sub>-H-V-L<sub>HC</sub>

**Live West Sak Crude Composition**

<b>Composition</b>	<b>mol%</b>	<b>Composition</b>	<b>mol%</b>	<b>Composition</b>	<b>mol%</b>
CO <sub>2</sub>	0.016	C <sub>7</sub>	0.016	C <sub>15</sub>	1.944
N <sub>2</sub>	0.032	C <sub>8</sub>	0.008	C <sub>16</sub>	1.795
C <sub>1</sub>	38.333	C <sub>9</sub>	0.823	C <sub>17</sub>	1.570
C <sub>2</sub>	0.857	C <sub>10</sub>	1.496	C <sub>18</sub>	1.795
C <sub>3</sub>	0.359	C <sub>11</sub>	1.720	C <sub>19</sub>	2.468
C <sub>4</sub>	0.179	C <sub>12</sub>	1.346	C <sub>20</sub>	2.841
C <sub>5</sub>	0.064	C <sub>13</sub>	1.496	C <sub>21</sub> <sup>+</sup>	39.037
C <sub>6</sub>	0.200	C <sub>14</sub>	1.795	Avg mol wt C <sub>21</sub>	455

**West Sak Crude PVT Properties**

<b>Pressure</b> <b>MPa</b>	<b>GOR</b> <b>SCF/STB</b>	<b>Density</b> <b>g/cc</b>	<b>Viscosity</b> <b>cp</b>	<b>Pressure</b> <b>MPa</b>	<b>GOR</b> <b>SCF/STB</b>	<b>Density</b> <b>g/cc</b>	<b>Viscosity</b> <b>cp</b>
11.65	210	0.902	35.4	4.93	93	0.917	68.4
10.34	188	0.905	40.0	3.45	68	0.920	82.5
8.96	165	0.908	45.2	2.07	42	0.923	102.1
7.58	141	0.911	51.2	0.69	15	0.927	127.6
6.21	117	0.914	58.5				

**Analysis of West Sak Separator Gas at 2.16 MPa and 291.5 K**

<b>Composition</b>	<b>mol%</b>	<b>Composition</b>	<b>mol%</b>	<b>Composition</b>	<b>mol%</b>
H <sub>2</sub> S	0.00	C <sub>2</sub>	0.24	i-C <sub>5</sub>	0.03
CO <sub>2</sub>	0.02	C <sub>3</sub>	0.31	n-C <sub>5</sub>	0.03
N <sub>2</sub>	0.16	i-C <sub>4</sub>	0.07	C <sub>6</sub>	0.02
C <sub>1</sub>	98.33	n-C <sub>4</sub>	0.12	C <sub>6</sub> <sup>+</sup>	0.02

(Continued)

**Continued****Constant Composition Expansion for West Sak Crude at 299.8 K**

Pressure		Pressure		Pressure	
MPa	Rel Liq Vol	MPa	Rel Liq Vol	MPa	Rel Liq Vol
11.75	1.00	8.68	0.934	4.87	0.762
9.98	0.974	7.04	0.878	4.10	0.685
9.46	0.954	6.26	0.844	3.17	0.6054

Rel Liq Vol = (Vol of Liq)/(Vol of Liq at Bub Pt Press).

**Saturation Pressures of West Sak Crude**

T (K)	P (MPa)						
299.8	11.75	310.9	14.12	366.5	16.24	394.3	17.20

**L<sub>W</sub>-H-V-L<sub>HC</sub> Data for West Sak Crude**

T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
279.8	5.36	281.6	6.38	282.4	7.03
280.8	6.03	282.0	6.79	284.0	8.30

*Hydrate:* Crude oil

*Reference:* Avlonitis (1988)

*Phases:* L<sub>W</sub>-H-V-L<sub>HC</sub>

**Characterization of Crude Oil**

Composition	mol%	Composition	mol%	Composition	mol%
N <sub>2</sub>	0.61	C <sub>3</sub> H <sub>8</sub>	8.06	n-C <sub>5</sub> H <sub>12</sub>	2.57
CO <sub>2</sub>	2.01	i-C <sub>4</sub> H <sub>10</sub>	1.34	n-C <sub>6</sub> H <sub>14</sub>	3.15
CH <sub>4</sub>	35.6	n-C <sub>4</sub> H <sub>10</sub>	4.26	C <sub>7</sub> <sup>+</sup>	31.26
C <sub>2</sub> H <sub>6</sub>	9.90	i-C <sub>5</sub> H <sub>12</sub>	1.28		

*Note:* The i = C<sub>7</sub><sup>+</sup> fraction is characterized by T<sub>C</sub> = 770 K, P<sub>C</sub> = 103.42 kPa,  $\omega$  = 0.690 and Equation-of-State  $\delta_{ij}$  interaction constants for the Soave equation of  $\delta_{C1} = 0.055$ ;  $\delta_{C2} = 0.030$ ;  $\delta_{N2} = 0.150$ ;  $\delta_{CO_2} = 0.120$ .

**Continued****L<sub>W</sub>-H-V-L<sub>HC</sub> Data**

<b>T (K)</b>	<b>P (MPa)</b>						
280.2	1.26	283.6	2.18	288.2	4.59	290.6	5.73
280.2	1.43	284.6	2.63	289.6	5.14	292.4	8.032
283.0	2.08	285.8	3.189				

**6.3.1.5 Equilibria with inhibitors**

The phase equilibria data for hydrates with inhibitors are presented below. As in previous results, data plots are provided for those systems which have been considered by more than one investigation, as a first order means of data evaluation. Individual investigators usually include plots of their data in the original reference. Unless otherwise indicated the mass concentration of the inhibitor in the aqueous phase is included in the column marked “wt%,” hydrocarbon/CO<sub>2</sub>/H<sub>2</sub>S/N<sub>2</sub> concentrations are mol% in vapor unless otherwise indicated.

*Simple methane hydrates with inhibitors*

*Hydrate:* Methane with methanol

*Reference:* Ng and Robinson (1985)

*Phases:* L<sub>W</sub>-H-V

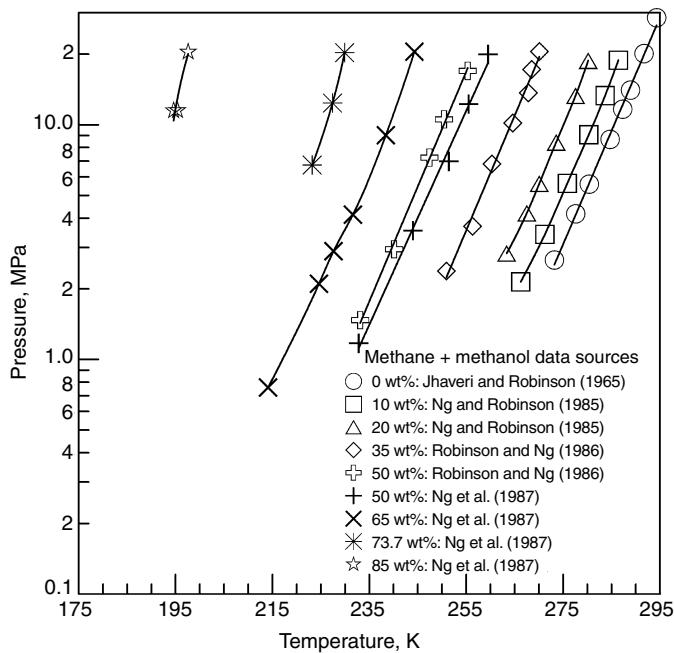
<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>
10.0	266.2	2.14	10.0	283.7	13.3	20.0	270.1	5.61
10.0	271.2	3.41	10.01	286.4	18.8	20.0	273.6	8.41
10.0	275.9	5.63	20.0	263.3	2.83	20.0	277.6	13.30
10.0	280.3	9.07	20.0	267.5	4.20	20.0	280.2	18.75

*Hydrate:* Methane with methanol

*Reference:* Robinson and Ng (1986)

*Phases:* L<sub>W</sub>-H-V

<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>
35	250.9	2.38	35	267.8	13.68	50	240.1	2.95
35	256.3	3.69	35	268.5	17.22	50	247.4	7.24
35	260.3	6.81	35	270.1	20.51	50	250.4	10.54
35	264.6	10.16	50	233.1	1.47	50	255.3	16.98



**FIGURE 6.41** Methanol inhibition of simple methane hydrates.

*Hydrate:* Methane with methanol

*Reference:* Ng et al. (1987b)

*Phases:* L<sub>W</sub>-H-V

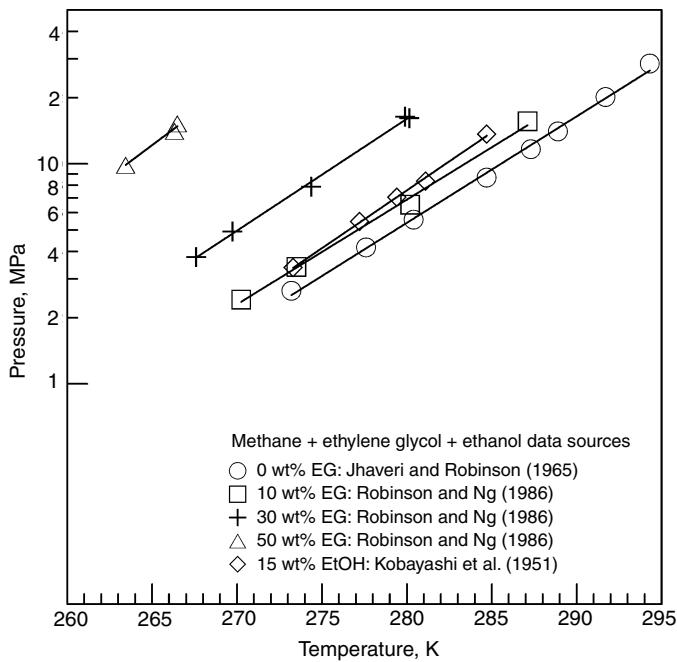
wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
50.0	232.8	1.17	65.0	224.6	2.10	73.7	227.4	12.37
50.0	244.0	3.54	65.0	227.6	2.89	73.7	229.9	20.30
50.0	251.4	6.98	65.0	231.6	4.14	85.0	194.6	11.49
50.0	255.5	12.26	65.0	238.4	9.03	85.0	195.4	11.51
50.0	259.5	19.93	65.0	244.3	20.49	85.0	197.6	20.42
65.0	214.1	0.76	73.7	223.2	6.73			

*Hydrate:* Methane with ethylene glycol

*Reference:* Robinson and Ng (1986)

*Phases:* L<sub>W</sub>-H-V

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
10	270.2	2.42	30	267.6	3.77	30	279.9	16.38
10	273.5	3.40	30	269.7	4.93	50	263.4	9.89
10	280.2	6.53	30	274.4	7.86	50	266.3	14.08
10	287.1	15.6	30	280.1	16.14	50	266.5	15.24



**FIGURE 6.42** Ethanol and ethylene glycol inhibition of simple methane hydrates.

*Hydrate:* Methane with triethylene glycol

*Reference:* Ross and Toczylkin (1992)

*Phases:* L<sub>W</sub>-H-V

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
10	274.6	3.17	20.2	275.0	4.37	40.0	274.5	7.27
10	276.0	3.87	20.2	276.0	4.97	40.0	276.0	9.87
10	278.0	4.77	20.2	278.0	6.32	40.0	278.0	15.27
10	283.0	8.02	20.2	283.0	11.32	40.0	280.5	23.02
10	288.0	14.72	20.2	288.0	21.62	40.0	283.0	35.17
10	293.0	25.57	20.2	293.0	39.87			

*Hydrate:* Methane with 15 wt% ethanol solution

*Reference:* Kobayashi et al. (1951)

*Phases:* L<sub>W</sub>-H-V

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
15	273.3	3.38	15	279.4	7.06	15	284.7	13.67
15	277.2	5.47	15	281.1	8.36			

*Hydrate:* Methane with sodium chloride solution

*Reference:* Kobayashi et al. (1951)

*Phases:* Lw–H–V

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
10	270.0	2.59	10	278.6	6.38	20	272.3	6.18
10	271.0	2.80	10	282.1	10.03	20	272.3	7.19
10	272.7	3.58	10	284.3	13.42	20	275.7	11.09
10	274.5	3.65	20	265.9	3.78	20	276.4	10.82
10	276.9	4.89	20	267.8	4.63	20	276.3	13.66

*Hydrate:* Methane with sodium chloride solutions

*Reference:* de Roo et al. (1983)

*Phases:* Lw–H–V

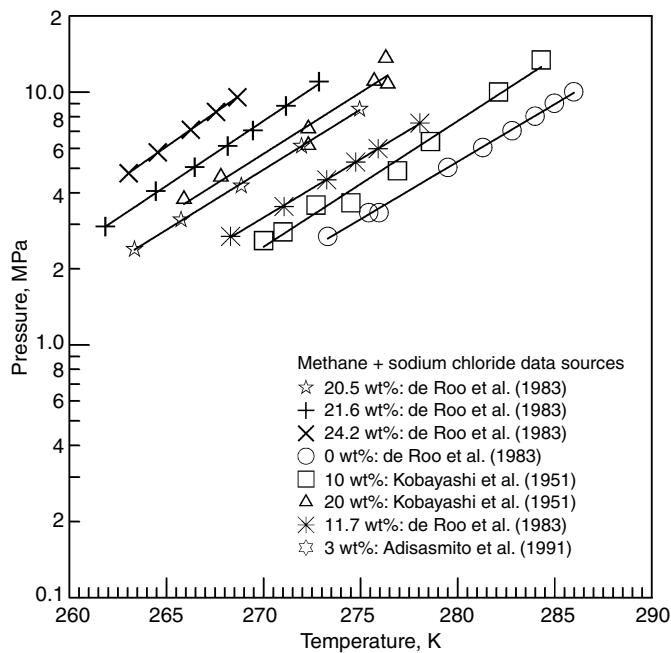
mol fraction			mol fraction			mol fraction		
NaCl	T (K)	P (MPa)	NaCl	T (K)	P (MPa)	NaCl	T (K)	P (MPa)
0.0394	268.3	2.69	0.0598	268.8	4.26	0.0778	271.2	8.83
0.0394	271.0	3.53	0.0598	272.0	6.12	0.0778	272.8	11.00
0.0394	273.2	4.50	0.0598	275.0	8.57	0.0891	263.0	4.78
0.0394	274.8	5.29	0.0778	261.8	2.94	0.0891	264.6	5.78
0.0394	275.9	5.98	0.0778	264.4	4.06	0.0891	266.2	7.11
0.0394	278.0	7.55	0.0778	266.4	5.05	0.0891	267.6	8.36
0.0598	263.4	2.39	0.0778	268.2	6.12	0.0891	268.6	9.55
0.0598	265.8	3.13	0.0778	269.4	7.05			

*Hydrate:* Methane and potassium formate

*Reference:* Fadnes et al. (1998)

*Phases:* Lw–H–V

wt%	HCOOK	T (K)	P (MPa)
0		285.45	10
0		285.75	10
10		283.15	10
10		289.55	20
10		288.15	20
20		278.35	9.6
20		278.55	10
20		283.65	20
30		272.75	10
30		277.05	20



**FIGURE 6.43** Sodium chloride inhibition of simple methane hydrates.

*Hydrate:* Methane and single and mixed electrolytes

*Reference:* Dholabhai et al. (1991)

*Phases:* L<sub>w</sub>-H-V

#### Compositions of Aqueous Solutions

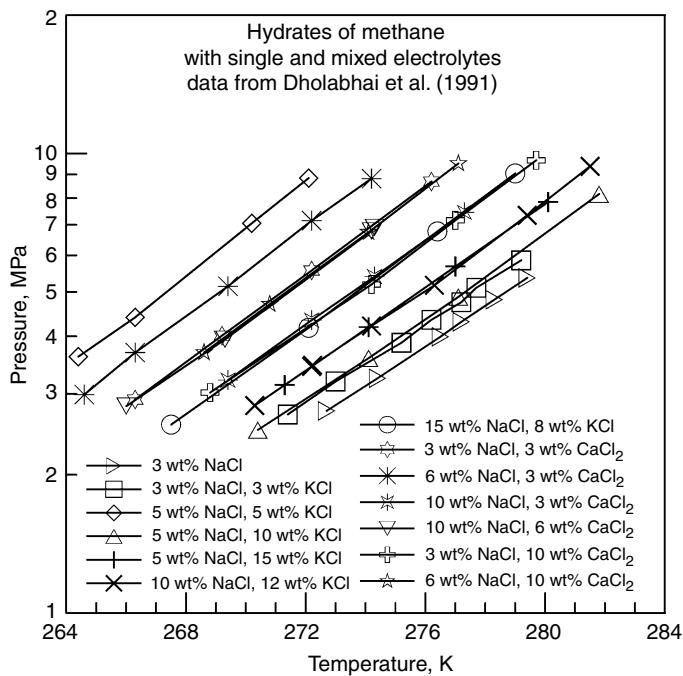
Solution ID	wt% NaCl	wt% KCl	wt% CaCl <sub>2</sub>	Molality
Na3	3.00	0	0	0.5287
Na3K3	3.00	3.00	0	0.7939
Na5K5	5.00	5.01	0	1.6975
Na5K10	5.00	9.98	0	2.5809
Na5K15	5.00	15.00	0	3.5869
Na10K12	10.01	12.00	0	4.2591
Na15K8	14.99	7.99	0	4.7189
Na3Ca3	3.00	0	3.00	1.2651
Na6Ca3	6.00	0	3.00	1.7221
Na10Ca3	10.00	0	3.00	2.7422
Na10Ca6	9.97	0	5.98	3.6321
Na3Ca10	3.00	0	10.00	3.1770
Na6Ca10	6.00	0	10.00	3.9019
SEA*	2.394	0.069	0.115	NA

\* = SEA also contains 0.401 wt% Na<sub>2</sub>SO<sub>4</sub>, 0.009 wt% NaF, 0.011 wt% KBr, 0.508 wt% MgCl<sub>2</sub>, and 0.002 wt% SrCl<sub>2</sub>.

