Inhibition of Gas Hydrates by Methanol

A molecular-thermodynamic correlation has been developed for calculating the inhibition effect of methanol on the formation of hydrates in moist gas mixtures. Six phases are potentially present in these mixtures: gas, aqueous liquid, hydrocarbon liquid, ice, and hydrate structures I and II. For a given temperature and system composition, the molecular-thermodynamic method described here allows computation of the hydrate-point pressure as well as relative amounts and compositions of all coexisting phases. Good agreement is obtained when calculated results are compared with diverse experimental data reported in the literature. The correlation given here may be useful for computer-aided design for gas processing and transportation.

F. E. Anderson and J. M. Prausnitz
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Chemical Engineering
University of California
Berkeley, CA 94720

SCOPE

Numerous articles are concerned with gas/hydrate phase equilibria (e.g., Berecz and Balla-Achs, 1983). Where no inhibitor is present, correlations for hydrate-system properties are restricted to selected parts of the general, multiphase-multicomponent diagram. A number of these studies are directed at the three-phase system hydrate/vapor/aqueous-liquid (or ice) (Parrish and Prausnitz, 1972; Ng and Robinson, 1976). Others have directed attention to the two-phase system hydrate/gas (Sloan et al., 1976; Ng and Robinson, 1980; Aoyagi et al., 1980; Song and Kobayashi, 1982). Limited studies of the three-phase system hydrate/aqueous-liquid/hydrocarbon-liquid have been made (Ng and Robinson, 1976, 1977). While several proprietary correlations exist (Gas Processors Assn.), no thermodynamically consistent overall multicomponent-multiphase correlation for this hydrate inhibition problem has appeared in the literature. Previous correlations for the effects of inhibitors on hydrate formation (Menten et al., 1981) have assumed that only condensed aqueous phases coexist with the gas and hydrate phases. This work covers all of the above-mentioned equilibria in a unified framework suitable for further development for computer-aided process design.

CONCLUSIONS AND SIGNIFICANCE

This work presents a method for predicting the amount of inhibitor that must be added to prevent hydrate formation in gas processing. The method, based on molecular-thermodynamic models and a computational framework, calculates hydrate-point pressures and temperatures, and coexisting-phase fractions and compositions for gas/water/methanol mixtures in the region from 220 to 320 K and pressures to 500 bar (50 MPa). Consideration is given to the possible existence of all of the six potential phases: gas, aqueous liquid, hydrocarbon liquid, ice, and hydrate structures I and II; these phases may occur in various combinations. The calculation procedure includes nitrogen, methane, ethane, propane, *n*-butane, isobutane, *n*-pentane, carbon dioxide, and hydrogen sulfide along with methanol and water.

Fugacities of all components in the gas phase are calculated using a modification of the Redlich-Kwong (1949) equation of state similar to that of de Santis et al. (1974). Fugacities for all condensible components are calculated using activity coefficients derived from a modified version of the UNIQUAC equation where energy-of-interaction parameters vary linearly with temperature. Liquid-phase fugacities for supercritical components are calculated using Henry's law. These molecular-thermodynamic models provide a good rep-

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F. E. Anderson is presently at Cabot Corp., Billerica, MA 01821.

resentation of the vapor-liquid-liquid equilibria present in gas/water/methanol systems. Fugacities of all components in the hydrate phases are calculated using the theory of van der Waals and Platteeuw (1959).

At a given temperature and composition, the hydrate-point pressure is that at which the fugacity of water in the hydrate phase is equal to that in all coexisting phases. The multiphase equilibrium computation routine uses four sequentially nested iterative procedures. Several special cases exist that allow elimination of one or two of these iterative routines.

Calculated results show good agreement with a wide variety of experimental data. The correlation presented here is compared with data for vapor-liquid-liquid equilibria, for methanol-water freezing-point depression, and for hydrate-formation pressures in both the gas/hydrate and condensed-fluid/hydrate regions of the phase diagram.

While the correlation presented here is consistently successful for relatively simple systems (e.g., water-methanol-methane), results are sometimes less successful for multicomponent systems, probably because of nonuniqueness of binary parameters. For better multicomponent results it may be necessary to add essentially empirical corrections. However, despite this limitation, the correlation given here can predict hydrate-point temperatures for multicomponent systems (at fixed pressure) to within about ±5° C of the experimental values.

Introduction

At low temperatures and high pressures, solid hydrates can precipitate from moist gas mixtures, interfering with gas processing and transportation. Hydrate formation can be inhibited by the addition of a hydrophilic fluid that lowers the fugacity of water; a suitable and inexpensive fluid is methanol.

This work presents a molecular-thermodynamic method for calculating phase equilibria in systems containing water, methanol, and both hydrate-forming and nonhydrate-forming gases as a function of temperature, pressure, and composition. Such calculations are useful first to determine operating conditions required to avoid hydrate formation, and second to determine the amount of methanol required to prevent hydrate formation at fixed operating conditions.

The thermodynamics of hydrate formation has been discussed by numerous authors, notably by Parrish and Prausnitz (1972), Sloan et al. (1976), Ng and Robinson (1976, 1977, 1980), Holder et al. (1980), Dharmawardhana et al. (1980), Menten et al. (1981), and John et al. (1985). With the exception of the treatment by John et al., these discussions make use of a statistical-thermodynamic theory presented by van der Waals and Platteeuw (1959); that theory is also used here. With the exception of the work by Sloan (1984), previous work has been restricted to selected parts of the general multiphase problem; this work treats the entire multiphase problem within a molecular-thermodynamic framework.