(Continued)

**Continued****L<sub>W</sub>–H–V Phase Equilibrium Results**

<b>Solution ID</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>Solution ID</b>	<b>T (K)</b>	<b>P (MPa)</b>
Na3	274.4	3.243	Na15K8	270.2	7.049
	276.5	3.993		266.3	4.400
	278.3	4.807		264.4	3.614
	279.4	5.361		272.1	8.839
	272.7	2.754			
	277.2	4.303		274.1	3.584
Na3K3				277.1	4.874
	277.2	4.746	Na6Ca3	281.8	8.159
	279.2	5.857		270.4	2.504
	275.2	3.873			
	271.4	2.704		274.1	4.189
	273.0	3.192		277.0	5.679
Na5K5	276.2	4.346		280.1	7.839
	277.7	5.106		271.3	3.134
			Na10Ca3	274.3	5.399
	272.23	3.464		272.2	4.339
	270.3	2.829		269.4	3.214
	274.2	4.215		277.3	7.444
Na5K10	276.3	5.169	Na10Ca6	274.2	6.779
	272.2	3.439		266.0	2.819
	281.5	9.379		269.3	3.939
	279.4	7.340			
				274.3	6.899
	272.1	4.174			
Na5K15	267.5	2.569	Na3Ca10	277.0	7.159
	279.0	9.046		279.7	9.664
	276.4	6.764		274.2	5.189
	272.2	5.564		268.8	3.019
	269.2	4.014			
Na10K12	266.3	2.914	Na6Ca10	274.1	6.739
	276.2	8.689		277.1	9.514
				270.8	4.699
	272.2	7.144			
	269.4	5.144		268.6	3.689
	266.3	3.689		277.0	4.364
	264.6	2.989	SEA	279.0	5.424
	274.2	8.819		281.2	6.659
				283.9	9.064



**FIGURE 6.44** Inhibition of simple methane hydrates with single and mixed electrolytes.

*Hydrate:* Methane + ethylene glycol (EG) + sodium chloride (NaCl)

*References:* Eichholz et al. (2004)

*Phases:* L<sub>w</sub>-H-V

EG mass %	NaCl mass % <sup>a</sup>	T (K)	P <sub>exp</sub> (MPa)	T <sup>b</sup> (K)	P <sub>b</sub> (MPa)
19.16	0	266.5	2.136	266.1	2.108
		272.6	3.815	272.6	3.769
		279.5	8.620	279.8	8.574
5.77	3.77	271.1	2.811	271	2.777
		274.5	3.968	274.6	3.932
		277.9	5.491	277.9	5.471
		282.2	8.109	281.1	8.076
15.36	3.77	267.1	2.392	267.1	2.353
		270.8	3.735	270.8	3.706
		274.3	5.314	274.4	5.264
		279.4	9.558	279.5	9.531
23.88	3.77	262.8	2.264	262.8	2.231
		266.6	3.308	266.7	3.291
		270.3	5.055	270.3	5.032
		276.1	9.489	276	9.450

(Continued)

**Continued**

<b>EG mass %</b>	<b>NaCl mass %<sup>a</sup></b>	<b>T (K)</b>	<b>P<sub>exp</sub> (MPa)</b>	<b>T<sup>b</sup> (K)</b>	<b>P<sub>b</sub> (MPa)</b>
3.77	15.67	264.9	2.772	264.9	2.732
		268.4	4.191	268.5	4.142
		272.2	6.384	272.2	6.345
12.07	15.01	263.6	3.497	263.5	3.448
		267.0	5.156	267.0	5.120
		270.6	7.690	270.5	7.637

<sup>a</sup> On wet basis (used without drying).

<sup>b</sup> Data denote the no hydrate point.

$P_{\text{exp}}$ : equilibrium pressure data.

$P_b$ : pressure where hydrates were not stable.

**Hydrate:** Methane + ethylene glycol (EG) + salt (NaCl, KCl, or CaCl<sub>2</sub>)

**References:** Masoudi et al. (2004, 2005)

**Phases:** L<sub>W</sub>-H-V

<b>Salt</b>	<b>Salt concentration wt%</b>	<b>EG concentration wt%</b>	<b>Hydrate conditions</b>	
			<b>T (K)</b>	<b>P (MPa)</b>
NaCl	15.0	21.3	262.3	5.068
			268.4	11.431
			274.3	27.758
			277.9	46.698
	12.0	30.8	262.4	6.957
			267.3	13.610
			270.5	22.946
			275.2	46.691
KCl	10.0	23.0	265.5	4.164
			273.4	10.356
			279.1	22.760
			283.9	44.513
	8.0	35.0	259.3	3.930
			267.0	9.935
			273.0	23.442
			277.6	45.050
CaCl <sub>2</sub>	15.0	21.3	269.4	4.027
			277.6	10.756
			283.1	22.918
			287.8	43.864

**Continued**

Salt	Salt concentration		Hydrate conditions	
	wt%	EG concentration wt%	T (K)	P (MPa)
CaCl <sub>2</sub>	15.3	13.4	265.1	3.971
			272.7	9.804
			279.5	25.090
			283.6	45.436
			261.5	3.907
	18.0	14.0	268.9	9.404
			275.2	22.994
			279.6	44.843
			261.6	4.675
			268.1	9.942
14.0	26.0	26.0	273.5	22.801
			277.9	43.347

*Hydrate:* Methane with aqueous glycerol*Reference:* Ng and Robinson (1994)*Phases:* L<sub>W</sub>-H-V

wt% glycerol	T (K)	P (MPa)	wt% glycerol	T (K)	P (MPa)
25.0	273.8	4.39	50.0	264.2	4.53
	278.0	6.91		267.8	6.65
	283.0	12.41		273.4	13.81
	286.2	20.53		276.2	20.53

**SIMPLE ETHANE HYDRATES WITH INHIBITORS***Hydrate:* Ethane with methanol*Reference:* Ng and Robinson (1985)*Phases:* L<sub>W</sub>-H-V, L<sub>W</sub>-H-V-L<sub>C<sub>2</sub>H<sub>6</sub></sub>, L<sub>W</sub>-H-L<sub>C<sub>2</sub>H<sub>6</sub></sub>**L<sub>W</sub>-H-V**

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
10	268.3	0.417	20	263.5	0.550
16	272.1	0.731	20	264.9	0.614

(Continued)

**Continued**

<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>
10	276.0	1.160	20	267.7	0.869
10	278.4	1.630	20	268.8	1.030
10	280.4	2.160	20	271.8	1.520
10	281.4	2.800	20	274.1	2.060
10	281.9	2.820			

**L<sub>W</sub>-H-L<sub>C<sub>2</sub>H<sub>6</sub></sub>**

<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>
10	282.2	2.91*	10	283.6	13.76
10	282.0	3.99	10	284.4	20.20
10	282.4	4.22	20	275.7	2.65*
10	282.0	5.65	20	276.3	5.89
10	282.0	6.59	20	277.0	10.03
10	282.7	7.30	20	277.8	15.12
10	282.9	10.36	20	278.6	20.40

\* = L<sub>W</sub>-H-V-L<sub>C<sub>2</sub>H<sub>6</sub></sub>.

*Hydrate:* Ethane with methanol

*Reference:* Ng et al. (1985a)

*Phases:* L<sub>W</sub>-H-V, L<sub>W</sub>-H-V-L<sub>C<sub>2</sub>H<sub>6</sub></sub>, L<sub>W</sub>-H-L<sub>C<sub>2</sub>H<sub>6</sub></sub>

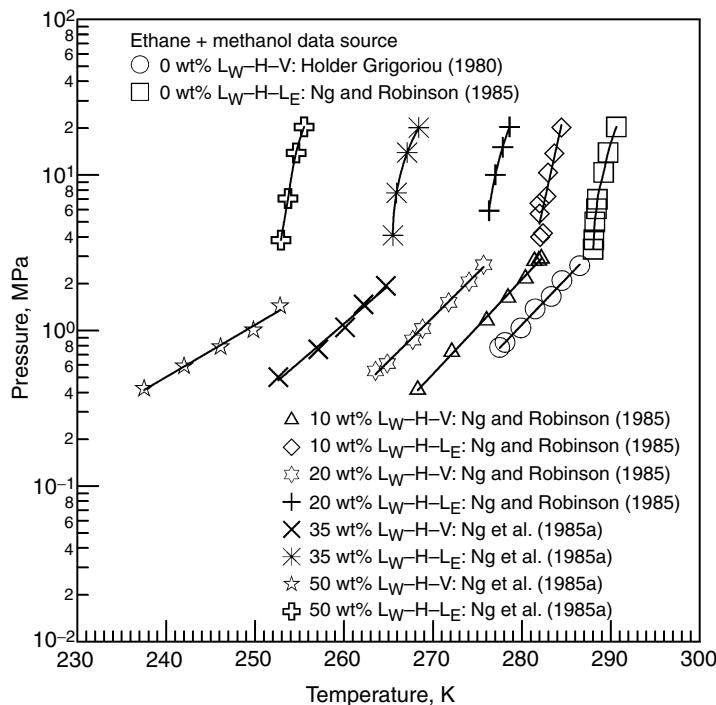
**L<sub>W</sub>-H-V**

<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>
35	252.6	0.502	50	237.5	0.423
35	257.1	0.758	50	242.0	0.592
35	260.1	1.050	50	246.1	0.786
35	262.2	1.48	50	249.8	1.007

**L<sub>W</sub>-H-L<sub>C<sub>2</sub>H<sub>6</sub></sub>**

<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>
35	264.7	1.937*	50	252.8	1.441*
35	265.5	4.095	50	252.9	3.820
35	265.9	7.695	50	253.7	7.074
35	267.1	13.93	50	254.6	13.89
35	268.4	20.18	50	255.5	20.35

\* = L<sub>W</sub>-H-V-L<sub>C<sub>2</sub>H<sub>6</sub></sub>.



**FIGURE 6.45** Methanol inhibition of simple ethane hydrates.

*Hydrate:* Ethane with triethylene glycol

*Reference:* Ross and Toczylkin (1992)

*Phases:* L<sub>W</sub>-H-V and L<sub>W</sub>-H-LC<sub>2</sub>H<sub>6</sub>

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
10	277.0	1.00	20.0	273.7	0.79	40.0	275.0	1.97
10	282.0	1.80	20.0	276.5	1.29	40.0	275.8	2.30
10	286.3	3.72*	20.0	278.0	1.54	40.0	277.9	3.30*
10	289.0	23.27*	20.0	283.0	2.63	40.0	281.7	20.77*
			20.0	285.5	9.72*	40.0	283.0	33.57*
			20.0	288.0	28.27*			
			20.0	289.0	36.27*			

\* = L<sub>W</sub>-H-LC<sub>2</sub>H<sub>6</sub>.

*Hydrate:* Ethane + NaCl

*References:* Tohidi et al. (1993)

*Phases:* Lw–H–V

wt% NaCl	T (K)	P (MPa)
10	273.7	0.883
	276.0	1.165
	277.6	1.455
	278.8	1.737
	280.4	2.165
15	272.7	1.082
	274.1	1.386
	277.1	2.151
20	266.2	0.689
	269.2	1.117
	271.2	1.469
	271.4	1.524

## SIMPLE PROPANE HYDRATES WITH INHIBITORS

*Hydrate:* Propane with methanol

*Reference:* Ng and Robinson (1985)

*Phases:* Lw–H–V, Lw–H–L<sub>C<sub>3</sub>H<sub>8</sub></sub>

### L<sub>w</sub>–H–V

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
5.00	272.1	0.234	10.39	269.2	0.228
5.00	272.6	0.259	10.39	270.9	0.360
5.00	273.3	0.316	10.39	271.0	0.352
5.00	274.2	0.405	10.39	271.6	0.415
5.00	274.8	0.468	10.39	271.8	0.434
10.39	268.3	0.185			

### L<sub>w</sub>–H–L<sub>C<sub>3</sub>H<sub>8</sub></sub>

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
5.00	275.0	0.794	10.39	272.1	0.984
5.00	275.1	1.720	10.39	272.1	2.737
5.00	275.0	6.340	10.39	272.1	6.510

*Hydrate:* Propane with methanol

*Reference:* Ng and Robinson (1984)

*Phases:* L<sub>w</sub>-H-V, L<sub>w</sub>-H-L<sub>C<sub>3</sub>H<sub>8</sub></sub>

### L<sub>w</sub>-H-V

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
35	248.0	0.137	50	229.7	0.090
35	250.2	0.207			

### L<sub>w</sub>-H-L<sub>C<sub>3</sub>H<sub>8</sub></sub>

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
35	250.6	0.876	50	229.9	1.970
35	251.1	6.090	50	229.3	7.830
35	251.0	9.770	50	229.3	19.710
35	251.3	20.38			

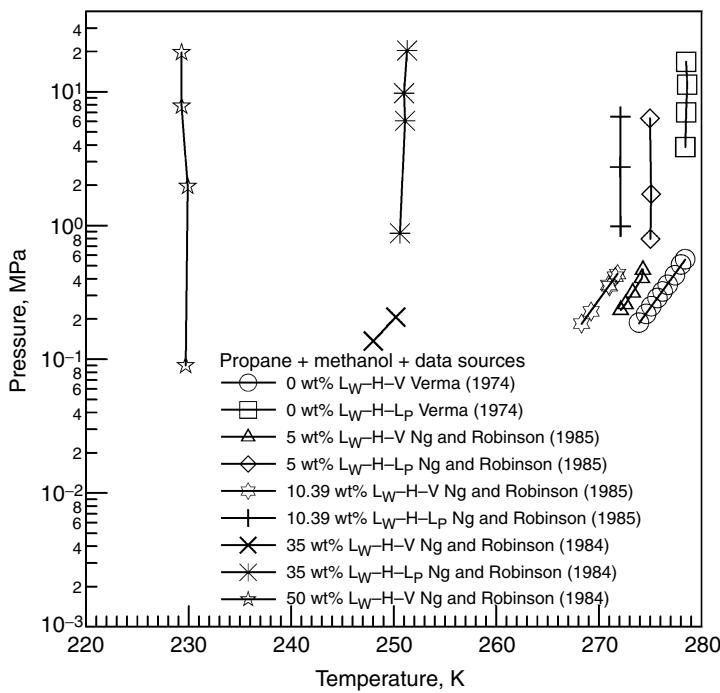


FIGURE 6.46 Methanol inhibition of simple propane hydrates.

*Hydrate:* Propane with sodium chloride

*Reference:* Kobayashi et al. (1951)

*Phases:* L<sub>W</sub>-H-V

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
10	268.3	0.122	10	272.4	0.370
10	269.7	0.170	10	272.8	0.479
10	271.8	0.278	10	273.0	1.118
10	272.0	0.309	10	273.1	1.911

*Hydrate:* Propane with sodium chloride

*Reference:* Patil (1987)

*Phases:* L<sub>W</sub>-H-V

wt%	T (K)	P (kPa)	wt%	T (K)	P (kPa)
3.0	272.2	179	5.0	274.4	324
3.0	274.2	290	5.0	275.6	448
3.0	275.4	366	10.0	270.8	191
3.0	276.2	455	10.0	272.2	259
5.0	271.2	185	10.0	273.6	355
5.0	272.6	241	10.0	274.6	450

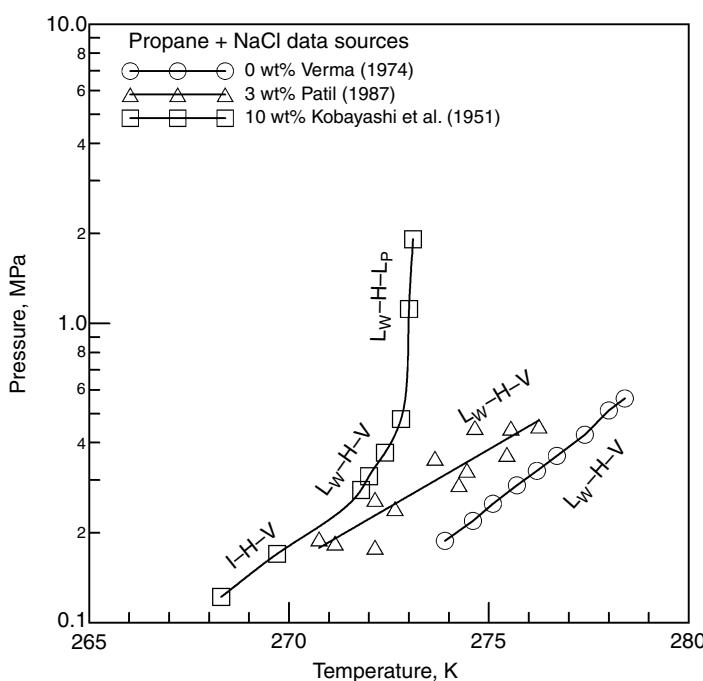


FIGURE 6.47 Sodium chloride inhibition of simple propane hydrates.