Hydrates are members of the general class of solid inclusion compounds called clathrates. They are formed when components with low molecular weights are in equilibrium with water at low temperature or high pressure. Water molecules form regular crystalline lattices that contain cavities (Byk and Fomina, 1968). These cavities encage gas molecules that stabilize the lattice by van der Waals forces. Hydrates occur in two distinct structures, I and II, which differ in cavity size. Inhibitors, such as methanol, act by lowering the fugacity of water in coexisting phases; as a result, hydrates are formed at lower temperatures and higher pressures than those encountered in the absence of methanol. This behavior is analogous to the freezing-point depression of water by methanol.

Hydrates are most frequently encountered in gas transportation and processing. Natural gas, as withdrawn from the well, is typically saturated with water. In cold climates, the water content of such natural gas is often sufficiently high to cause hydrate formation in downstream transportation networks. Hydrate formation in these piping systems is undesired as it causes large pressure drops through the lines and can halt the flow of the natural gas. Hydrate formation also occurs in association with natural gas cryogenic liquefaction and separations. To prevent hydrate formation in these transportation networks and separation operations, two alternatives are available. The first, removal of the water at the well head, is expensive, as the level to which removal must be accomplished is often very low. The second, addition of a component to the natural gas-water mixture to prevent hydrate formation, can often be accomplished economically using methanol.

Molecular Thermodynamic Models and Data Reduction

At equilibrium, the fugacity f of any component i is the same in all phases:

$$f_i^G = f_i^{L1} = f_i^{L2} = f_i^{H1} = f_i^{H2} = (f_w^\alpha) \tag{1}$$

where G stands for gas, $L1$ for aqueous liquid, $L2$ for hydrocarbon liquid, $H1$ and $H2$ for hydrate structures I and II, and α for ice. Consistent with the phase rule, all of the phases referred to in Eq. 1 do not coexist simultaneously. The fugacity of water in the ice phase is in parentheses to indicate that the ice phase is assumed to be pure. Methanol is not incorporated into the hydrate structure, as indicated by Davidson et al. (1981). Given temperature, overall composition of the mixture, and expressions for the fugacities of each component in each phase, Eq. 1 is solved to obtain the pressure where hydrate first forms (hydrate-point pressure) and to determine the proportions and compositions of each of the coexisting phases. Condensed phases need not coexist with the hydrate phase; hydrate formation may occur directly from a gas phase. In such cases, the inhibition effect of methanol is greatly reduced since water and methanol are only sparingly soluble in the gas phase. Necessary molecu-

Table 1. Redlich-Kwong $a(T)$ Parameters for Polar Components

	$a_i^{(0)}\left(\frac{10^{-7}\,\mathrm{cm}^6\cdot\mathrm{bar}}{\mathrm{mol}^2}\right)$	$a_i^{(1)}\left(\frac{10^{-14}\,\mathrm{cm}^6\cdot\mathrm{bar}\cdot\mathrm{K}^3}{\mathrm{mol}^2}\right)$
Water	4.38	122.0
Methanol	43.1	226.9
Hydrogen sulfide	7.75	6.395
Carbon dioxide	6.03	1.680

SI conversion: kPa = bar × 100.
Data valid between 220 and 320 K.

lar-thermodynamic models used for each of the six possible phases are described below.

Gas-phase fugacities

The fugacity of any component i in the gas phase is calculated using fugacity coefficient ϕ_i:

$$f_i^G = y_i \phi_i P \tag{2}$$

where y_i is the gas phase mole fraction and where ϕ_i is obtained from a modification of the Redlich-Kwong (1949) equation of state:

$$P = \frac{\rho RT}{(1 - b_M \rho)} - \frac{a(T)_M \rho^2}{T^{1/2}(1 + b_M \rho)} \tag{3}$$

Conventional mixing rules relate mixture constants $a(T)_M$ and b_M to the composition and to pure-component constants $a(T)_{ii}$ and b_i:

$$a(T)_M = \sum_i \sum_j y_i y_j a_{ij} \tag{4}$$

and

$$b_M = \sum_i y_i b_i \tag{5}$$

Indices i and j in Eq. 4 and 5 run over all components in the mixture.

Parameter b_i is evaluated for all components using the corresponding-states expression of Chueh and Prausnitz (1967). Following de Santis et al. (1974), we separate the temperature-dependent $a(T)_{ii}$ parameter into nonpolar and polar contributions:

$$a(T)_{ii} = a_i^{(0)} + \frac{a_i^{(1)}}{T^3} \tag{6}$$

For nonpolar components, $a_i^{(1)}$ is zero; for water, methanol, hydrogen sulfide, and carbon dioxode $a_i^{(1)} > 0$. For nonpolar components $a_i^{(0)}$ is evluated using critical properties. Redlich-Kwong constants $a(T)_{ii}$ and b_i are related to the second virial coefficient, B_{ii}:

$$B_{ii} = b_i - \frac{a(T)_{ii}}{RT} \tag{7}$$

Similarly,

$$B_{ij} = \frac{(b_i + b_j)}{2} - \frac{a(T)_{ij}}{RT} \tag{8}$$

Following de Santis et al., for polar components, $a_i^{(0)}$ and $a_i^{(1)}$ are evaluated using Eq. 7 and data for the temperature dependence of the second virial coefficient. Table 1 gives $a_i^{(0)}$ and $a_i^{(1)}$ for all polar components.