*Hydrate:* Propane and single and mixed electrolytes

*Reference:* Englezos and Ngan (1993)

*Phases:* L<sub>W</sub>-H-V

<b>Electrolyte (wt%)</b>					
<b>CaCl<sub>2</sub> · 2H<sub>2</sub>O</b>	<b>NaCl</b>	<b>KCl</b>	<b>CaCl<sub>2</sub></b>	<b>T (K)</b>	<b>P (MPa)</b>
15.00	0	0	0	268.7	0.205
				269.8	0.270
				270.3	0.317
				271.1	0.376
				271.7	0.412
7.5	7.5	0	0	265.9	0.172
				266.4	0.186
				267.6	0.248
				268.5	0.312
				269.4	0.385
				269.8	0.418
0	7.5	7.5	0	265.2	0.157
				266.2	0.206
				267.4	0.259
				268.5	0.321
				269.0	0.372
0	0	7.5	7.5	266.3	0.181
				266.9	0.206
				267.5	0.230
				268.1	0.263
				268.6	0.294
				269.5	0.370
				270.1	0.432
0	7.5	7.5	5.0	261.9	0.172
				262.3	0.192
				262.8	0.214
				263.4	0.249
				263.6	0.267
				264.2	0.286
				264.4	0.303
				264.5	0.303
				265.1	0.342
				265.2	0.352

*Hydrate:* Propane with single salts of NaCl, KCl, CaCl<sub>2</sub>

*Reference:* Tohidi et al. (1993)

*Phases:* L<sub>w</sub>-H-V

Salt	wt%	T (K)	P (MPa)	Salt	wt%	T (K)	P (MPa)
NaCl	3.1	273.2	0.221	KCl	15.0	269.0	0.221
		273.8	0.248			269.8	0.269
		274.6	0.303			270.4	0.324
		275.4	0.365			270.6	0.345
		276.0	0.414			271.2	0.393
NaCl	10.0	270.0	0.241	KCl	20.0	266.4	0.228
		270.8	0.283			266.8	0.262
		271.6	0.359			267.2	0.290
		272.2	0.421			267.4	0.310
		272.8	0.531*			267.6	0.338
NaCl	15.0	266.2	0.221	CaCl <sub>2</sub>	7.5	271.6	0.234
		266.8	0.241			272.0	0.269
		267.4	0.290			272.8	0.317
		268.2	0.379			273.6	0.379
		268.6	0.455*			274.2	0.427
NaCl	20.0	261.0	0.200	CaCl <sub>2</sub>	11.3	269.6	0.248
		261.6	0.228			270.0	0.283
		262.6	0.283			270.6	0.324
		263.0	0.331			271.4	0.372
KCl	10.0	271.0	0.228	CaCl <sub>2</sub>	15.2	266.4	0.234
		271.8	0.283			267.0	0.262
		272.6	0.331			267.2	0.303
		273.0	0.379			267.8	0.345
		273.4	0.421			268.0	0.359

\* = L<sub>w</sub>-H-V-L<sub>C<sub>3</sub>H<sub>8</sub></sub>.

*Hydrate:* Propane with single and salts of NaCl, KCl, CaCl<sub>2</sub>

*Reference:* Tohidi et al. (1994a)

*Phases:* L<sub>w</sub>-H-V and phase fractions

Salt	Original wt% salt	T (K)	P (MPa)	C <sub>3</sub> H <sub>8</sub> mol%	wt% salt in H <sub>2</sub> O	Hydrate phase fraction
CaCl <sub>2</sub>	7.274	272.2	0.317	3.248	8.533	0.163
CaCl <sub>2</sub>	11.343	269.4	0.310	3.639	12.265	0.088
CaCl <sub>2</sub>	15.121	266.0	0.324	3.783	16.346	0.089
NaCl	3.078	273.2	0.255	2.968	3.914	0.226

**Continued**

Salt	Original wt% salt	T (K)	P (MPa)	C <sub>3</sub> H <sub>8</sub> mol%	wt% salt in H <sub>2</sub> O	Hydrate phase fraction
NaCl	20.03	260.0	0.283	3.646	21.324	0.080
KCl	9.976	270.8	0.290	3.834	12.245	0.210
KCl	15.067	268.6	0.296	4.777	16.829	0.125
NaCl	4.820	271.15	0.324	2.940	5.589	0.154
CaCl <sub>2</sub>	3.710				4.301	
NaCl	5.109	270.2	0.296	3.107	5.863	0.148
KCl	5.109				5.863	

*Hydrate:* Propane + (mixed salts and two North Sea brines)

*References:* Tohidi et al. (1997b)

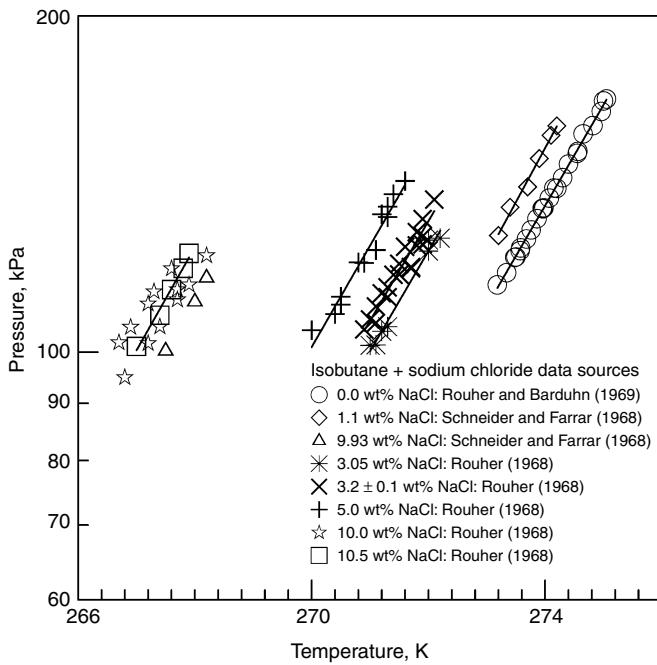
*Phases:* Lw–H–V

### Composition of North Sea Brine and Forties Formation Water

Salt	North Sea brine wt%	Forties formation H <sub>2</sub> O wt%
NaCl	2.354	6.993
CaCl <sub>2</sub>	0.116	0.735
MgCl <sub>2</sub>	0.524	0.186
KCl	0.086	0.066
Na <sub>2</sub> SO <sub>4</sub>	0.428	—
SrCl <sub>2</sub>	—	0.099
BaCl <sub>2</sub>	—	0.036

### Hydrate Dissociation Conditions with Salts

Salt (wt%)	T (K)	P (MPa)	Salt	T (K)	P (MPa)
5.0% NaCl + 5.0% KCl	270.4	0.234	North Sea brine	272.7	0.234
	270.9	0.269		273.7	0.269
	272.4	0.379		274.3	0.296
	272.8	0.441		274.8	0.324
				275.0	0.352
4.9% NaCl + 3.8% CaCl <sub>2</sub>	270.9	0.234	Forties formation H <sub>2</sub> O	275.9	0.427
	271.4	0.290		270.6	0.241
	272.2	0.331		271.2	0.269
	272.6	0.379		271.8	0.317
	273.5	0.441		272.9	0.393
				273.5	0.448



**FIGURE 6.48** Sodium chloride inhibition of simple isobutane hydrates.

### SIMPLE ISOBUTANE HYDRATES WITH INHIBITORS

*Hydrate:* Isobutane with sodium chloride

*Reference:* Schneider and Farrar (1968)

*Phases:* L<sub>W</sub>-H-V

NaCl (wt%)	T (K)	P (kPa)	NaCl (wt%)	T (K)	P (kPa)
1.10	273.2	127.2	1.08	274.2	159.5
1.10	273.4	134.8	9.93	268.2	116.6
1.10	273.7	140.6	9.93	268.0	111.0
1.09	273.9	149.1	9.93	267.5	100.3
1.10	274.1	156.4			

*Hydrate:* Isobutane with sodium chloride

*Reference:* Rouher (1968)

*Phases:* L<sub>W</sub>-H-V

NaCl (wt%)	T (K)	P (kPa)	NaCl (wt%)	T (K)	P (kPa)
5.00	270.5	110.3	3.05*	271.7	119.2
5.00	270.8	120.3	3.05*	271.8	124.6
5.00	271.1	123.5	3.05*	271.9	124.9
5.00	271.3	135.0	3.05*	271.9	127.0

**Continued**

<b>NaCl (wt%)</b>	<b>T (K)</b>	<b>P (kPa)</b>	<b>NaCl (wt%)</b>	<b>T (K)</b>	<b>P (kPa)</b>
5.00	270.0	104.6	3.32*	271.0	101.4
5.00	270.4	108.2	3.32*	271.2	104.4
5.00	270.5	112.1	3.32*	272.0	126.0
5.00	270.9	120.2	3.27*	271.1	101.5
5.00	271.1	123.4	3.21*	272.0	123.2
5.00	271.2	132.9	3.16*	271.3	105.4
5.00	271.3	132.1	3.16*	272.2	126.5
5.00	271.4	138.5	10.0	266.7	102.0
5.00	271.6	142.3	10.0	266.9	105.3
3.05*	270.9	104.8	10.0	267.2	110.5
3.05*	271.0	107.0	10.0	267.3	113.3
3.05*	271.1	109.9	10.0	267.6	118.8
3.05*	271.2	112.9	10.0	266.8	94.9
3.05*	271.3	114.3	10.0	267.2	101.8
3.05*	271.4	117.3	10.0	267.4	105.4
3.05*	271.5	120.0	10.0	267.7	113.8
3.05*	271.6	124.3	10.0	267.7	111.4
3.05*	271.8	128.1	10.0	267.9	114.9
3.05*	271.9	131.6	10.0	268.2	122.0
3.05*	272.1	137.0	10.55	267.0	101.2
3.05*	271.1	106.2	10.55	267.4	107.9
3.05*	271.3	112.0	10.5	267.6	113.8
3.05*	271.5	117.4	10.5	267.8	118.9
3.05*	271.7	118.9	10.5	267.9	122.6

\* = Sea water with 3.05 wt% NaCl equivalent activity.

**SIMPLE CARBON DIOXIDE HYDRATE WITH INHIBITORS**

*Hydrate:* Carbon dioxide with hydrogen chloride

*Reference:* Larson (1955)

*Phases:* L<sub>W</sub>–H–V

<b>HCl</b>	<b>T (K)</b>	<b>P (kPa)</b>	<b>HCl</b>	<b>T (K)</b>	<b>P (kPa)</b>
0.1 N	274.2	1379	0.5 N	281.0	3716
0.1 N	278.5	2351	0.5 N	282.0	4371Q <sub>2</sub>
0.1 N	282.2	3916	1.0 N	273.5	1565
0.1 N	283.1	4489Q <sub>2</sub>	1.0 N	276.6	2262
0.5 N	272.6	1310	1.0 N	278.5	2903
0.5 N	277.0	2172	1.0 N	281.2	4289Q <sub>2</sub>

Q<sub>2</sub> = Inhibited upper quadruple point (L<sub>W</sub>–H–V–L<sub>CO<sub>2</sub></sub>).

*Hydrate:* Carbon dioxide with sodium hydroxide

*Reference:* Larson (1955)

*Phases:* L<sub>W</sub>-H-V

NaOH	T (K)	P (kPa)	NaOH	T (K)	P (kPa)
0.1 N	273.5	1324	0.5 N	279.0	2868
0.1 N	276.3	1834	0.5 N	281.0	3827
0.1 N	279.1	2592	0.5 N	282.0	4378Q <sub>2</sub>
0.1 N	282.2	3923	1.0 N	273.9	1600
0.1 N	283.0	4482Q <sub>2</sub>	1.0 N	276.6	2220
0.5 N	273.3	1393	1.0 N	279.6	3358
0.5 N	276.3	2000	1.0 N	281.3	4296Q <sub>2</sub>

Q<sub>2</sub> = Inhibited upper quadruple point (L<sub>W</sub>-H-V-L<sub>CO<sub>2</sub></sub>)

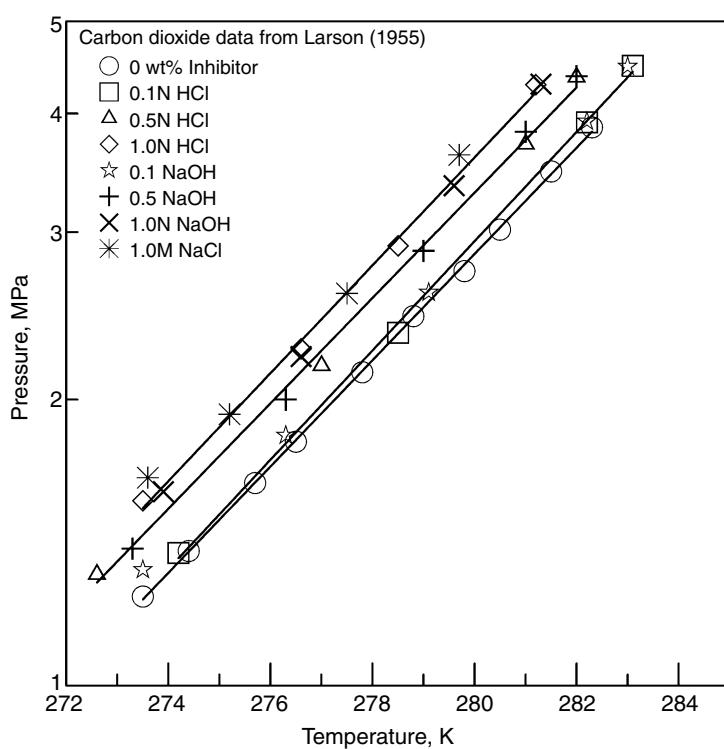


FIGURE 6.49 Acid, base, and salt inhibition of simple carbon dioxide hydrates.

*Hydrate:* Carbon dioxide with sodium chloride

*Reference:* Larson (1955)

*Phases:* L<sub>W</sub>-H-V

NaCl	T (K)	P (kPa)	NaCl	T (K)	P (kPa)
1.0 M	273.6	1655	1.0 M	277.5	2586
1.0 M	275.2	1931	1.0 M	279.7	3619

*Hydrate:* Carbon dioxide and sodium chloride

*Reference:* Vlahakis et al. (1972)

*Phases:* L<sub>W</sub>-H-V

wt% NaCl	T (K)	P (MPa)	wt% NaCl	T (K)	P (MPa)
5.42	276.1	2.297	5.949	278.2	3.072
5.28	277.2	2.596	5.632	278.7	3.222
5.30	279.2	3.371	5.568	279.2	3.438
4.865	279.6	3.468	10.17	271.6	1.735
5.37	280.0	2.877	10.33	272.6	2.024
5.27	275.9	2.158	10.30	273.2	2.095
5.72	276.4	2.333	10.31	274.2	2.384
5.76	277.0	2.534	10.50	274.7	2.651
5.80	277.5	2.795	10.30	275.2	2.786
5.545	277.9	2.886	10.46	275.7	3.040
5.445	278.6	3.231	10.26	276.2	3.185
5.45	279.3	3.530	10.37	276.7	3.434
5.53	279.7	3.727	10.27	277.2	3.619
4.79	271.6	1.319	10.21	277.4	3.767
5.215	272.1	1.398	10.59	268.2	1.189
5.375	272.6	1.502	10.55	269.1	1.339
5.26	273.1	1.589	10.38	270.1	1.488
5.385	273.6	1.709	10.22	271.1	1.648
4.665	274.1	1.737	10.25	272.2	1.919
5.715	274.6	1.927	10.22	273.7	2.261
4.81	275.3	2.018	10.20	274.5	2.488
5.875	280.4	4.227	10.32	275.3	2.892
5.871	273.2	1.653	10.30	275.4	2.878
5.917	274.2	1.865	10.19	276.3	3.233
5.834	275.1	2.056	10.29	276.5	3.333
5.764	276.2	2.355	10.16	276.9	3.454
6.132	276.6	2.555	10.41	277.0	3.567
5.733	277.2	2.675	10.20	277.2	3.681
5.860	277.7	2.899			

*Hydrate:* Carbon dioxide with methanol

*Reference:* Ng and Robinson (1985)

*Phases:* L<sub>W</sub>-H-V, L<sub>W</sub>-H-L<sub>CO<sub>2</sub></sub>

### L<sub>W</sub>-H-V

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
10.00	269.5	1.59	20.02	264.5	1.83
10.00	269.6	1.58	20.02	265.2	1.98
10.00	271.3	2.06	20.02	266.4	2.21
10.00	273.8	2.89	20.02	267.2	2.53
10.00	273.8	2.85	20.02	268.1	2.74
10.00	274.9	3.48	20.02	268.9	2.94
20.02	264.0	1.59			

### L<sub>W</sub>-H-L<sub>CO<sub>2</sub></sub>

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
10.00	276.0	4.60	20.02	270.1	7.68
10.00	276.8	7.23	20.02	270.5	11.27
10.00	277.4	10.09	20.02	270.7	11.40
10.00	278.1	13.98	20.02	271.6	15.89
20.02	269.1	3.34	20.02	271.8	16.09
20.02	269.6	5.50			

*Hydrate:* Carbon dioxide with methanol

*Reference:* Robinson and Ng (1986)

*Phases:* L<sub>W</sub>-H-V, L<sub>W</sub>-H-L<sub>CO<sub>2</sub></sub>

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
<b>L<sub>W</sub>-V-H</b>					
35	242.0	0.379	50	232.6	0.496
35	247.6	0.724	50	235.5	0.676
35	250.1	1.030	50	241.3	1.310
35	252.4	1.390			
35	255.1	1.770			
<b>L<sub>W</sub>-H-L<sub>CO<sub>2</sub></sub></b>					
35	256.9	2.18	50	241.1	8.83
35	257.5	2.87	50	241.8	12.36
35	257.8	5.91	50	241.3	14.62
35	257.9	6.87	50	241.1	19.53
35	258.0	13.34			
35	258.5	20.70			

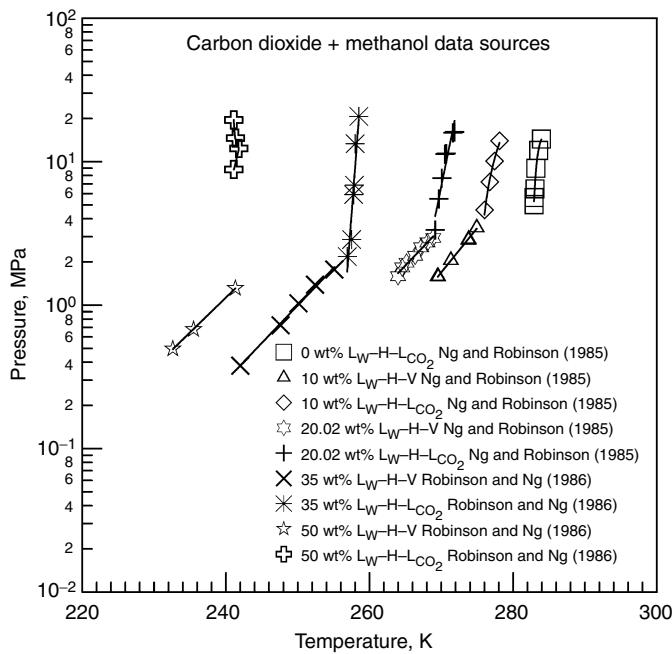


FIGURE 6.50 Methanol inhibition of simple carbon dioxide hydrates.

Hydrate: Carbon dioxide + seawater

Reference: Ohgaki et al. (1993)

Phases:  $L_W-H-V$ ,  $H-L_W-L_{CO_2}$ ,  $L_W-L_{CO_2}-V$  (no hydrate)

$T$ (K)	$P$ (MPa)	$T$ (K)	$P$ (MPa)
<b>H-L<sub>W</sub>-V</b>			
<i>T-cycle method, formation</i>			
273.87	1.710	278.79	3.165
273.95	1.711	279.67	3.537
275.57	2.095	279.74	3.549
275.66	2.103	280.08	3.970
277.43	2.652	280.36	3.980
277.48	2.654		
<i>T-cycle method, dissociation</i>			
274.75	1.730	280.42	3.561
276.57	2.121	281.28	4.014
278.34	2.677	281.46	4.020
279.68	3.182		

(Continued)

**Continued**

<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)
<i>T</i> -cycle method, stationary point			
273.78	1.59	279.73	3.426
275.56	1.945	280.03	3.625
277.47	2.532	280.36	3.743
278.70	2.986		
<b>H-Lw-L<sub>CO<sub>2</sub></sub></b>			
<i>T</i> -cycle method, formation			
280.57	4.891		
<i>T</i> -cycle method, dissociation			
282.01	5.436		
<b>H-L<sub>CO<sub>2</sub></sub>-V</b>			
<i>First freezing point method</i>			
279.62	4.1494		
<b>Lw-L<sub>CO<sub>2</sub></sub>-V</b>			
<i>First freezing point method</i>			
281.59	4.361		
282.56	4.464		
283.52	4.573		
284.15	4.681		

For T-cycle methods, refer to the description given in [Section 6.3.1.1](#). Ohgaki et al. (1993).

*Hydrate:* Carbon dioxide and single and mixed electrolytes

*Reference:* Dholabhai et al. (1993c)

*Phases:* L<sub>w</sub>-H-V

**Composition of Aqueous Solutions**

Solution ID	wt% NaCl	wt% KCl	wt% CaCl <sub>2</sub>	Solution ID	wt% NaCl	wt% KCl	wt% CaCl <sub>2</sub>
Na3-1	3.00	0	0	Na5-1	5.00	0	0
Na3-2	3.02	0	0	Na5-2	5.00	0	0
Na3-3	3.02	0	0				
Na10-1	10.02	0	0	Na15	15.00	0	0
Na10-2	10.0	0	0				
Na20	20.03	0	0	K3	0	3.00	0
K5	0	5.01	0	K10	0	10.02	0
K15	0	14.97	0	Ca3	0	0	3.03
Ca5	0	0	5.02	Ca10	0	0	9.99
Ca15	0	0	14.97	Ca20	0	0	19.96
Na3K3	3.01	3.02	0	Na5K5	5.00	5.01	0
Na7K10	6.99	10.00	0	Na15K5	15.01	5.03	0
Na15K5	15.01	5.03	0	Na3Ca3	3.03	0	3.03
Na2Ca8	2.02	0	8.00	Na8Ca2	8.01	0	2.03
Na5Ca15	5.02	0	14.7	Na15Ca5	15.01	0	5.03

**Continued**

<b>Solution</b>		<b>P</b>	<b>Solution</b>		<b>P</b>	<b>Solution</b>		<b>P</b>
<b>ID</b>	<b>T (K)</b>	(MPa)	<b>ID</b>	<b>T (K)</b>	(MPa)	<b>ID</b>	<b>T (K)</b>	(MPa)
Pure H <sub>2</sub> O	273.8	1.340	Na3-1	279.0	2.955	Na3-2	273.2	1.434
	275.5	1.640		277.0	2.309	Na3-3	280.9	3.907
	277.1	1.985		275.2	1.837			
	279.0	2.52		272.2	1.304			
Na5-1	278.0	3.004	Na10-1	277.2	3.781	Na15	273.0	3.239
	275.0	2.016		277.0	3.671		271.0	2.469
	273.0	1.597	Na10-2	276.1	3.155		268.2	1.703
	271.2	1.306		276.1	3.149		265.4	1.212
Na5-2	278.0	3.766		274.1	2.409			
				271.0	1.656			
				268.0	1.162			
			K3	281.1	3.834	K5	280.5	3.905
Na20	266.8	2.63		280.0	3.233		280.4	3.861
	265.3	2.208		278.7	2.760		279.4	3.324
	263.3	1.606		276.8	2.154		278.6	2.960
				274.6	1.654		276.0	2.129
K10	277.9	3.485	K15	269.0	1.415	Ca3	275.5	1.827
	276.3	2.807		272.2	2.095		272.6	1.302
	273.1	1.848		274.6	2.901		278.2	2.529
	269.0	1.130		276.0	3.575		280.9	3.702
Ca5	278.2	2.805	Ca10	270.8	1.511	Ca15	273.2	3.221
	280.1	3.657		268.0	1.102		270.1	2.138
	275.1	1.872		274.0	2.198		267.4	1.497
	271.1	1.184		277.3	3.460		263.4	0.960
Ca20	266.6	2.690	Na3K3	279.9	3.976	Na5K5	270.0	1.347
	264.6	2.052		279.3	3.573		271.7	1.660
	262.0	1.504		276.1	2.317		274.1	2.258
	259.2	1.051		274.0	1.814		277.3	3.432
Na7K10				271.5	1.326			
	267.6	1.482	Na15K5	262.9	1.218	Na3Ca3	279.2	3.595
	270.5	2.180		266.3	1.872		277.3	2.738
	273.1	3.044		268.2	2.388		275.7	2.227
Na8Ca2	274.1	3.455		269.8	3.050		271.8	1.375
							271.0	1.258
	267.8	1.086	Na2Ca8	277.5	3.697	Na5Ca15	267.3	2.935
	271.1	1.623		276.3	3.101		266.3	2.490
Na15Ca5	273.2	2.112		272.7	1.909		264.1	1.878
	276.0	3.089		267.8	1.053		261.1	1.288
							259.2	1.042
	267.4	2.665	SEA	274.6	1.688			
	265.7	2.112		275.9	2.001			
	263.5	1.609		277.9	2.556			
	259.0	0.909		281.1	4.072			
				272.1	1.288			

*Hydrate:* Carbon dioxide with 25 wt% glycerol

*Reference:* Ng and Robinson (1994)

*Phases:* L<sub>w</sub>-H-V and L<sub>w</sub>-H-L<sub>CO<sub>2</sub></sub>

Phases	T (K)	P (MPa)	Phases	T (K)	P (MPa)
L <sub>w</sub> -H-V	269.6	1.48	L <sub>w</sub> -H-L <sub>CO<sub>2</sub></sub>	277.2	8.47
L <sub>w</sub> -H-V	274.4	2.83		278.8	20.67
L <sub>w</sub> -H-V	276.8	3.96			

*Hydrate:* Carbon dioxide with glycerol

*Reference:* Breland and Englezos (1996)

*Phases:* L<sub>w</sub>-H-V

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
10	272.3	1.391	20	270.4	1.502	30	270.1	2.030
10	274.6	1.786	20	270.6	1.556	30	270.6	2.096
10	276.1	2.191	20	272.3	1.776	30	271.4	2.340
10	277.7	2.640	20	273.6	2.096	30	272.3	2.651
10	278.4	2.942	20	274.1	2.281	30	273.2	2.981
10	279.3	3.345	20	275.5	2.721			
			20	276.2	3.001			
			20	277.1	3.556			

*Hydrate:* Carbon dioxide + sodium chloride or potassium chloride

*References:* Tohidi et al. (1997b)

*Phases:* L<sub>w</sub>-H-V

wt%	T (K)	P (MPa)
10% NaCl	273.2	2.151
	276.0	3.151
	271.9	1.862
	276.1	3.227
20% NaCl	263.2	1.517
	266.5	2.248
	267.2	2.489
	268.8	3.116
10% KCl	273.5	1.937
	275.2	2.517
	276.9	3.047
	278.4	3.613

*Hydrate:* Carbon dioxide with methanol and monoethylene glycol

*Reference:* Fan et al. (2000)

*Phases:* L<sub>W</sub>-H-V

wt% inhibitor	T (K)	P (MPa)	wt% inhibitor	T (K)	P (MPa)
10% MeOH	271.6	1.74	10% MEG	270.9	1.15
	273.8	2.35		273.1	1.74
				275.8	2.40
				278.3	3.20

### SIMPLE HYDROGEN SULFIDE HYDRATES WITH INHIBITORS

*Hydrate:* Hydrogen sulfide with methanol

*Reference:* Bond and Russell (1949)

*Phases:* L<sub>W</sub>-H-V

wt%	T (K)	P (kPa)	wt%	T (K)	P (kPa)
16.5	273.2	275.80	16.5	290.1	1496.20
16.5	283.2	730.86			

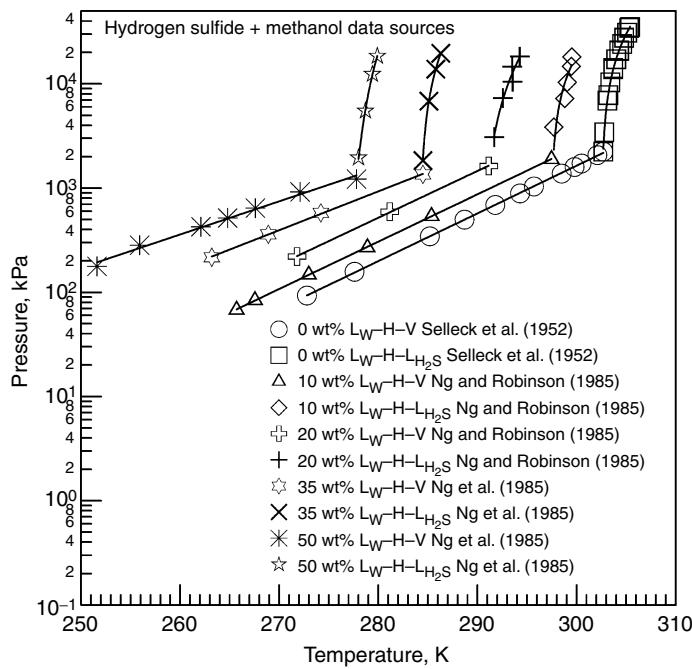
*Hydrate:* Hydrogen sulfide with methanol

*Reference:* Ng and Robinson (1985)

*Phases:* L<sub>W</sub>-H-V, L<sub>W</sub>-H-V-L<sub>H<sub>2</sub>S</sub>, L<sub>W</sub>-H-L<sub>H<sub>2</sub>S</sub>

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
<b>L<sub>W</sub>-H-V</b>					
10.0	265.7	0.068	10.0	285.4	0.541
10.0	267.5	0.084	10.0	291.8	1.080
10.0	273.0	0.148	20.0	271.8	0.221
10.0	278.9	0.270	20.0	281.2	0.593
<b>L<sub>W</sub>-H-L<sub>H<sub>2</sub>S</sub></b>					
10.0	297.5	1.90*	20.0	291.1	1.63*
10.0	297.7	3.85	20.0	291.7	3.09
10.0	298.8	7.23	20.0	292.6	7.29
10.0	299.1	10.35	20.0	293.6	10.46
10.0	299.5	14.71	20.0	293.5	14.57
10.0	299.5	18.16	20.0	294.2	18.26

\* = L<sub>W</sub>-H-V-L<sub>H<sub>2</sub>S</sub>.



**FIGURE 6.51** Methanol inhibition of simple hydrogen sulfide hydrates.

*Hydrate:* Hydrogen sulfide with methanol

*Reference:* Ng et al. (1985b)

*Phases:*  $L_w$ -H-V,  $L_w$ -H-V- $L_{H_2S}$ ,  $L_w$ -H- $L_{H_2S}$

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
$L_w$ -V-H					
35	263.2	0.217	50	255.9	0.283
35	268.9	0.361	50	262.1	0.426
35	274.2	0.579	50	264.8	0.517
35	284.5	1.351	50	267.6	0.642
50	251.6	0.177	50	272.1	0.920
50	277.8	1.220*			
$L_w$ -H- $L_{H_2S}$					
35	284.5	1.834	50	278.0	1.951
35	285.1	6.812	50	278.7	5.516
35	285.8	13.84	50	279.4	12.36
35	286.3	19.65	50	279.9	18.48

\* =  $L_w$ -H-V- $L_{H_2S}$ .

*Hydrate:* Hydrogen sulfide with sodium chloride

*Reference:* Bond and Russell (1949)

*Phases:* L<sub>w</sub>-H-V

wt%	T (K)	P (kPa)	wt%	T (K)	P (kPa)
10.0	274.8	206.8	26.4	276.2	668.8
10.0	287.1	648.1	26.4	278.2	1020.4
10.0	294.8	1875.0	26.4	280.2	1303.1
26.4	269.2	420.6	26.4	280.2	1447.9

*Hydrate:* Hydrogen sulfide with calcium chloride

*Reference:* Bond and Russell (1949)

*Phases:* L<sub>w</sub>-H-V

wt%	T (K)	P (kPa)	wt%	T (K)	P (kPa)
10.0	274.8	172.4	21.1	277.2	655.0
10.0	288.4	724.0	21.1	281.2	917.0
10.0	295.4	1896.0	21.1	284.2	1489.0
21.1	271.7	365.4	21.1	284.3	1565.0
			36.0	265.4	882.55

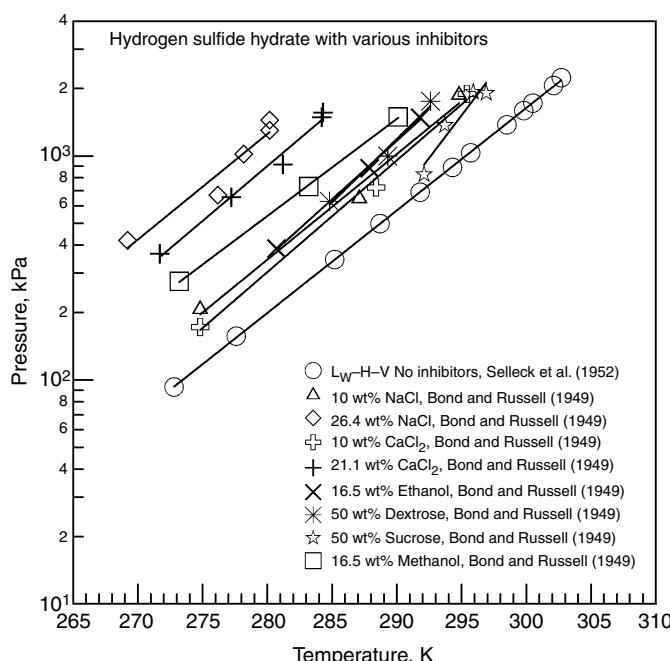


FIGURE 6.52 Simple hydrogen sulfide hydrates with various inhibitors.

*Hydrate:* Hydrogen sulfide with ethanol

*Reference:* Bond and Russell (1949)

*Phases:* L<sub>W</sub>–H–V

wt%	T (K)	P (kPa)	wt%	T (K)	P (kPa)
16.5	280.7	386.12	16.5	291.8	1482.4
16.5	287.9	882.55			

*Hydrate:* Hydrogen sulfide with dextrose

*Reference:* Bond and Russell (1949)

*Phases:* L<sub>W</sub>–H–V

wt%	T (K)	P (kPa)	wt%	T (K)	P (kPa)
50.0	284.8	627.4	50.0	292.6	1758.2
50.0	289.3	999.8			

*Hydrate:* Hydrogen sulfide with sucrose

*Reference:* Bond and Russell (1949)

*Phases:* L<sub>W</sub>–H–V

wt%	T (K)	P (kPa)	wt%	T (K)	P (kPa)
50.0	292.1	827.4	50.0	295.9	1930.6
50.0	293.7	1372.1	50.0	295.9	1909.9

## BINARY MIXTURES OF METHANE + ETHANE WITH INHIBITORS

*Hydrate:* 89.51 mol% methane and 10.49% ethane with methanol

*Reference:* Ng and Robinson (1983)

*Phases:* L<sub>W</sub>–H–V

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
10.02	268.7	1.40	20.01	263.9	1.49
10.02	270.9	1.78	20.01	267.0	2.11
10.02	273.6	2.32	20.01	272.3	3.76
10.02	277.1	3.28	20.01	275.2	5.49
10.02	280.4	4.78	20.01	278.1	8.34
10.02	284.9	8.42	20.01	281.3	13.22
10.02	287.5	13.21	20.01	283.61	19.1
10.02	289.4	18.89			

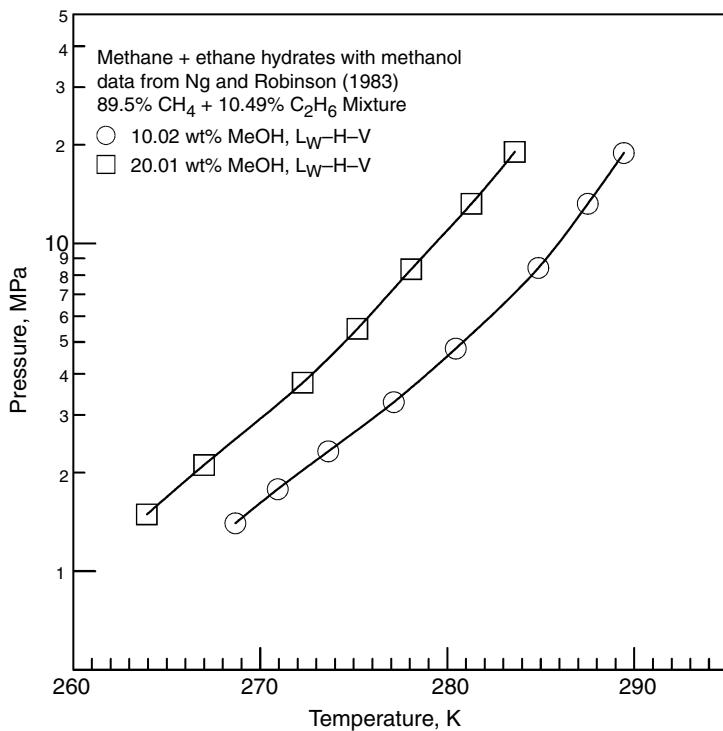


FIGURE 6.53 Methanol inhibition of methane + ethane hydrates.