For polar-polar binaries a_{ij} is calculated from:

$$a(T)_{ij} = \left\{[a_i^{(0)} a_j^{(0)}]^{1/2} + \frac{[a_i^{(1)} a_j^{(1)}]^{1/2}}{T^3}\right\}(1 - k_{ij}) \tag{9}$$

All other a_{ij} parameters are calculated from:

$$a(T)_{ij} = [a_i^{(0)} a_j^{(0)}]^{1/2}(1 - k_{ij}) \tag{10}$$

Binary parameters k_{ij} are fixed using two methods. Most k_{ij} values were obtained using second-virial cross-coefficient data and Eq. 8; for some binaries, however, such data are unavailable. For these systems, k_{ij} were obtained from a fit of our model to binary vapor-liquid equilibrium (VLE) data. In a few cases, the k_{ij} values obtained from second-virial cross-coefficient data gave poor representations of VLE data; in these cases the k_{ij} values were modified to improve agreement with VLE data. Table 2 presents all k_{ij} values used in this work.

Table 2. $10^3\,k_{ij}$ Parameters

	Methanol	Hydrogen Sulfide	Carbon Dioxide	Methane	Nitrogen	Ethane	Propane	*n*-Butane	Isobutane	*n*-Pentane
Water	0	24	120	62	0	35	35	35	35	35
Methanol	—	376	418	350	408	403	8	8	8	8
Hydrogen sulfide	—	—	325	0	0	86	375	10	10	118
Carbon dioxide	—	—	—	138	0	145	113	121	121	103
Methane	—	—	—	—	89	0	17	20	76	144
Nitrogen	—	—	—	—	—	9	32	151	151	158
Ethane	—	—	—	—	—	—	0	0	0	0
Propane	—	—	—	—	—	—	—	0	0	0
n-Butane	—	—	—	—	—	—	—	—	0	0
Isobutane	—	—	—	—	—	—	—	—	—	0

Data valid between 220 and 320 K.

Liquid-phase fugacities

Natural-gas/water/inhibitor mixtures contain two types of components: condensible components (e.g., water, methanol, propane) and noncondensible components (methane and nitrogen). For condensible components, we calculate fugacities in any liquid phase from:

$$f_i^L = x_i \gamma_i f_i^\circ \tag{11}$$

where f_i° is the fugacity of pure liquid i at system temperature. Activity coefficients, γ_i, are obtained from a modification of the UNIQUAC equation (Abrams and Prausnitz, 1975). Binary UNIQUAC energy-of-interaction parameters ($\Delta U_{ij}/R$ and $\Delta U_{ji}/R$) are assumed to vary linearly with temperature:

$$\frac{\Delta U_{ij}}{R} = U_{ij}^{(0)} + U_{ij}^{(1)}\,T \tag{12}$$

With the exception of the water-methanol binary, coefficient $U_{ij}^{(1)}$ is taken as zero for binary systems where no liquid-liquid equilibrium (LLE) exists. Binary parameters are obtained by fitting binary VLE and LLE data. Figure 1 shows a correlation of vapor-liquid-liquid equilibria (VLLE) for the water-propane system, and Figure 2 shows a correlation for the water/hydrogen sulfide binary. Table 3 gives all UNIQUAC parameters used in this work.

UNIQUAC parameters for the water-methanol system are of particular importance because the fugacity of water in the aqueous liquid phase is the key quantity that determines hydrate inhibition. Parameters for this binary were obtained from a fit to water-methanol freezing-point-depression data (Miller and Carpenter, 1964; Ross, 1954) and from data on methanol inhibition of methane hydrate (Ng and Robinson, 1983, 1984). Figure 3 shows a correlation for the freezing-point depression of water by methanol.

An economic analysis of any hydrate-inhibition process using methanol is intimately tied to the amount of methanol required per mole of water in the natural gas mixture. Methanol losses in most processes are directly related to the solubility of methanol in natural gas liquids. Using binary methanol-hydrocarbon VLE, LLE, and ternary VLLE for methanol-hydrocarbon-water systems (Noda et al., 1975; Ng and Robinson, 1983), methanol-hydrocarbon UNIQUAC parameters were determined to maximize the accuracy of the predicted partition coefficient of methanol between aqueous and natural gas liquid phases.

For condensible components, the standard state fugacity is

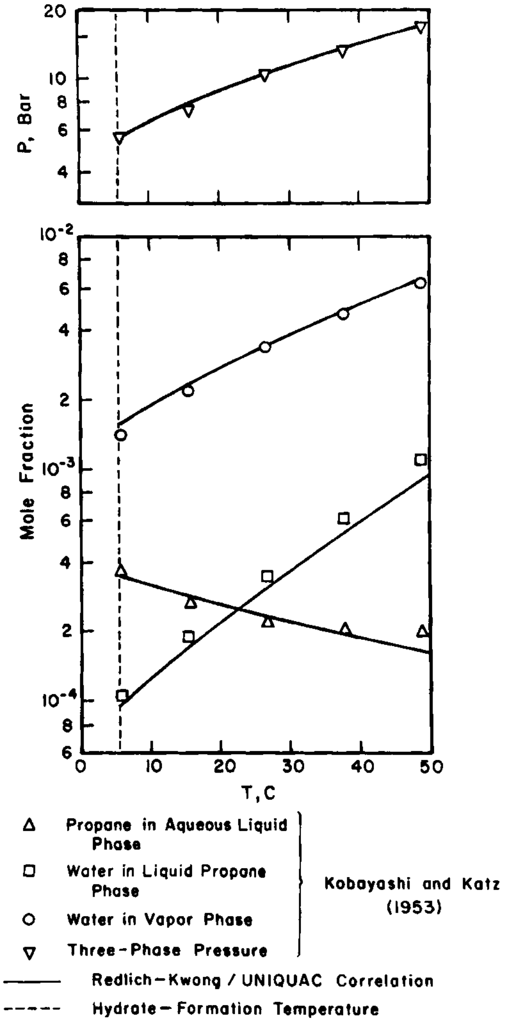

Figure 1. Three-phase compositions and pressures for water-propane mixtures.

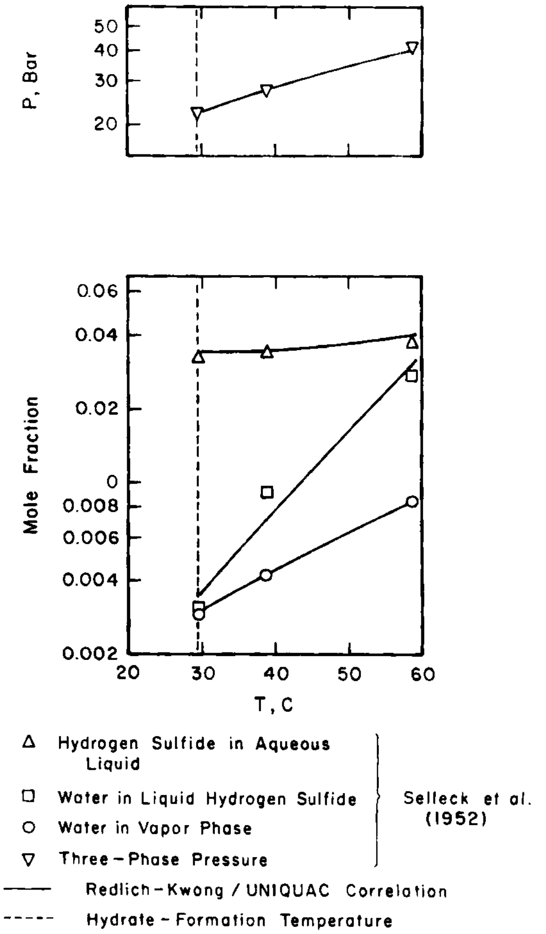

Figure 2. Three-phase compositions and pressures for water-hydrogen sulfide mixtures.

Table 3. Parameters for Modified UNIQUAC Model

	R		Q	H_2O	CH_3OH	H_2S	CO_2	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}
H_2O	0.9200	1.400	(0)	—	365.7	−378.1	−105.3	−770.7	−736.3	−284.5	−283.5	−168.0
			(1)	—	−38.06	363.2	197.4	521.6	471.6	304.7	299.4	257.2
CH_3OH	1.4311	1.432	(0)	−184.0	—	−13.48	54.77	−425.0	109.1	−276.7	158.7	96.77
			(1)	−26.85	—	—	—	200.5	—	125.1	—	−34.91
H_2S	1.0000	1.000	(0)	4813.0	412.1	—	345.3	112.4	91.85	−65.50	81.34	−50.08
			(1)	−1300.0	—	—	—	—	—	—	—	—
CO_2	1.3200	1.280	(0)	1577.0	540.5	−28.85	—	74.71	19.70	−23.30	−13.57	281.0
			(1)	−235.3	—	—	—	—	—	—	—	—
C_2H_6	1.8022	1.696	(0)	3468.0	576.9	230.4	114.5	—	156.0	−76.10	68.55	11.55
			(1)	−112.7	−6.31	—	—	—	—	—	—	—
C_3H_8	2.4766	2.236	(0)	3338.0	860.0	225.9	169.3	−104.5	—	−18.15	43.74	−235.9
			(1)	−662.9	—	—	—	—	—	—	—	—
n-C_4H_{10}	3.1510	2.776	(0)	4155.0	1109.0	352.5	286.0	131.6	15.64	—	−42.15	−155.2
			(1)	−919.8	−125.8	—	—	—	—	—	—	—
i-C_4H_{10}	3.1502	2.772	(0)	4754.0	239.4	186.2	261.4	−30.02	−62.13	42.17	—	−206.3
			(1)	−1140.0	—	—	—	—	—	—	—	—
n-C_5H_{12}	3.8254	3.316	(0)	3402.0	176.1	368.1	61.38	83.76	520.9	257.5	348.7	—
			(1)	−690.8	−429.4	—	—	—	—	—	—	—

Data valid between 220 and 320 K for Eq. 12.
$U_{ij}^{(0)}$ in K; $10^2\, U_{ij}^{(1)}$ dimensionless.

given by:

$$f_i^\circ = P_i^{sat}\phi_i^{sat} \exp\left[\frac{v_i^L(P - P_i^{sat})}{RT}\right] \quad (13)$$

where P_i^{sat} is the vapor pressure of i, ϕ_i^{sat} is the fugacity coefficient of saturated gas i, and v_i^L is the molar volume of i. For all components except water, vapor pressures are given by the Antoine equation. For water above the ice point, the equation of Bain (1964) is used for vapor pressure. The molar volume, corrected for temperature and pressure variations, was obtained from pure-component data where possible, and elsewhere from the liquid-density correlation of Chueh and Prausnitz (1969).