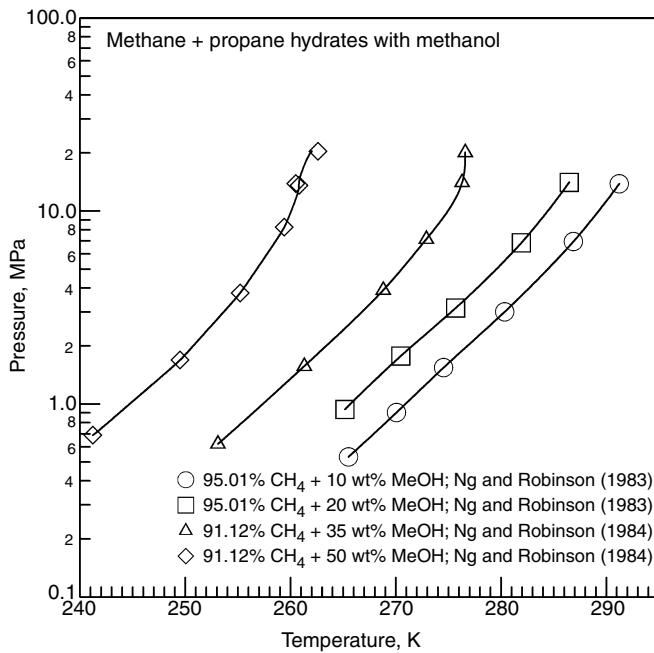
### BINARY MIXTURES OF METHANE + PROPANE WITH INHIBITORS

Hydrate: 95.01 mol% methane and 4.99% propane with methanol

Reference: Ng and Robinson (1983)

Phases: L<sub>W</sub>-H-V

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
10.0	265.5	0.532	20.0	265.2	0.938
10.0	270.1	0.903	20.0	270.5	1.772
10.0	274.5	1.544	20.0	275.7	3.144
10.0	280.4	3.006	20.0	281.9	6.846
10.0	286.9	6.950	20.0	286.5	14.100
10.0	291.2	13.831			



**FIGURE 6.54** Methanol inhibition of methane + propane hydrates.

*Hydrate:* 91.12 mol% methane and 8.88% propane with methanol

*Reference:* Ng and Robinson (1984)

*Phases:* L<sub>W</sub>-H-V

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
35	253.1	0.621	50	249.5	1.690
35	261.3	1.570	50	255.2	3.760
35	268.8	3.890	50	259.4	8.240
35	272.9	7.150	50	260.8	13.580
35	276.3	14.070	50	260.5	13.860
35	276.6	20.110	50	262.6	20.420
50	241.2	0.689			

*Hydrate:* 88.13 mol% methane + 11.87% propane with methanol and ethylene glycol

*Reference:* Song and Kobayashi (1989)

*Phases:* L<sub>W</sub>-H-V

Inhibitor (wt%)	T (K)	P (MPa)	T (K)	P (MPa)
Methanol (7.0 wt%)	278.5	0.824	295.3	10.717
	286.8	2.735	295.4	10.742
	288.9	3.677	297.6	17.979
	292.4	6.314		

**Continued**

<b>Inhibitor (wt%)</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
Methanol (15.0 wt%)	276.9	1.365	289.1	12.664
	281.9	3.732	289.8	17.834
	288.6	12.640		
Methanol (35.0 wt%)	281.3	0.980	280.2	11.198
	274.2	2.345	280.5	13.831
	277.0	5.561		
Ethylene glycol (5.0 wt%)	282.2	1.230	296.6	10.260
	288.8	3.168	298.2	15.640
	293.8	6.246		
Ethylene glycol (25.0 wt%)	279.6	1.944	289.6	8.092
	285.2	3.725	291.4	13.331
	288.6	5.420		
Ethylene glycol (40.0 wt%)	276.2	1.051	283.2	8.106
	283.5	5.294	283.6	10.941
	283.2	7.212	284.1	13.305
	282.8	8.099		
Ethylene glycol (50.0 wt%)	273.2	2.359	279.8	9.069
	277.2	3.966	280.8	14.883
	279.2	7.379	280.8	17.441

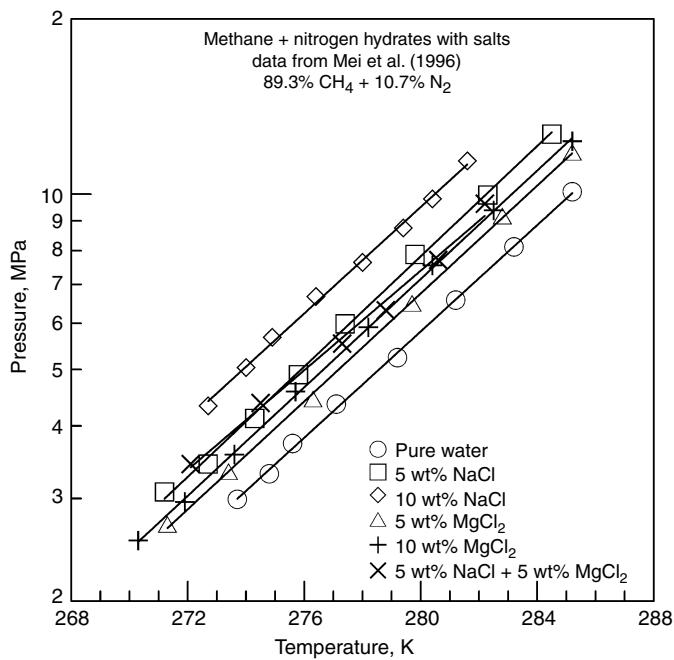
**BINARY MIXTURES OF METHANE + NITROGEN WITH INHIBITORS***Hydrate:* Methane + Nitrogen + (single and mixed salts)*References:* Mei et al. (1996a)*Phases:* L<sub>W</sub>-H-V**Vapor Phase is 89.26% CH<sub>4</sub> + 10.74% N<sub>2</sub>**

<b>Salt (wt%)</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>Salt (wt%)</b>	<b>T (K)</b>	<b>P (MPa)</b>
Pure water	273.7	2.99	NaHCO <sub>3</sub> (5%)	271.0	2.45
	274.8	3.31		273.2	3.16
	275.6	3.73		275.5	4.15
	277.1	4.36		278.0	5.34
	279.2	5.24		279.8	6.83
	281.2	6.58		282.3	8.62
	283.2	8.12		283.7	10.31
	285.3	10.10		285.4	12.57
NaCl (5%)	271.2	3.08	MgCl <sub>2</sub> (5%)	271.3	2.71
	272.7	3.44		273.4	3.34
	274.3	4.12		276.3	4.45
	275.8	4.90		279.7	6.50
	277.4	5.99		282.8	9.18
	279.8	7.88		285.2	11.82
	282.3	9.97			
	284.5	12.68			

(Continued)

## Continued

<b>Salt (wt%)</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>Salt (wt%)</b>	<b>T (K)</b>	<b>P (MPa)</b>
NaCl (10%)	272.7	4.33	MgCl <sub>2</sub> (10%)	270.3	2.54
	274.0	5.04		271.9	2.96
	274.9	5.68		273.6	3.57
	276.4	6.67		275.7	4.58
	278.0	7.64		278.2	5.91
	279.4	8.75		280.4	7.55
	280.4	9.82		282.5	9.38
NaHCO <sub>3</sub> (3%)	281.6	11.41		285.2	12.33
	269.8	2.05	CaCl <sub>2</sub> (10%) + NaCl (10%)	269.9	3.72
	272.1	2.62		271.6	4.40
	273.2	3.00		273.0	5.14
	275.8	3.98		273.9	5.71
	278.1	5.02		276.0	7.09
	280.4	6.48		277.9	8.92
NaCl (5%) + MgCl <sub>2</sub> (5%)	283.0	8.54		279.8	11.16
	285.8	11.31	NaCl (5%) + MgCl <sub>2</sub> (5%) + CaCl <sub>2</sub> (5%)	270.2	2.41
	272.1	3.44		272.2	3.05
	274.5	4.38		273.5	3.82
	277.3	5.54		275.1	4.88
	278.8	6.32		276.9	6.30
	280.6	7.71		278.1	7.36
NaCl (5%) + NaHCO <sub>3</sub> (3%)	282.8	9.63		279.3	8.75
	285.2	12.26		280.4	10.09
	268.1	2.40	NaCl (5%) + KCl (5%) + CaCl <sub>2</sub> (3%) + MgCl <sub>2</sub> (3%)	269.2	2.53
	271.1	3.24		270.6	2.53
	273.1	3.89		272.1	3.72
	275.3	4.92		273.5	4.48
	277.9	6.32		275.0	5.62
CaCl <sub>2</sub> (10%) + MgCl <sub>2</sub> (5%)	279.2	7.23		276.5	6.95
	281.1	8.76		278.0	8.56
	283.2	10.79		279.4	10.49
	269.6	3.16			
	271.6	3.91			
	273.9	5.01			
	275.4	5.82			
	277.0	6.97			
	278.7	8.10			
	280.2	9.61			
	281.8	11.34			



**FIGURE 6.55** Inhibition of methane + nitrogen hydrates with sodium chloride and magnesium chloride.

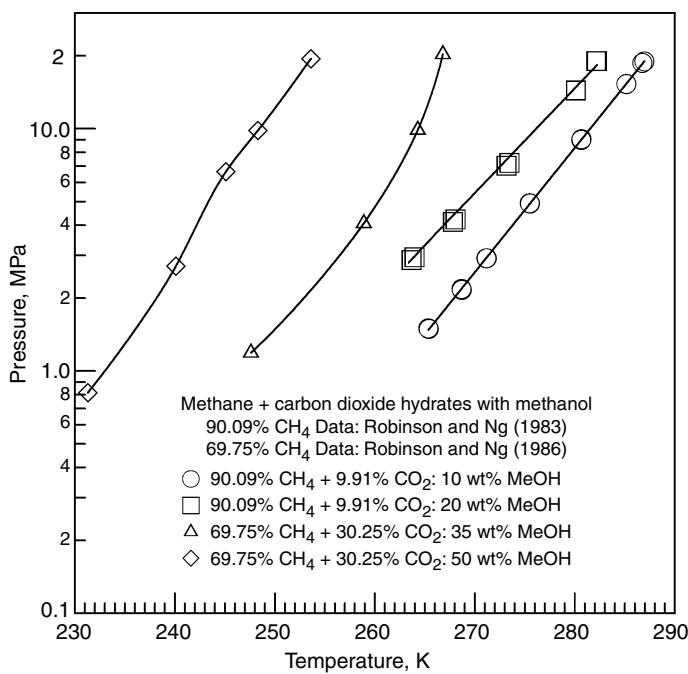
### BINARY MIXTURES OF METHANE + CARBON DIOXIDE WITH INHIBITORS

*Hydrate:* 90.09 mol% methane and 9.91% carbon dioxide with methanol

*Reference:* Ng and Robinson (1983)

*Phases:* Lw–H–V

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
10.0	265.4	1.49	10.0	287.0	18.95
10.0	265.4	1.50	20.0	263.4	2.76
10.0	268.7	2.16	20.0	263.6	2.81
10.0	268.7	2.18	20.0	267.0	4.12
10.0	271.2	2.92	20.0	267.1	4.21
10.0	271.2	2.92	20.0	267.1	4.27
10.0	275.5	4.91	20.0	272.9	6.98
10.0	275.5	4.93	20.0	273.2	7.03
10.0	280.6	8.98	20.0	280.1	14.36
10.0	280.7	9.05	20.0	280.1	14.40
10.0	285.2	15.28	20.0	282.2	19.00
10.0	285.2	15.29	20.0	282.1	19.01
10.0	286.8	18.66			



**FIGURE 6.56** Methanol inhibition of methane + carbon dioxide hydrates.

*Hydrate:* 69.75 mol% methane and 30.25% carbon dioxide with methanol

*Reference:* Robinson and Ng (1986)

*Phases:* L<sub>W</sub>-H-V

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
35	247.6	1.190	50	240.1	2.710
35	258.9	4.070	50	245.1	6.640
35	264.3	9.890	50	248.3	9.830
35	266.8	20.270	50	253.6	19.430
50	231.3	0.814			

*Hydrate:* Methane + carbon dioxide and single and mixed electrolytes

*Reference:* Dholabhai and Bishnoi (1994)

*Phases:* L<sub>W</sub>-H-V

### Composition of Aqueous Solutions

Solution ID	wt% NaCl	wt% KCl	wt% CaCl <sub>2</sub>	Molality
Na5	5.02	0	0	0.9044
Na10	9.99	0	0	1.8992
Na15	15.00	0	0	3.0197

**Continued**

<b>Solution ID</b>	<b>wt% NaCl</b>	<b>wt% KCl</b>	<b>wt% CaCl<sub>2</sub></b>	<b>Molality</b>
Na20-1	20.00	0	0	4.2779
Na20-2	20.01	0	0	4.2806
K5	0	5.00	0	0.7060
K10	0	10.00	0	1.4904
K15	0	15.01	0	2.3690
Ca10	0	0	9.91	2.9733
Ca15	0	0	15.00	4.7699
Ca20	0	0	20.00	6.7574
Na5K10	5.00	10.00	0	2.5847
Na10K5	10.00	5.00	0	2.8022
K10Ca5	0	10.00	5.00	3.1681
Na5Ca10	5.01	0	10.00	4.1890
Na10Ca10	10.0	0	10.00	5.5176
Na10Ca10	10.17	0	5.08	3.6736
Na6K5Ca4-1	6.01	5.00	3.99	3.2677
Na6K5Ca4-2	6.00	5.00	4.00	3.2689

**Hydrate Formation Conditions (Initial Gas Composition = 80 mol% CH<sub>4</sub> + 20% CO<sub>2</sub>)**

<b>Solution</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>%CO<sub>2</sub></b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>%CO<sub>2</sub></b>
H <sub>2</sub> O	277.6	3.41	15.3	274.1	2.36	16.4
	281.5	5.14	16.7	284.8	7.53	17.9
Na5	282.0	6.98	17.7	275.0	3.26	16.1
	279.2	5.08	17.2	271.6	2.30	15.2
Na10	279.0	6.56	17.4	276.1	4.66	19.4
	272.1	3.10	16.1	268.5	2.03	19.3
Na15	277.2	7.31	18.9	273.1	4.40	19.8
	269.1	2.88	19.4	264.8	1.86	17.3
Na20-1	270.4	5.42	19.3	267.5	3.85	19.8
	262.0	2.12	19.1			
Na20-2	274.3	9.15	19.9			
K5	271.4	2.04	19.7	275.0	2.96	19.8
	278.8	4.46	19.8	282.0	6.43	19.8
K10	275.9	3.94	19.6	272.2	2.59	19.8
	269.2	1.83	19.7	279.0	5.56	19.8
K15	267.0	1.89	18.4	272.7	3.45	19.5
	270.1	2.62	19.0	277.1	5.63	19.7

(Continued)

**Continued**

<b>Solution</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>%CO<sub>2</sub></b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>%CO<sub>2</sub></b>
Ca10	268.6	1.96	18.7	272.0	2.80	19.4
	276.0	4.32	19.7	279.1	6.08	19.7
Ca15	273.1	4.61	19.0	266.6	1.88	19.6
	269.1	3.00	19.7	276.9	7.09	19.7
Ca20	263.8	2.89	19.8	267.6	4.30	19.8
	271.3	7.24	19.9	273.7	9.46	19.9
Na5Ca10	273.7	5.04	19.4	265.5	2.06	19.7
	269.4	3.12	19.8	276.7	7.14	19.9
K10Ca5	265.1	1.65	19.8	269.4	2.46	19.8
	274.8	4.60	19.9	281.6	10.61	19.9
Na5K10	269.3	2.59	19.2	275.2	4.99	19.7
	281.3	10.41	19.8	265.1	1.66	20.3
Na10Ca5	275.1	6.07	19.5	269.2	3.10	20.0
	265.5	2.11	20.1	278.7	9.71	19.4
Na6K5Ca4-1	275.1	5.23	19.9	269.0	2.67	19.9
	278.2	7.65	19.7	265.5	1.85	20.3

**Hydrate Formation Conditions (Initial Gas Composition =  
50 mol% CH<sub>4</sub> + 50% CO<sub>2</sub>)**

<b>Solution ID</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>% CO<sub>2</sub></b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>% CO<sub>2</sub></b>
Na10Ca10	268.1	3.53	48.6	270.8	5.16	49.4
	264.1	2.15	49.7	268.2	3.52	49.7
Na10K5	275.5	4.59	46.5	268.0	1.82	49.8
	271.6	2.78	49.5	265.8	1.38	50.0
Na6K5Ca4-2	275.5	4.46	47.5	266.0	1.45	48.1
	271.9	2.80	50.0	268.1	1.81	49.6