Below the ice-point temperature, the fugacity of pure hypothetical-liquid water is calculated from:

$$f_w^\circ = f_w^\alpha(T, P_w^{sat,\alpha}) \exp\left[\frac{\Delta h_w^{fus}(T_t)}{RT}\left(1 - \frac{T}{T_t}\right) + \frac{1}{RT}\int_{T_t}^{T} \Delta C_p^{L-\alpha}\, dT - \int_{T_t}^{T} \frac{\Delta C_p^{L-\alpha}}{RT}\, dT\right] \exp\left[\frac{v_w^L(P - P_w^{sat,\alpha})}{RT}\right] \quad (14)$$

Above the ice-point temperature Eq. 13 is used for f_w°. The heat capacity difference between ice and liquid water is calculated from:

$$\Delta C_p^{L-\alpha} = \Delta c_p^{(0)} + \frac{\Delta c_p^{(1)}}{T} + \frac{\Delta c_p^{(2)}}{T^2} + \frac{\Delta c_p^{(3)}}{T^3} \quad (15)$$

The constants in Eq. 15 are evaluated using the heat capacity data of Angell et al. (1973) for subcooled liquid water and the heat capacity data of Giauque and Stout (1936) for ice. Equation 14 produces excellent agreement with the data of Kraus and Greer (1984) for the vapor pressures of subcooled liquid water. Table 4 gives the enthalpy of fusion and the constants $\Delta c_p^{(0)}$,

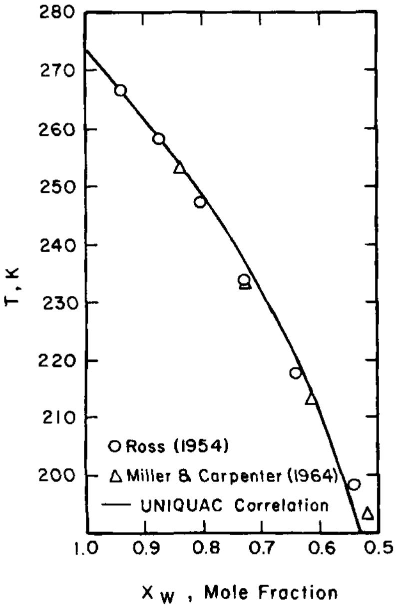

Figure 3. Freezing point of water-methanol solutions.

Table 4. Thermophysical Properties of Water

$$\frac{\Delta h_w^{fus}}{R} = 7.225 \times 10^2 \text{ K}$$

$$\frac{\Delta c_p^{(0)}}{R} = -2.054 \times 10^3$$

$$\frac{\Delta c_p^{(1)}}{R} = 1.638 \times 10^6 \text{ K}$$

$$\frac{\Delta c_p^{(2)}}{R} = -4.348 \times 10^8 \text{ K}^2$$

$$\frac{\Delta c_p^{(3)}}{R} = 3.852 \times 10^{10} \text{ K}^3$$

Eqs. 14 and 15; data valid between 220 and 273.15 K.

$\Delta c_p^{(1)}$, $\Delta c_p^{(2)}$, and $\Delta c_p^{(3)}$. The fugacity of water in the ice phase is calculated from:

$$f_w^\alpha = P_w^{sat,\alpha}\phi_w^{sat,\alpha}\exp\left[\frac{v_w^\alpha(P - P_w^{sat,\alpha})}{RT}\right] \tag{16}$$

The vapor pressure of ice is given by Jansco et al. (1970).

For components that are supercritical in part of the temperature range of interest (carbon dioxide and ethane), f_i^o is calculated using the corresponding-states method of Lyckman et al. (1965). This correlation is used for all temperatures. For such components, the reference pressure for Poynting corrections is taken to be zero, consistent with the work by Lyckman et al.

For supercritical components (nitrogen and methane), fugacities in the liquid phase are obtained from a pressure-corrected Henry's law:

$$f_i^L = x_i H_{iM}\exp\left(\frac{\bar{v}_i^\infty P}{RT}\right) \tag{17}$$

where H_{iM}, Henry's constant of component i in the liquid mixture, is related to Henry's constants of components i in pure condensible components j, H_{ij}, by:

$$\ln H_{iM} = \sum_j \ln H_{ij}\left(\frac{x_j v_j^L}{\sum_k x_k v_k^L}\right) \tag{18}$$

Indices j and k are carried over all condensible components in the mixture. Mole fractions x_j and x_k are normalized such that they reflect only condensible components in the liquid phase. The partial molar volume of component i at infinite dilution, $\bar{v}_i^\infty$ is evaluated from the method presented by Lyckman et al. (1965). For the temperature range of interest here, Henry's constants are given by:

$$\ln H_{ij} = H_{ij}^{(0)} - \frac{H_{ij}^{(1)}}{T} \tag{19}$$

where the fitting constants are obtained from vapor-liquid equilibrium data for each binary pair. These constants are listed in Table 5.

Table 5. Parameters for Henry's Constants

	Nitrogen		Methane	
Solvent	$H_{ij}^{(0)}$	$10^{-2}H_{ij}^{(1)}$	$H_{ij}^{(0)}$	$10^{-2}H_{ij}^{(1)}$
Water	14.11	8.032	13.99	10.12
Methanol	8.003	−1.163	14.50	19.36
Hydrogen sulfide	4.215	−9.196	5.154	−2.096
Carbon dioxide	3.752	−5.202	5.265	3.315
Ethane	3.259	−5.627	6.036	4.388
Propane	5.267	−1.849	5.780	2.819
n-butane	4.069	−6.566	6.580	4.745
Isobutane	3.951	−6.913	5.455	1.459
n-pentane	5.892	−1.312	7.130	5.996

Data valid between 220 and 320 K for Eq. 19.

$H_{ij}^{(0)}$ is dimensionless, with reference pressure of 1.01325 bar (101.325 kPa); $H_{ij}^{(1)}$ in K.