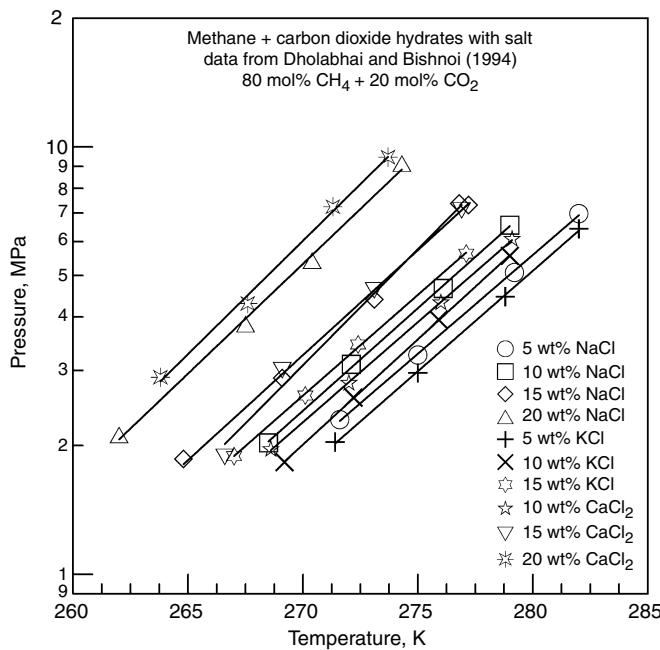
*Hydrate:* Methane + carbon dioxide with 9.45 wt% sodium chloride

*Reference:* Fan and Guo (1999)

*Phases:* L<sub>W</sub>-H-V

**5.02% CH<sub>4</sub>**

<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
267.9	1.24	274.1	2.43
271.0	1.76	275.1	2.85
273.3	2.22	277.4	3.75
273.5	2.35		



**FIGURE 6.57** Inhibition of methane + carbon dioxide hydrates with salts.

*Hydrate:* Methane + carbon dioxide with 10 wt% monoethylene glycol

*Reference:* Fan et al. (2000)

*Phases:* L<sub>w</sub>-H-V

### 3.48 mol% CH<sub>4</sub>

T (K)	P (MPa)	T (K)	P (MPa)
268.7	1.14	274.2	2.26
271.3	1.60	278.0	3.22

## BINARY MIXTURES OF METHANE + HYDROGEN SULFIDE WITH INHIBITORS

*Hydrate:* Methane and hydrogen sulfide with 20 wt% methanol

*Reference:* Ng et al. (1985a)

*Phases:* L<sub>w</sub>-H-V

CH <sub>4</sub>	H <sub>2</sub> S	T (K)	P (MPa)	CH <sub>4</sub>	H <sub>2</sub> S	T (K)	P (MPa)
0.896	0.104	264.5	0.945	0.780	0.220	287.0	11.670
0.897	0.103	271.8	2.130	0.741	0.259	290.3	18.710
0.837	0.163	281.4	5.750				

## BINARY MIXTURES OF ETHANE + CARBON DIOXIDE WITH INHIBITORS

*Hydrate:* 75% ethane and 25 mol% carbon dioxide with methanol

*Reference:* Ng et al. (1985b)

*Phases:* L<sub>W</sub>-H-V, L<sub>W</sub>-H-V-L<sub>MIX</sub>, L<sub>W</sub>-H-L<sub>MIX</sub>

### L<sub>W</sub>-H-V

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
20	266.4	0.738	35	266.8	2.110
20	271.1	1.400	50	237.0	0.319
20	275.3	2.689	50	242.1	0.494
35	251.4	0.422	50	248.4	0.862
35	256.9	0.724	50	251.5	1.172
35	260.2	0.993	50	254.3	1.593
35	263.9	1.586	50	255.3	1.800

### L<sub>W</sub>-H-V-L<sub>MIX</sub>

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
20	276.9	3.523	50	255.5	1.855
35	267.8	2.627	50	255.8	2.096
35	268.1	2.806			

### L<sub>W</sub>-H-L<sub>MIX</sub>

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
20	277.1	4.254	35	270.4	13.960
20	278.3	9.080	35	271.6	20.170
20	279.3	14.470	50	256.5	3.999
20	280.5	20.770	50	257.9	8.267
35	268.6	4.192	50	259.4	15.010
35	269.2	6.998	50	260.6	20.420

*Hydrate:* Ethane + carbon dioxide with 10 wt% sodium chloride

*Reference:* Fan and Guo (1999)

*Phases:* L<sub>W</sub>-H-V

### 5.31 mol% C<sub>2</sub>H<sub>6</sub>

T (K)	P (MPa)	T (K)	P (MPa)
269.1	1.17	272.9	1.88
270.9	1.50	274.2	2.30

*Hydrate:* Ethane + carbon dioxide with 10.6 wt% monoethylene glycol

*Reference:* Fan et al. (2000)

*Phases:* L<sub>w</sub>-H-V

### 5.31 mol% C<sub>2</sub>H<sub>6</sub>

T (K)	P (MPa)	T (K)	P (MPa)
269.1	0.85	274.9	1.82
271.0	1.03	276.4	2.31
272.9	1.31		

## BINARY MIXTURES OF PROPANE + *n*-BUTANE WITH INHIBITORS

*Hydrate:* Propane + *n*-butane with sodium chloride

*Reference:* Paranjpe et al. (1987)

*Phases:* L<sub>w</sub>-H-V and L<sub>w</sub>-H-V-L<sub>HC</sub>

### L<sub>w</sub>-H-V

wt% NaCl	mol% C <sub>3</sub> H <sub>8</sub>	T (K)	P (MPa)	wt% NaCl	mol% C <sub>3</sub> H <sub>8</sub>	T (K)	P (MPa)
3.0	0.999	275.2	350.3	5.0	0.984	273.2	299.2
3.0	0.955	275.2	373.7	5.0	0.952	273.2	307.3
3.0	0.906	275.2	391.6	5.0	0.927	273.2	317.2
3.0	0.997	273.2	224.8	5.0	0.894	273.2	330.9
3.0	0.921	273.2	246.8	5.0	0.906	273.2	336.5
3.0	0.854	273.2	273.7	5.0	0.981	272.2	242.7
3.0	1.000	272.2	197.2	5.0	0.930	272.2	255.1
3.0	0.964	272.2	209.6	5.0	0.905	272.2	262.7
3.0	0.833	272.2	221.3	5.0	0.878	272.2	272.3
3.0	0.826	272.2	238.6				

### L<sub>w</sub>-H-V-L<sub>HC</sub>

wt% NaCl	mol% C <sub>3</sub> H <sub>8</sub>	T (K)	P (MPa)	wt% NaCl	mol% C <sub>3</sub> H <sub>8</sub>	T (K)	P (MPa)
3.0	NA	275.2	373.7	5.0	NA	274.2	412.3
3.0	NA	274.2	332.3	5.0	NA	273.2	350.3
3.0	NA	273.2	281.3	5.0	NA	272.2	284.1
3.0	NA	272.2	241.3	5.0	NA	271.2	241.3
3.0	NA	271.3	214.4	5.0	NA	270.2	209.6

## BINARY MIXTURES OF NITROGEN + CARBON DIOXIDE WITH INHIBITORS

*Hydrate:* Nitrogen + carbon dioxide with 9.41 wt% sodium chloride

*Reference:* Fan and Guo (1999)

*Phases:* L<sub>W</sub>-H-V

**9.01 mol% N<sub>2</sub>**

%CO <sub>2</sub>	T (K)	P (MPa)	%CO <sub>2</sub>	T (K)	P (MPa)
90.99	266.9	1.12	90.99	272.9	2.03
90.99	269.3	1.40	90.99	275.0	2.89
90.99	271.7	1.72	90.99	276.2	3.16
90.99	271.8	1.74			

*Hydrate:* Nitrogen + carbon dioxide with monoethylene glycol

*Reference:* Fan et al. (2000)

*Phases:* L<sub>W</sub>-H-V

mol% CO <sub>2</sub>	T (K)	P (MPa)	mol%	T (K)	P (MPa)
			CO <sub>2</sub>		
96.52	10 wt% MEG	268.9	1.00	90.99	267.2
96.52		272.1	1.35	90.99	267.9
96.52		273.4	1.62	90.99	270.2
96.52		276.1	2.49	90.99	271.9
				90.99	273.7
				90.99	274.2
				90.99	275.3
				90.99	276.5
					0.93
					1.03
					1.20
					1.76
					2.15
					2.49
					2.80
					3.39

## TERNARY AND MULTICOMPONENT MIXTURES WITH INHIBITORS

*Hydrate:* Methane + carbon dioxide + hydrogen sulfide with methanol

*Reference:* Ng et al. (1985b)

*Phases:* L<sub>W</sub>-V-H

<b>MeOH</b>					
wt%	CH <sub>4</sub>	CO <sub>2</sub>	H <sub>2</sub> S	T (K)	P (MPa)
10	0.7647	0.1639	0.0714	264.9	0.556
10	0.7648	0.1654	0.0698	267.7	0.734
10	0.6980	0.2059	0.0961	275.7	1.411
10	0.6941	0.1998	0.1061	280.9	2.237
10	0.6635	0.2167	0.1198	285.6	3.900

**Continued**

MeOH		wt%	CH <sub>4</sub>	CO <sub>2</sub>	H <sub>2</sub> S	T (K)	P (MPa)
10	0.6106	0.2350	0.1544	291.0	6.546		
20	0.6938	0.2161	0.0901	267.5	1.072		
20	0.6463	0.2334	0.1209	273.5	1.627		
20	0.6263	0.2338	0.1399	277.8	2.455		
20	0.6119	0.2408	0.1473	280.7	3.344		
20	0.6060	0.2408	0.1532	283.6	4.909		
20	0.5873	0.2434	0.1693	285.7	6.705		
20	0.5924	0.2470	0.1606	284.5	5.634		
20	0.5320	0.1988	0.2642	270.0	0.575		

*Hydrate:* Quaternary gas mixture with single; mixed salts; methanol; salts + methanol inhibitors

*Reference:* Mei et al. (1998)

*Phases:* L<sub>W</sub>-H-V

Methane + Ethane + Propane + 2-Methylpropane

**Gas Composition**

Composition	mol%	Composition	mol%
CH <sub>4</sub>	97.25	C <sub>3</sub> H <sub>8</sub>	1.08
C <sub>2</sub> H <sub>6</sub>	1.42	n-C <sub>4</sub> H <sub>10</sub>	0.25

Sol wt%	T (K)	P (MPa)	Sol wt%	T (K)	P (MPa)
10% NaCl	267.1	0.81	10% MeOH	266.8	0.61
	269.2	1.01		269.0	0.79
	271.0	1.30		271.2	1.00
	273.4	1.66		273.2	1.03
	275.5	2.12		275.4	1.68
	277.6	2.66		277.5	2.14
	277.7	2.68		279.5	2.71
	279.8	3.43			
10% KCl			20% MeOH	264.5	0.74
				266.0	1.20
				268.6	1.51
				270.6	1.91
				272.8	2.48
				275.4	3.40
				277.6	4.50

(Continued)

## Continued

Sol wt%	T (K)	P (MPa)	Sol wt%	T (K)	P (MPa)
10% CaCl <sub>2</sub>	{ 266.7 269.2 271.1 273.5 275.4 277.4 279.7	{ 0.63 0.88 1.14 1.44 1.88 2.48 3.34	30% MeOH	{ 262.6 264.7 266.9 267.9 268.9 270.2	{ 1.60 1.97 2.24 2.56 2.85 3.20
2% NaCl + 0.5% CaCl <sub>2</sub> + 0.5% KCl	{ 270.9 273.2 275.2 277.4 279.2 281.2	{ 0.60 0.93 1.20 1.60 2.06 2.75	10% NaCl + 20% MeOH	{ 260.8 262.4 264 265.5 267.5 269	{ 1.70 2.06 2.56 3.06 3.98 4.96
10% KCl + 10% MeOH	{ 266.5 269.3 270.9 273.4 275.5 277.5 279.5	{ 1.16 1.42 1.84 2.67 3.47 4.61 6.03	10% KCl + 20% MeOH	{ 264.6 266.6 268.6 271.3 273.4 275.5	{ 1.80 2.50 3.46 5.53 7.76 11.18
10% NaCl + 10% MeOH	{ 264.7 267.0 269.0 271.0 273.4 275.4 277.5	{ 1.05 1.40 1.78 2.47 3.18 3.98 4.90	10% CaCl <sub>2</sub> + 20% MeOH	{ 264.5 266.1 267.6 269.1 270.7 272.4	{ 1.47 2.05 2.66 3.44 4.34 5.89
10% CaCl <sub>2</sub> + 10% MeOH	{ 267.0 273.8 269.0 270.8 273.5 275.5 277.5 279.4	{ 1.10 1.66 1.58 1.84 2.57 3.42 4.43 5.95	2% NaCl + 0.5% CaCl <sub>2</sub> + 0.5% KCl + 10% MeOH	{ 268.6 271.3 276.4 278.9 281.5 266.5 270.7 272.9 274.8 268.7 276.9 279	{ 0.78 1.18 2.48 3.46 4.69 1.47 2.57 3.40 4.52 1.96 5.92 7.88

*Hydrate:* Quaternary gas mixture with 10 wt% monoethylene glycol (mol% gas composition: 88.53% CO<sub>2</sub> + 6.83% CH<sub>4</sub> + 0.38% C<sub>2</sub>H<sub>6</sub> + 4.26% N<sub>2</sub>)

*Reference:* Fan et al. (2000)

*Phases:* L<sub>W</sub>-H-V

T (K)	P (MPa)	T (K)	P (MPa)
268.8	0.80	276.4	2.41
270.7	1.16	278.1	2.85
274.4	1.82	279.3	3.50

*Hydrate:* Synthetic natural gas mixture with methanol

*Reference:* Ng and Robinson (1983)

*Phases:* L<sub>W</sub>-H-V

### Gas Composition

Composition	mol%	Composition	mol%	Composition	mol%
N <sub>2</sub>	7.00	C <sub>2</sub> H <sub>6</sub>	4.67	n-C <sub>4</sub> H <sub>10</sub>	0.93
CH <sub>4</sub>	84.13	C <sub>3</sub> H <sub>8</sub>	2.34	n-C <sub>5</sub> H <sub>12</sub>	0.93

wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)	wt%	T (K)	P (MPa)
10.0	267.7	0.90	10.0	288.6	17.19	20.0	275.0	4.66
10.0	273.5	1.80	10.0	288.9	18.82	20.0	279.2	8.92
10.0	279.2	3.57	20.0	264.8	1.26	20.0	281.4	13.73
10.0	283.5	6.78	20.0	270.0	2.38	20.0	283.3	18.82
10.0	286.3	10.86						

*Hydrate:* Synthetic natural gas mixture containing carbon dioxide with methanol

*Reference:* Ng and Robinson (1983)

*Phases:* L<sub>W</sub>-H-V

### Gas composition

Composition	mol%	Composition	mol%	Composition	mol%
N <sub>2</sub>	5.96	C <sub>3</sub> H <sub>8</sub>	1.94	n-C <sub>5</sub> H <sub>12</sub>	0.79
CH <sub>4</sub>	71.60	n-C <sub>4</sub> H <sub>10</sub>	0.79	CO <sub>2</sub>	14.19
C <sub>2</sub> H <sub>6</sub>	4.73				

(Continued)

**Continued**

<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>
10.0	268.3	1.04	10.0	286.5	13.91	20.0	276.3	6.94
10.0	271.0	1.46	10.0	287.7	17.44	20.0	278.0	9.53
10.0	276.6	2.76	10.0	288.3	19.03	20.0	278.8	12.14
10.0	281.5	5.52	20.0	264.4	1.41	20.0	279.5	15.04
10.0	283.9	8.42	20.0	270.4	2.83	20.0	280.3	16.75
10.0	285.0	10.73	20.0	274.1	4.77	20.0	281.0	19.15

*Hydrate:* Seven-component mixture with methanol

*Reference:* Robinson and Ng (1986)

*Phases:* L<sub>W</sub>-H-V, L<sub>W</sub>-H-V-L<sub>HC</sub>, L<sub>W</sub>-H-L<sub>HC</sub>

<b>Composition mol%</b>	<b>Composition mol%</b>	<b>Composition mol%</b>	<b>Composition mol%</b>
N <sub>2</sub>	5.26	CH <sub>4</sub>	73.90
CO <sub>2</sub>	13.37	C <sub>2</sub> H <sub>6</sub>	3.85
		C <sub>3</sub> H <sub>8</sub>	2.02
		n-C <sub>4</sub> H <sub>10</sub>	0.80
		n-C <sub>5</sub> H <sub>10</sub>	0.80

**L<sub>W</sub>-H-V**

<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>
35	244.9	0.362	35	248.2	0.600

**L<sub>W</sub>-H-V-L<sub>HC</sub>**

<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>
35	256.1	1.390	50	234.4	0.518
35	262.6	3.610	50	241.5	1.410
35	266.8	7.290	50	250.1	3.450
			50	254.5	7.250
35	269.9	13.82	50	256.3	13.57
35	273.1	20.35	50	256.8	14.22
			50	258.5	20.28

*Hydrate:* Gas liquid and condensate with methanol and ethylene glycol

*Reference:* Ng et al. (1987a)

### Composition of Hydrocarbon Liquids (mol%)

Component	Gas C	Gas D
Nitrogen	0.16	0.64
Methane	26.19	73.03
Carbon dioxide	2.10	3.11
Ethane	8.27	8.04
Propane	7.50	4.28
Isobutane	1.83	0.73
<i>n</i> -Butane	4.05	1.50
Isopentane	1.85	0.54
<i>n</i> -Pentane	2.45	0.60
Hexanes plus	45.60	7.53
Mol.Wt.	90.2	32.4
Satn. <i>P</i> (MPa) at <i>Ts</i>	8.95 <sup>B</sup>	43.94 <sup>R</sup>
<i>Ts</i> (K)	310.95	416.15

B = Bubble point pressure.

R = Retrograde dew point pressure.