Hydrate-phase fugacities

As discussed by van der Waals and Platteeuw (1959), hydrate-forming molecules are viewed as adsorbed in the cavity sites; this adsorption is described by a Langmuir adsorption model. The van der Waals-Platteeuw theory uses the Gibbs-Duhem equation to provide a model for the fugacity of water in a hydrate phase as a function of f_j, the fugacities of hydrate-forming components in coexisting phases. Each cavity is envisioned as spherical, and the gas-cavity wall interaction is described by the Kihara potential function. The reference fugacity for water, f_w^β, is that in the hypothetical empty hydrate lattice. The fugacity of water in the hydrate phase, f_w^H, is found from:

$$f_w^H = f_w^\beta \exp\left(\frac{-\Delta\mu_w^{\beta-H}}{RT}\right) \tag{20}$$

where

$$\Delta\mu_w^{\beta-H} = \mu_w^\beta - \mu_w^H \tag{21}$$

The difference in chemical potential, $\Delta\mu_w^{\beta-H}$ is obtained from the van der Waals-Platteeuw expression (Parrish and Prausnitz, 1972; van der Waals and Platteeuw, 1959):

$$\Delta\mu_w^{\beta-H} = RT\sum_m \nu_m \ln\left(1 + \sum_j C_{mj}f_j\right) \tag{22}$$

The Langmuir constant $C_{mj}(T)$ accounts for gas-water interactions in the hydrate cavities; this constant is calculated from:

$$C_{mj}(T) = \frac{4\pi}{kT}\int_0^\infty \exp\left(\frac{-\omega_{mj}(r)}{kT}\right) r^2\,dr \tag{23}$$

As shown by McKoy and Sinanoglu (1963), a sum of all gas-water interactions in the cavity yields $\omega_{mj}(r)$, the spherically symmetric cell-potential function in terms of Kihara parameters ϵ_j, σ_j, and a_j. The integral in Eq. 23 is evaluated using Gaussian integration. The Kihara hard-core parameter a_j, is determined from second virial coefficient data (Parrish and Prausnitz, 1972), while Kihara energy and size parameters ϵ_j and σ_j are determined by a fit of the model to hydrate dissociation pressure data. All Kihara parameters are given in Table 6.

The fugacity of water f_w^β in the empty hydrate lattice is calculated as a function of temperature and pressure using the difference in chemical potential of water between the empty hydrate lattice and ice (or liquid water) following the method outlined by Holder et al. (1980). If the temperature is below the ice point,

Table 6. Kihara Parameters for Hydrate-Gas Interactions

Gas	ϵ/k, K	$10^2\sigma$, nm	10^2a, nm
Methane	153.39	32.578	3.00
Nitrogen	128.57	32.677	3.50
Ethane	175.94	34.381	4.00
Propane	189.84	36.002	6.80
Isobutane	207.04	32.422	8.00
Hydrogen sulfide	199.34	32.561	3.60
Carbon dioxide	169.44	29.561	7.20

we define:

$$\Delta\mu_w^{\beta-\alpha} = \mu_w^\beta - \mu_w^\alpha \tag{24}$$

and if the temperature is above the ice point, we define:

$$\Delta\mu_w^{\beta-L} = \mu_w^\beta - \mu_w^L \tag{25}$$

We calculate f_w^β from:

$$f_w^\beta = f_w^\alpha \exp\left(\frac{\Delta\mu_w^{\beta-\alpha}}{RT}\right) \tag{26}$$

or

$$f_w^\beta = f_w^{L^o} \exp\left(\frac{\Delta\mu_w^{\beta-L}}{RT}\right) \tag{27}$$

depending on the temperature. The chemical potential differences defined by Eqs. 24 and 25 are calculated using the method outlined by Holder et al.:

$$\frac{\Delta\mu_w^{\beta-\alpha}}{RT} = \frac{\Delta\mu_w^o}{RT^o} - \int_{T^o}^{T} \frac{\Delta h_w^{\beta-\alpha}}{RT^2}\,dT + \int_0^P \frac{\Delta v_w^{\beta-\alpha}}{RT}\,dP \tag{28}$$

and

$$\frac{\Delta\mu_w^{\beta-L}}{RT} = \frac{\Delta\mu_w^o}{RT^o} - \int_{T^o}^{T} \frac{\Delta h_w^{\beta-\alpha} + \Delta h_w^{fus}}{RT^2}\,dT + \int_0^P \frac{\Delta v_w^{\beta-\alpha} + \Delta v_w^{fus}}{RT}\,dP \tag{29}$$

Molar volume differences here are assumed to be temperature-independent; however, the molar enthalpy difference is given by:

$$\Delta h_w^{\beta-\alpha} = \Delta h_w^{\beta-\alpha^o} + \int_{T^o}^{T} \Delta C_p^{\beta-\alpha,L}\,dT \tag{30}$$

Values of $\Delta\mu^o$ and $\Delta h_w^{\beta-\alpha}$ determined by Dharmawardhana et al. (1980) were used. The heat capacity difference in Eq. 30 is correlated using the expression provided by Holder et al.

Parameters for the molar volume difference between the empty hydrate lattice and ice are slightly different from those used by Dharmawardhana et al. For structure I hydrate we follow Dharmawardhana et al. and use 3.0 cm^3/mol, but for structure II hydrate we use 1.2 cm^3/mol instead of the previously reported 3.4 cm^3/mol. This change is necessary to calculate equilibria in the liquid-hydrocarbon/hydrate region of the propane-water phase diagram. In this region, the fugacity of propane in the liquid phase is used in Eq. 22. The Poynting corrections contained in the liquid propane fugacity and in the empty hydrate lattice fugacity cause the hydrate-phase water fugacity to increase with pressure. Without our modification, the increase of the hydrate-phase water fugacity with pressure is greater than that of water in the liquid phase, and calculation of phase equilibria is not possible. This modification is only important for propane hydrate due to its particularly rapid increase of hydrate formation pressure with temperature. The volume difference parameters used by Dharmawardhana et al. were obtained from x-ray crystallographic studies on filled hydrate lattices of von Stackelberg and Muller (1954).

Results and Discussion

Figure 4 shows the inhibiting effect of methanol on the formation of methane hydrate. Calculated results agree well with

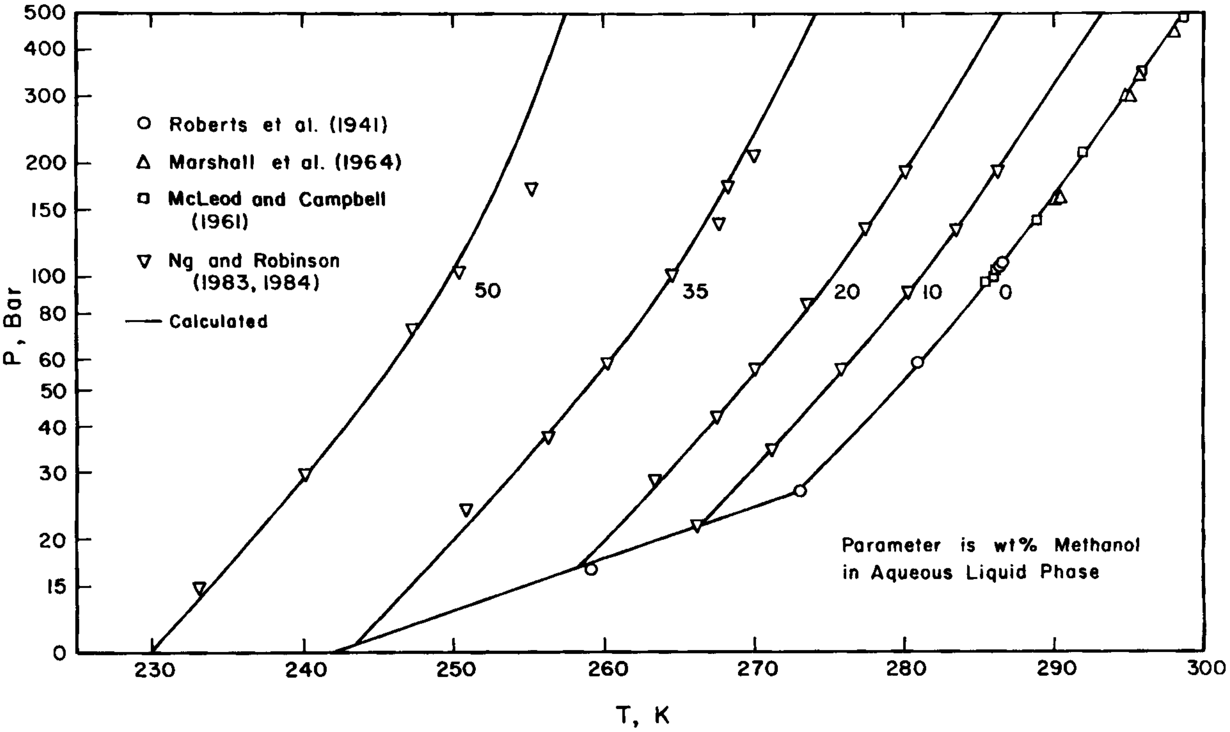

Figure 4. Inhibition of methane hydrate by methanol.

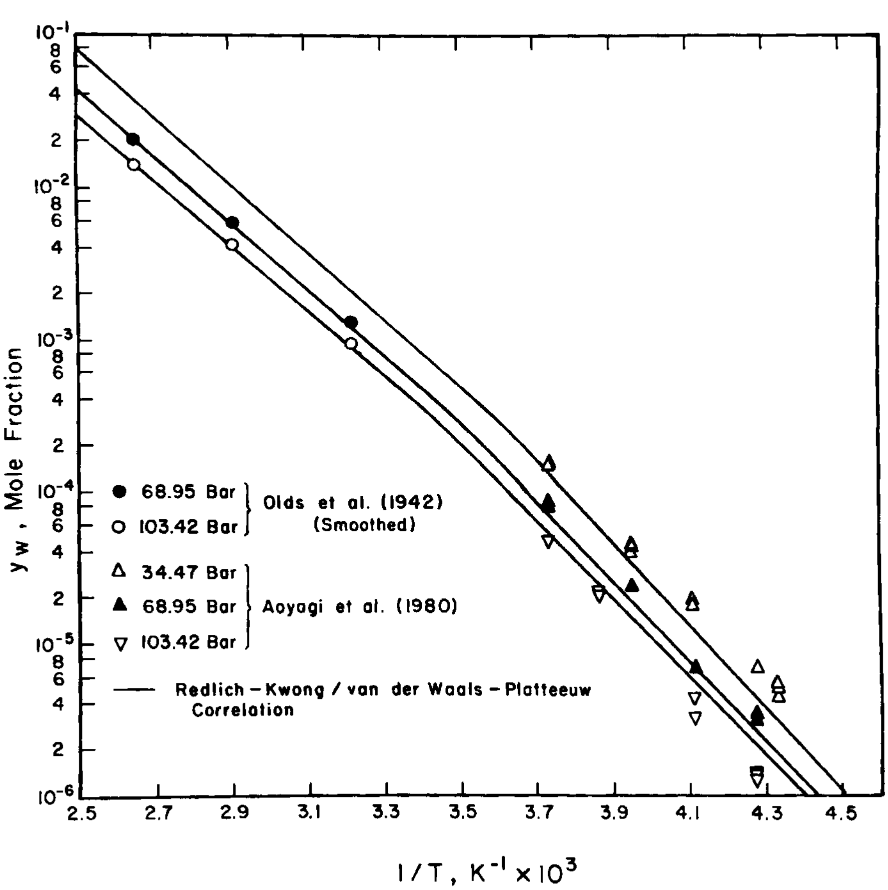

Figure 5. Water content of saturated methane gas.