### Liquid C

Sol (wt%)	<i>T</i> (K)	<i>P</i> (MPa)	Phases	Sol (wt%)	<i>T</i> (K)	<i>P</i> (MPa)	Phases
13% MeOH	281.0	3.91	L <sub>W</sub> -H-V-L <sub>HC</sub>	20% MEG	281.2	3.94	L <sub>W</sub> -H-V-L <sub>HC</sub>
	285.8	7.40	L <sub>W</sub> -H-V-L <sub>HC</sub>		285.6	7.37	L <sub>W</sub> -H-V-L <sub>HC</sub>
	286.2	12.00	L <sub>W</sub> -H-L <sub>HC</sub>		286.4	12.00	L <sub>W</sub> -H-L <sub>HC</sub>
	287.6	20.00	L <sub>W</sub> -H-L <sub>HC</sub>		287.8	20.00	L <sub>W</sub> -H-L <sub>HC</sub>
24% MeOH	275.2	4.02	L <sub>W</sub> -H-V-L <sub>HC</sub>	39% MEG	274.4	4.08	L <sub>W</sub> -H-V-L <sub>HC</sub>
	278.8	6.97	L <sub>W</sub> -H-V-L <sub>HC</sub>		278.4	6.92	L <sub>W</sub> -H-V-L <sub>HC</sub>
	279.0	11.99	L <sub>W</sub> -H-L <sub>HC</sub>		278.8	12.06	L <sub>W</sub> -H-L <sub>HC</sub>
	280.4	19.99	L <sub>W</sub> -H-L <sub>HC</sub>		280.0	19.99	L <sub>W</sub> -H-L <sub>HC</sub>

(Continued)

**Continued****Liquid D**

<b>Aqueous solution wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>Phases</b>
16% MeOH	283.2	6.00	L <sub>W</sub> -H-V-L <sub>HC</sub>
	286.4	11.03	L <sub>W</sub> -H-V-L <sub>HC</sub>
	288.0	15.01	L <sub>W</sub> -H-V-L <sub>HC</sub>
	288.95	19.99	L <sub>W</sub> -H-V-L <sub>HC</sub>
29% MeOH	276.0	6.03	L <sub>W</sub> -H-V-L <sub>HC</sub>
	278.8	10.99	L <sub>W</sub> -H-V-L <sub>HC</sub>
	280.0	14.97	L <sub>W</sub> -H-V-L <sub>HC</sub>
	281.6	20.00	L <sub>W</sub> -H-V-L <sub>HC</sub>

*Hydrate:* Lean gas and rich gas with methanol

*Reference:* Ng et al. (1987b)

*Phases:* L<sub>W</sub>-H-V-L<sub>LG</sub>, L<sub>W</sub>-H-L<sub>LG</sub>, L<sub>W</sub>-H-V-L<sub>RG</sub>, L<sub>W</sub>-H-L<sub>RG</sub>

**Mol Fraction**

<b>Component</b>	<b>Lean gas</b>	<b>Rich gas</b>
CH <sub>4</sub>	0.9351	0.8999
C <sub>2</sub> H <sub>6</sub>	0.0458	0.0631
C <sub>3</sub> H <sub>8</sub>	0.0131	0.0240
i-C <sub>4</sub> H <sub>10</sub>	0.0010	0.0030
n-C <sub>4</sub> H <sub>10</sub>	0.0020	0.0050
i-C <sub>5</sub> H <sub>12</sub>	0.0010	0.0010
n-C <sub>5</sub> H <sub>12</sub>	0.0010	0.0010
n-C <sub>6</sub> H <sub>14</sub>	0.0010	0.0030

**Lean Gas**  
**L<sub>W</sub>-H-V-L<sub>LG</sub>**

<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>
65.0	225.8	0.66	73.7	229.2	2.90
65.0	235.0	1.61	73.7	235.1	5.79
65.0	244.4	4.25	85.0	199.8	2.08
73.7	221.9	1.37	85.0	204.4	4.63

**Continued****L<sub>W</sub>-H-L<sub>LG</sub>**

<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>
65.0	248.9	10.29	73.7	237.2	20.07
65.0	250.4	19.75	85.0	205.8	11.34
73.7	236.4	9.51	85.0	206.8	20.37
73.7	235.9	10.17			

**Rich Gas  
L<sub>W</sub>-H-V-L<sub>RG</sub>**

<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>
65.0	229.4	0.77	73.7	228.9	
65.0	238.2	1.70	73.7	236.4	
65.0	46.0	4.28	785.0	198.1	
73.7	218.2	0.76	85.0	207.4	

**L<sub>W</sub>-H-L<sub>RG</sub>**

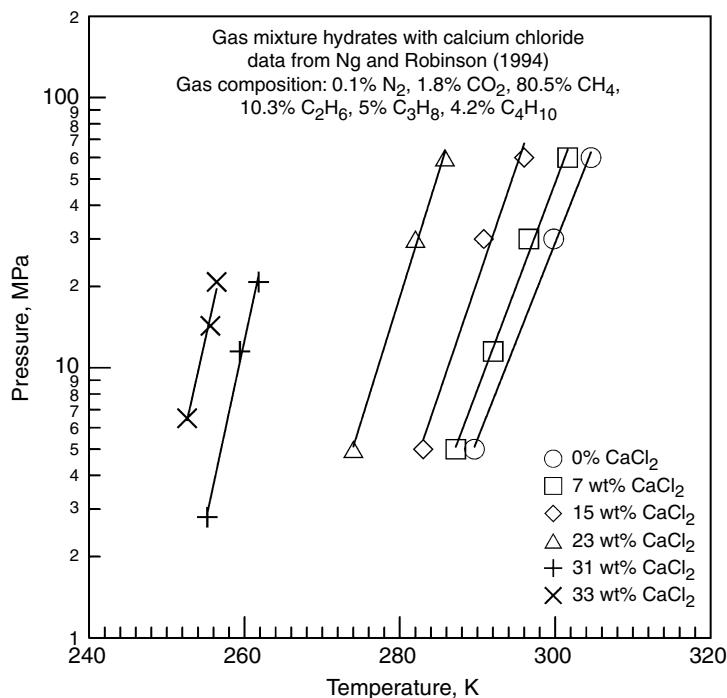
<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>wt%</b>	<b>T (K)</b>	<b>P (MPa)</b>
65.0	250.0	10.54	73.7	238.6	
65.0	251.2	20.17	85.0	211.1	
73.7	237.7	10.23	85.0	212.4	

*Hydrate:* Gas mixture with calcium chloride (0.1% N<sub>2</sub>, 1.8% CO<sub>2</sub>, 80.5% CH<sub>4</sub>, 10.3% C<sub>2</sub>H<sub>6</sub>, 5% C<sub>3</sub>H<sub>8</sub>, 4.3% C<sub>4</sub>H<sub>10</sub>)

*Reference:* Ng and Robinson (1994)

*Phases:* L<sub>W</sub>-H-V

<b>wt% CaCl<sub>2</sub></b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>wt% CaCl<sub>2</sub></b>	<b>T (K)</b>	<b>P (MPa)</b>
0	289.6	5.0	23.0	274.0	5.0
	299.8	30.0		282.0	30.0
	304.6	60.0		285.8	60.0
7.0	287.2	5.0	31.0	255.2	3.8
	292.0	11.5		259.4	11.5
	296.6	30.0		261.8	20.8
	301.6	60.0			
15.0	283.0	5.0	33.0	252.6	6.5
	290.8	30.0		255.6	14.3
	296.0	60.0		256.4	20.8



**FIGURE 6.58** Calcium chloride inhibition of a multicomponent gas mixture.

*Hydrate:* Reservoir fluid with methanol and formation water

*Reference:* Ng and Robinson (1994)

*Phases:* L<sub>W</sub>-H-V-L<sub>HC</sub> and L<sub>W</sub>-H-L<sub>HC</sub>

Reservoir fluid: 1.05 mol% CO<sub>2</sub>, 0.29% N<sub>2</sub>, 61.07% CH<sub>4</sub>, 4.58% C<sub>2</sub>H<sub>6</sub>, 3.16% C<sub>3</sub>H<sub>8</sub>, 1.98% C<sub>4</sub>H<sub>10</sub>, 1.35% C<sub>5</sub>H<sub>12</sub>, 1.92% C<sub>6</sub>H<sub>14</sub>, 24.6% C<sub>7</sub>H<sub>16</sub><sup>+</sup>

Fraction concentrations: CH<sub>4</sub> (60 mol%), C<sub>7</sub>H<sub>16</sub><sup>+</sup> (25 mol%)

Salt content of formation water = 3 wt%

<b>Formation water</b>			<b>20 wt% MeOH/80% formation H<sub>2</sub>O</b>		
<b>T (K)</b>	<b>P (MPa)</b>	<b>Phases</b>	<b>T (K)</b>	<b>P (MPa)</b>	<b>Phases</b>
280.2	2.48	L <sub>W</sub> -H-V-L <sub>HC</sub>	272.6	3.10	L <sub>W</sub> -H-V-L <sub>HC</sub>
288.2	7.47	L <sub>W</sub> -H-V-L <sub>HC</sub>	279.0	7.65	L <sub>W</sub> -H-V-L <sub>HC</sub>
294.0	20.6	L <sub>W</sub> -H-V-L <sub>HC</sub>	284.0	20.7	L <sub>W</sub> -H-V-L <sub>HC</sub>
298.9	44.0	L <sub>W</sub> -H-L <sub>HC</sub>	288.2	43.2	L <sub>W</sub> -H-L <sub>HC</sub>

*Hydrate:* Natural gas and condensate in distilled and saline water and in methanol

*Reference:* Tohidi et al. (1994a, 1995b, 1996b)

*Phases:* L<sub>w</sub>-H-V and phase fractions

### Composition of Mixture, Condensate, and Salt Water

Component	Gas mixture	Gas condensate	Forties Formation H <sub>2</sub> O salt concentration (wt%)	H <sub>2</sub> O
CH <sub>4</sub>	85.93	73.9	NaCl	6.993
C <sub>2</sub> H <sub>6</sub>	6.75	7.50	CaCl <sub>2</sub>	0.735
C <sub>3</sub> H <sub>8</sub>	3.13	4.08	MgCl <sub>2</sub>	0.186
i-C <sub>4</sub> H <sub>10</sub>	0.71	0.61	KCl	0.066
n-C <sub>4</sub> H <sub>10</sub>	0.88	1.58	SrCl <sub>2</sub>	0.099
i-C <sub>5</sub> H <sub>12</sub>		0.50	BaCl <sub>2</sub>	0.036
n-C <sub>5</sub> H <sub>12</sub>	0.57	0.74		
C <sub>6</sub> H <sub>14</sub>		0.89		
C <sub>7</sub> H <sub>16</sub> <sup>+</sup>		7.19		
CO <sub>2</sub>	1.31	2.38		
N <sub>2</sub>	0.72	0.58		

### Hydrate Formation Conditions

Gas mixture				Gas condensate			
Distilled water		Forties Formation H <sub>2</sub> O		Distilled water		30.5 wt% MeOH	
T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
280.5	1.634	277.5	1.613	277.3	0.993	262.4	1.151
283.9	2.468	281.8	2.916	277.6	1.082	264.4	1.627
287.8	3.916	286.8	5.681	278.2	1.207	267.2	2.268
				278.8	1.289	269.4	2.923
				279.4	1.386	271.2	3.723
				280.6	1.620	271.8	3.944
				281.2	1.758	272.2	4.185
				281.8	1.924		
				283.4	2.289		
				284.4	2.558		
				286.0	3.096		

(Continued)

**Continued**

**Phase Fractions, Compositions, and Temperature and Pressure**

Phase	Gas mixture				Gas condensate	
	Pure water		Forties Formation H <sub>2</sub> O		Pure water	30 wt% MeOH
	284.8 K	3.591 MPa	284.5 K	5.366 MPa	283.3 K	270.2 K
mol H <sub>2</sub> O/ mol gas	5.029		4.987		13.354	3.632
N <sub>2</sub>	*	*	*	*	0.65	0.96
CO <sub>2</sub>	1.68	0.37	1.28		1.76	1.99
CH <sub>4</sub>	88.57	67.89	87.43	69.9	86.46	86.88
C <sub>2</sub> H <sub>6</sub>	6.47	8.63	6.47	8.54	7.29	6.92
C <sub>3</sub> H <sub>8</sub>	1.67	17.29	3.04	16.69	2.03	1.94
i-C <sub>4</sub> H <sub>10</sub>	0.29	4.54	0.40	3.73	0.21	0.20
n-C <sub>4</sub> H <sub>10</sub>	0.80	1.28	0.85	1.14	0.69	0.41
i-C <sub>5</sub> H <sub>12</sub>					0.13	0.05
n-C <sub>5</sub> H <sub>12</sub>	0.52	0.14			0.15	0.08
C <sub>6</sub> H <sub>14</sub> <sup>+</sup>					0.63	0.44
MeOH						0.13
Vapor%		14.85		15.06		
Hydrate%	11.63 (calc'd)		9.96 (calc'd)			
Water%	73.52		74.98			
mol gas in hydrate	0.022		0.019			
mol% vapor					5.30	13.68
mol H <sub>2</sub> O converted to hydrate					0.042	0.048

\* = Vapor phase composition on a nitrogen-free and water-free basis.

*Hydrate:* Natural gas and black oil with synthetic salts and North Sea brines

*References:* Tohidi et al. (1997b)

*Phases:* L<sub>W</sub>-H-V and L<sub>W</sub>-H-V-L<sub>HC</sub>

Component	Black oil MW = 131.8 mol%	Specific gravity at 60°F/60°F	Composition of gas mixture
N <sub>2</sub>			0.84
CO <sub>2</sub>			0.25

**Continued**

<b>Component</b>	<b>Black oil MW = 131.8 mol%</b>	<b>Specific gravity at 60°F/60°F</b>	<b>Composition of gas mixture</b>
CH <sub>4</sub>	23.96		85.47
C <sub>2</sub> H <sub>6</sub>	3.98		7.72
C <sub>3</sub> H <sub>8</sub>	5.65		3.30
i-C <sub>4</sub> H <sub>10</sub>	2.00		0.81
n-C <sub>4</sub> H <sub>10</sub>	4.12		1.01
i-C <sub>5</sub> H <sub>12</sub>	2.09		0.30
n-C <sub>5</sub> H <sub>12</sub>	2.89		0.30
C <sub>6</sub> 's	4.10	0.666	
C <sub>7</sub> 's	6.25	0.714	
C <sub>8</sub> 's	6.55	0.738	
C <sub>9</sub> 's	5.20	0.761	
C <sub>10</sub> 's	4.06	0.776	
C <sub>11</sub> 's	3.31	0.790	
C <sub>12</sub> 's	2.64	0.801	
C <sub>13</sub> 's	2.36	0.815	
C <sub>14</sub> 's	2.18	0.831	
C <sub>15</sub> 's	1.95	0.837	
C <sub>16</sub> 's	1.61	0.844	
C <sub>17</sub> 's	1.28	0.849	
C <sub>18</sub> 's	1.27	0.856	
C <sub>19</sub> 's	1.05	0.863	
C <sub>20</sub> <sup>+</sup>	11.50	0.947	

**Composition of North Sea Brine and  
Forties Formation Water**

<b>Salt</b>	<b>North Sea brine</b>	<b>Forties Formation H<sub>2</sub>O</b>
	<b>wt%</b>	<b>wt%</b>
NaCl	2.354	6.993
CaCl <sub>2</sub>	0.116	0.735
MgCl <sub>2</sub>	0.524	0.186
KCl	0.086	0.066
Na <sub>2</sub> SO <sub>4</sub>	0.428	—
SrCl <sub>2</sub>	—	0.099
BaCl <sub>2</sub>	—	0.036

(Continued)

**Continued****Hydrate Formation from Natural Gas  
with Mixed Salt Inhibitors**

<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
10 wt% NaCl			
275.8	1.427	283.8	3.558
281.0	2.217	291.0	13.155
2.87 wt% NaCl + 2.87% KCl + 2.89% CaCl <sub>2</sub>			
278.4	1.682	288.7	5.192
282.3	2.496	290.2	6.964
284.7	3.516	292.6	13.224
5.55 wt% NaCl + 1.85% KCl + 1.85% CaCl <sub>2</sub>			
276.8	1.413	287.7	5.364
280.4	2.124	289.2	6.964
283.0	2.979	291.0	10.342
285.7	4.199	291.9	13.066
287.2	5.171		
North Sea brine			
2788	1.434	288.3	4.730
281.7	1.937	291.0	6.957
283.6	2.620	293.6	10.632
286.0	3.468		
Forties Formation water			
275.3	1.165	283.0	2.923
278.0	1.586	286.7	4.309
280.6	2.151	290.0	6.943

**Hydrate Formation from Black Oil  
with Mixed Salt Inhibitors**

<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
Distilled water			
275.0	0.779	282.3	2.193
276.6	0.958	282.9	2.379
277.7	1.082	283.6	2.599
277.8	1.158	284.6	3.075
278.7	1.310	285.4	3.427
279.9	1.531		
6.01 wt% NaCl + 1.49% CaCl <sub>2</sub> + 0.19% MgCl <sub>2</sub>			
276.1	1.296	280.3	2.723
278.4	2.041		
8.46 wt% NaCl + 3.04% CaCl <sub>2</sub> + 0.87% MgCl <sub>2</sub>			
270.9	1.055	275.9	2.103
272.2	1.289	277.0	2.461
274.0	1.737	277.8	3.130

**Continued**

<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
Forties Formation water			
274.9	1.165	282.0	3.447
278.5	1.924	284.3	4.868
Forties Formation H <sub>2</sub> O + 8.67 wt% methanol			
270.9	1.255	277.8	3.392
274.5	2.075	281.1	5.330

*Hydrate:* Gas, condensate with distilled water, salty water, and methanol

*Reference:* Tohidi et al. (1994b)

*Phases:* L<sub>W</sub>-H-V and L<sub>W</sub>-H-L<sub>HC</sub> with inhibitors

**Composition of Gas and Gas Condensate**

<b>Component</b>	<b>Gas condensate</b>	
	<b>Gas (mol%)</b>	<b>(mol%)</b>
CH <sub>4</sub>	85.93	73.9
C <sub>2</sub> H <sub>6</sub>	6.75	7.50
C <sub>3</sub> H <sub>8</sub>	3.13	4.08
i-C <sub>4</sub> H <sub>10</sub>	0.71	0.61
n-C <sub>4</sub> H <sub>10</sub>	0.88	1.58
i-C <sub>5</sub> H <sub>12</sub>	—	0.50
n-C <sub>5</sub> H <sub>12</sub>	0.57	0.74
C <sub>6</sub> H <sub>14</sub>	—	0.89
C <sub>7</sub> H <sub>16</sub> <sup>+</sup>	—	7.19
CO <sub>2</sub>	1.31	2.38
N <sub>2</sub>	0.72	0.58

**Composition of Forties Formation (Salt) Water**

Salt	NaCl	CaCl <sub>2</sub>	MgCl <sub>2</sub>	KCl	SrCl <sub>2</sub>	BaCl <sub>2</sub>
Concentration wt%	6.993	0.735	0.186	0.066	0.099	0.036

**Hydrate Conditions for Gas in Pure Water and Forties Formation (Salt) Water**

<b>Distilled water</b>		<b>Forties formation water</b>	
<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
280.5	1.634	277.5	1.613
283.9	2.468	281.8	2.916
287.8	3.916	286.8	5.681

(Continued)

**Continued****Hydrate Conditions for Condensate in Pure Water  
and 30.5 wt% Methanol**

<b>Distilled water</b>		<b>30.5 wt% methanol</b>	
<b>T (K)</b>	<b>P (MPa)</b>	<b>T (K)</b>	<b>P (MPa)</b>
277.25	0.993	262.35	1.151
277.65	1.082	264.35	1.627
278.25	1.207	267.25	2.268
278.75	1.289	269.35	2.923
279.45	1.386	271.25	3.723
280.55	1.620	271.75	3.944
281.25	1.758	272.15	4.185
281.85	1.924		
283.35	2.289		
284.35	2.558		
285.95	3.096		

**Compositions for Gas in Pure Water and Forties  
Formation (Salt) Water**

<b>Component</b>	<b>With distilled water at 284.8 K and 5.03 MPa. Init mol H<sub>2</sub>O/mol gas = 5.03</b>		<b>With Forties water at water at 284.5 K and 5.366 MPa. Init mol H<sub>2</sub>O/mol gas = 4.99</b>	
	<b>Vapor mol%</b>	<b>Hydrate mol%</b>	<b>Vapor mol%</b>	<b>Hydrate mol%</b>
CH <sub>4</sub>	88.57	67.89	87.43	69.9
C <sub>2</sub> H <sub>6</sub>	6.47	8.63	6.47	8.54
C <sub>3</sub> H <sub>8</sub>	1.67	17.29	3.04	16.69
i-C <sub>4</sub> H <sub>10</sub>	0.29	4.54	0.40	3.73
n-C <sub>4</sub> H <sub>10</sub>	0.80	1.28	0.85	1.14
n-C <sub>5</sub> H <sub>12</sub>	0.52	—	0.53	0.0
CO <sub>2</sub>	1.68	0.37	1.28	—
<b>Phase</b>	<b>Amount of each phase (mol%) at equilibrium</b>			
Vapor	14.85			
Hydrate	11.63			
Water	73.52			
Mol gas	0.022			
released from hydrate				

\* As a result of hydrate formation, salt concentration in the free water phases increased to 8.9 wt% from an initial value of 8.1 wt%.

**Continued**

**Vapor Compositions and Moles of Water  
Converted to Hydrate for Gas Condensate**

Component	With distilled water at 283.25 K and 2.85 MPa. mol H <sub>2</sub> O/ mol condensate = 13.354 vapor mol%	With water/methanol at 270.2 K and 4.027 MPa. mol H <sub>2</sub> O/ mol condensate = 3.632 vapor mol%
CO <sub>2</sub>	1.76	1.99
N <sub>2</sub>	0.65	0.96
CH <sub>4</sub>	86.46	86.88
C <sub>2</sub> H <sub>6</sub>	7.29	6.92
C <sub>3</sub> H <sub>8</sub>	2.03	1.94
i-C <sub>4</sub> H <sub>10</sub>	0.21	0.20
n-C <sub>4</sub> H <sub>10</sub>	0.69	0.41
i-C <sub>5</sub> H <sub>12</sub>	0.13	0.05
n-C <sub>5</sub> H <sub>12</sub>	0.15	0.08
C <sub>6</sub> H <sub>14</sub> +	0.63	0.44
Methanol	—	0.13
H <sub>2</sub> O	—	—
Mol% vapor	5.30	13.68
Mol of H <sub>2</sub> O converted to hydrates	0.042	0.048

*Hydrate:* Near critical natural fluid with distilled water, salty water, and methanol

*Reference:* Tohidi et al. (2001a)

*Phases:* L<sub>W</sub>-H-V-L<sub>HC</sub> with inhibitors

**Composition of Synthetic Formation Water**

Salt Concentration, wt%	NaCl	CaCl <sub>2</sub>	MgCl <sub>2</sub>	KCl	SrCl <sub>2</sub>	BaCl <sub>2</sub>
12.06	1.04	0.12	0.56	0.04	0.01	

**Composition of Original Near Critical Fluid, and  
Liquid Compositions and Vapor Phase Amounts from  
High and Medium Pressure Separators**

Component	Original fluid mol%	Specific gravity at 288.7 K	Composition of separator liquid at 298.1 K and 17.189 MPa, mol%	Composition of separator liquid at 298.0 K and 4.089 MPa, mol%
N <sub>2</sub>	0.36		0.38	0.37
CO <sub>2</sub>	0.27		0.28	0.27

(Continued)

## Continued

Component	Original fluid mol%	Specific gravity at 288.7 K	Composition of separator liquid at 298.1 K and 17.189 MPa, mol%	Composition of separator liquid at 298.0 K and 4.089 MPa, mol%
CH <sub>4</sub>	68.73		50.04	16.79
C <sub>2</sub> H <sub>6</sub>	9.88		10.23	9.23
C <sub>3</sub> H <sub>8</sub>	4.22		5.43	7.70
i-C <sub>4</sub> H <sub>10</sub>	0.48		0.69	1.14
n-C <sub>4</sub> H <sub>10</sub>	1.49		2.26	3.96
i-C <sub>5</sub> H <sub>12</sub>	0.32		0.53	0.99
n-C <sub>5</sub> H <sub>12</sub>	0.86		1.48	2.82
C <sub>6</sub> 's	1.00	0.670	1.88	3.66
C <sub>7</sub> 's	2.02	0.724	4.11	8.10
C <sub>8</sub> 's	2.33	0.758	4.93	9.74
C <sub>9</sub> 's	1.78	0.774	3.83	7.58
C <sub>10</sub> 's	1.25	0.783	2.78	5.51
C <sub>11</sub> 's	0.89	0.784	1.98	3.93
C <sub>12</sub> 's	0.64	0.798	1.42	2.83
C <sub>13</sub> 's	0.52	0.814	1.16	2.30
C <sub>14</sub> 's	0.65	0.823	1.45	2.87
C <sub>15</sub> 's	0.48	0.835	1.07	2.12
C <sub>16</sub> 's	0.36	0.843	0.80	1.59
C <sub>17</sub> 's	0.24	0.840	0.53	1.06
C <sub>18</sub> 's	0.25	0.841	0.56	1.10
C <sub>19</sub> 's	0.20	0.850	0.44	0.88
C <sub>20</sub> <sup>+</sup>	0.78	0.868	1.74	3.46
Vapor mol fraction	NA		0.55	0.50

**Hydrate Dissociation Conditions for  
Near Critical Fluid with Distilled Water,  
Salt Formation Water, and Methanol**

Distilled water		Formation water		10.41 wt% methanol	
T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
277.2	1.069	276.2	2.103	276.3	5.330
280.4	1.627	281.3	4.137	280.7	11.349
284.5	2.772	285.2	7.805	283.6	24.256
288.4	4.702	287.8	13.914		

**Continued**

**Dissociation Conditions of Liquids from  
the High Pressure and Medium Pressure  
Separators, in the Presence of Distilled  
Water, Flashed to below Conditions**

298.1 K, 17.18 MPa high pressure liquid feed separator		298.0 K, 4.089 MPa medium pressure liquid feed separator	
T (K)	P (MPa)	T (K)	P (MPa)
278.4	1.193	279.7	1.400
283.8	2.510	283.3	2.275
289.3	6.095	287.2	3.944
		287.7*	11.721

\* For this run only no vapor phase was present and the dissociation was observed visually.

### 6.3.2 Thermal Property Data

In this section the hydrate data for heat capacity and enthalpy of dissociation are presented. The other thermal properties such as thermal conductivity and thermal expansion are presented in [Chapter 2](#) with their analogs for ice.

#### 6.3.2.1 Heat capacity and heat of dissociation

Since there is a paucity of data, the data for the heat capacity and enthalpy of dissociation are presented by investigation without discrimination, other than the accuracy statements presented in Section 6.1.2. The reader is also referred to Section 4.6.1 for a discussion of heat of dissociation values.

*Compounds:* Methane, ethane, and propane

*Reference:* Handa (1986a)

*Properties:* Molar heat capacity and enthalpy of dissociation

**Constant Pressure Heat Capacity  
J/(K · mol)**

T (K)	CH <sub>4</sub> 6.0 H <sub>2</sub> O	C <sub>2</sub> H <sub>6</sub> · 7.67 H <sub>2</sub> O	C <sub>3</sub> H <sub>8</sub> · 17.0 H <sub>2</sub> O
85	107.7	149.6	281.7
90	112.1	156.0	294.0
100	121.4	167.2	318.8
110	131.5	177.2	342.0

(Continued)

**Continued**

<i>T</i> (K)	$\text{CH}_4 \cdot 6.0 \text{ H}_2\text{O}$	$\text{C}_2\text{H}_6 \cdot 7.67 \text{ H}_2\text{O}$	$\text{C}_3\text{H}_8 \cdot 17.0 \text{ H}_2\text{O}$
120	140.3	188.6	366.5
130	149.0	199.4	392.4
140	156.8	210.0	415.9
150	164.2	219.6	437.6
160	171.1	229.0	459.3
170	178.6	237.9	481.0
180	186.3	248.2	502.4
190	194.1	259.1	524.8
200	201.4	269.2	548.3
210	209.8	277.4	573.5
220	219.3	292.8	599.5
230	225.9	301.7	617.7
240	233.7	310.9	644.0
250	240.4	323.0	674.4
260	248.4	337.8	710.2
270	257.6		

<b>Compound</b>	<b><i>T</i> (K) range</b>	<b><math>\Delta H</math> (kJ/mol gas)</b>	
		<b><math>\text{H} \leftrightarrow \text{I} + \text{G}</math></b>	<b><math>\text{H} \leftrightarrow \text{L} + \text{G}</math></b>
$\text{CH}_4$	160–210	$18.13 \pm 0.27$	$54.19 \pm 0.28$
$\text{C}_2\text{H}_6$	190–250	$25.70 \pm 0.37$	$71.80 \pm 0.38$
$\text{C}_3\text{H}_8$	210–260	$27.00 \pm 0.33$	$129.2 \pm 0.4$

*Compounds:* Isobutane and two naturally occurring hydrates

*Reference:* Handa (1986b, 1988)

*Properties:* Enthalpy of dissociation

### Composition of Naturally Occurring Hydrates (mol%)

<b>Composition</b>	<b>Mid-America</b>	
	<b>Gulf of Mexico</b>	<b>trench</b>
$\text{CH}_4$	66.0	99.93
$\text{C}_2\text{H}_6$	2.9	0.01
$\text{C}_3\text{H}_8$	14.7	0.01
i- $\text{C}_4\text{H}_{10}$	3.7	0.05
<i>n</i> - $\text{C}_4\text{H}_{10}$	0.08	
neo- $\text{C}_5\text{H}_{12}$	0.13	

**Continued**

<b>Composition</b>	<b>Gulf of Mexico</b>	<b>Mid-America trench</b>
i-C <sub>5</sub> H <sub>12</sub>	0.01	
cy-C <sub>5</sub> H <sub>12</sub>	0.01	
CO <sub>2</sub>	7.8	
H <sub>2</sub> S	0.49	
N <sub>2</sub>	4.0	
wt% Sdmnt	7.4	0.764

**Standard Molar Enthalpy of Dissociation  $\Delta H'$** 

<b>Hydrate sample</b>	<b><math>H \leftrightarrow I + G</math></b>	<b><math>H \leftrightarrow L + G</math></b>
Isobutane	$18.13 \pm 0.27$ (KJ/mol)	$54.19 \pm 0.28$ (KJ/mol)
Gulf of Mexico	27.8 (J/g)	33.1 (J/g)
Assumption	all water = hydrate	20% water = ice
Mid-America trench	17.5 (kJ/mol)	(19.2 mass% water as ice)

*Compound:* Methane*Reference:* Lievois (1987)*Property:* Enthalpy of dissociation

<b>T (K)</b>	<b><math>\Delta H</math> (J/gmol CH<sub>4</sub>)</b>
278.2	57,739
278.2	57,358
278.2	57,697
283.2	52,798
283.2	53,610

*Compound:* Methane*Reference:* Rueff et al. (1988)*Property:* Constant volume heat capacity and enthalpy of dissociation

<b>T (K)</b>	<b>C<sub>v</sub> (J/g-K)</b>	<b>T (K)</b>	<b><math>\Delta H</math> (J/g)</b>
245	1.62	285	429.66
255	1.56		
255	1.61		
256	1.70		
257	1.66		
259	1.61		

*Compound:* Methane, carbon dioxide, nitrogen, carbon dioxide + nitrogen, carbon dioxide + nitrogen + tetrahydrofuran

*Reference:* Kang et al. (2001)

*Property:* Enthalpy of dissociation

Guest(s)	$\Delta H/\text{kJmol}^{-1}$	Hydrate composition
CH <sub>4</sub>	56.84 ± 0.89	<i>n</i> = 6.38
CO <sub>2</sub>	65.22 ± 1.03	<i>n</i> = 7.23
N <sub>2</sub>	65.81 ± 1.04	<i>n</i> = 5.94
0.17CO <sub>2</sub> + 0.83N <sub>2</sub>	64.59 ± 1.02	<i>x</i> = 5.43, <i>y</i> = 1.89
0.70CO <sub>2</sub> + 0.30N <sub>2</sub>	63.41 ± 1.00	<i>x</i> = 7.08, <i>y</i> = 0.25
0.17CO <sub>2</sub> + 0.83N <sub>2</sub> with 0.01C <sub>4</sub> H <sub>8</sub> O + 0.99H <sub>2</sub> O	109.01 ± 1.72	<i>x</i> = 2.96, <i>y</i> = 9.47, <i>z</i> = 11.39
0.17CO <sub>2</sub> + 0.83N <sub>2</sub> with 0.03C <sub>4</sub> H <sub>8</sub> O + 0.97H <sub>2</sub> O	118.94 ± 1.87	<i>x</i> = 2.35, <i>y</i> = 7.42, <i>z</i> = 12.53
0.70CO <sub>2</sub> + 0.30N <sub>2</sub> with 0.01C <sub>4</sub> H <sub>8</sub> O + 0.99H <sub>2</sub> O	107.18 ± 1.69	<i>x</i> = 9.97, <i>y</i> = 2.58, <i>z</i> = 10.94
0.70CO <sub>2</sub> + 0.30N <sub>2</sub> with 0.03C <sub>4</sub> H <sub>8</sub> O + 0.97H <sub>2</sub> O	113.66 ± 1.79	<i>x</i> = 8.11, <i>y</i> = 2.19, <i>z</i> = 13.16

Enthalpies of dissociation for pure and mixed gases were measured three times and average values reported above. G · *n*H<sub>2</sub>O: *n* is the number of water molecules in the unit cell and G is the pure guest. *x*CO<sub>2</sub> · *y*N<sub>2</sub> · 46H<sub>2</sub>O: *x* and *y* are the calculated numbers of CO<sub>2</sub> and N<sub>2</sub> molecules, respectively, in sI. *x*CO<sub>2</sub> · *y*N<sub>2</sub> · *z*C<sub>4</sub>H<sub>8</sub>O · 136H<sub>2</sub>O: *x*, *y*, and *z* are the calculated numbers of CO<sub>2</sub>, N<sub>2</sub>, and THF molecules, respectively, in sII [THF = C<sub>4</sub>H<sub>8</sub>O].

*Compound:* Methane

*Reference:* Gupta (2007)

*Property:* Constant volume heat capacity and enthalpy of dissociation

$T_{\text{onset}}/\text{K}$	$P/\text{MPa}$	$\Delta H_d \pm 11.72$ (J/gm-hydrate)	$\Delta H_d \pm 13.3$ (J/gm-water)	$\Delta H_d \pm 1.45$ (kJ/mol-gas)
280.60	5.5	442.21	508.29	54.90
285.65	9.8	420.60	483.45	52.21
288.15	12.8	433.96	498.80	53.87
288.45	13.2	428.58	492.62	53.20
289.85	15.0	455.01	523.00	56.48
292.16	18.5	441.39	507.35	54.79
291.65	19.3	448.02	514.97	55.62

**Continued**

<b>T/K</b>	<b>P/MPa</b>	<b>Cp (J/gm hydrate/K)</b>	<b>T/K</b>	<b>P/MPa</b>	<b>Cp (J/gm hydrate/K)</b>
247.91	20.00	1.797	266.57	20.00	1.947
250.58	20.00	1.827	278.61	20.00	2.082
253.24	20.00	1.850	280.11	20.00	2.132
255.91	20.00	1.870	281.61	20.00	2.172
258.57	20.00	1.883	283.11	20.00	2.217
261.24	20.00	1.898	284.61	20.00	2.281
263.90	20.00	1.904			

**6.4 SUMMARY AND RELATIONSHIP TO CHAPTERS THAT FOLLOW**

The object of this chapter is to provide an overview of the experimental methods, the phase equilibria data, and the thermal property data available on hydrates since Hammerschmidt (1934) on hydrates in natural gas systems. The tabulations and figures illustrate that more data are needed, particularly for phase equilibria mixtures of noncombustible components, structure H components, and for thermal property data.

Chapters 7 and 8 consider two applications of the data in this chapter and the correlation methods of Chapters 4 and 5. Chapter 7 considers the impact of hydrate on energy, climate, and geohazards in the earth, as examples of phase equilibria and thermal property data application. In Chapter 8, applications caused by hydrates in gas processing and production are described.

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