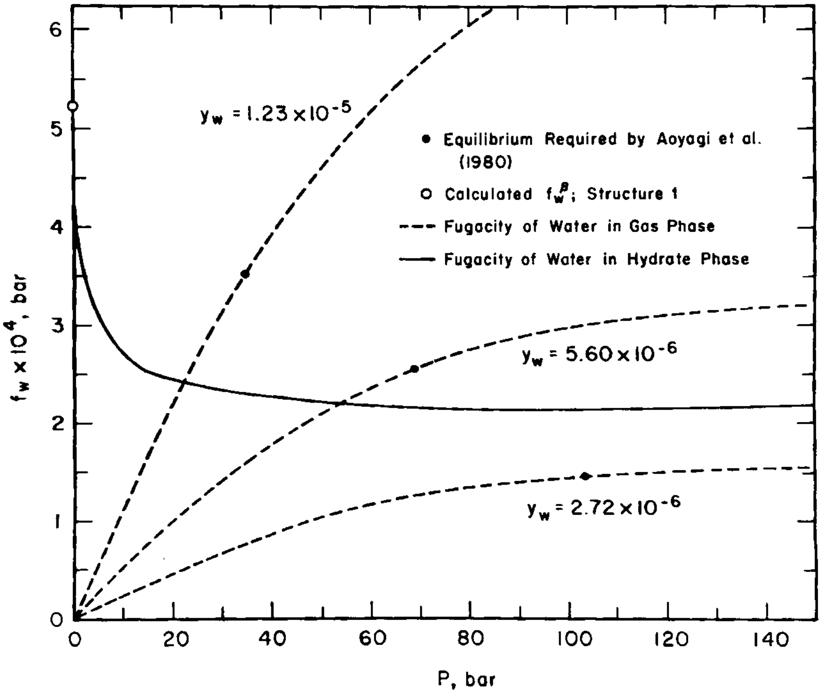

Figure 6. Calculated fugacities of water in methane gas and hydrate phases at 240 K.

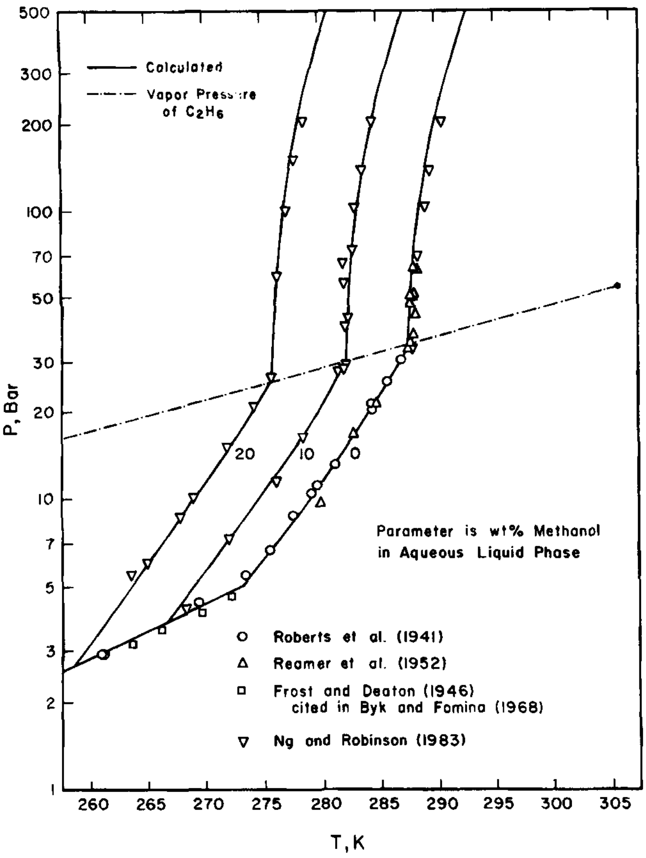

Figure 7. Inhibition of ethane hydrate by methanol.

methanol inhibition data of Ng and Robinson (1983, 1984). Figure 5 shows the water content of methane gas in equilibrium with liquid water and hydrate for several isobars. At low inverse temperature calculated results are compared with the dew-point data of Olds et al. (1942) and at high inverse temperature our correlation is compared to the hydrate-point data of Aoyagi et al. (1980). Slight discrepancies occur at low temperature due to inadequacies of the van der Waals-Platteeuw model. At low temperatures, calculated water fugacities are based on Kihara parameters obtained from experimental high-temperature data.

Figure 6 shows calculated gas-phase fugacities that correspond to the smoothed hydrate-point compositions given by Aoyagi et al. (1980). For each composition, the solid points in Figure 6 denote the hydrate formation pressure measured by Aoyagi et al. This figure also gives the calculated fugacity of water in the hydrate phase based on Kihara parameters determined from experimental three-phase hydrate/aqueous-liquid/gas data. Intersections of fugacity curves correspond to the equilibrium conditions shown in Figure 5. To match the data of Aoyagi et al., calculated intersections must occur at the pressures denoted by points in Figure 6. For such matching, the pressure dependence of the hydrate-phase water fugacity must be different. An accurate fit of all experimental data is limited by results of the van der Waals-Platteeuw theory.

Ng and Robinson (1976) proposed an empirical modification of the van der Waals-Platteeuw model directed toward improving the fit of hydrate pressures for gas mixtures. However, since Ng and Robinson (1980) found that their empirical modification is insufficient to fit the data of Aoyagi et al., they proposed an ad hoc method for correcting their hydrate-phase fugacities.

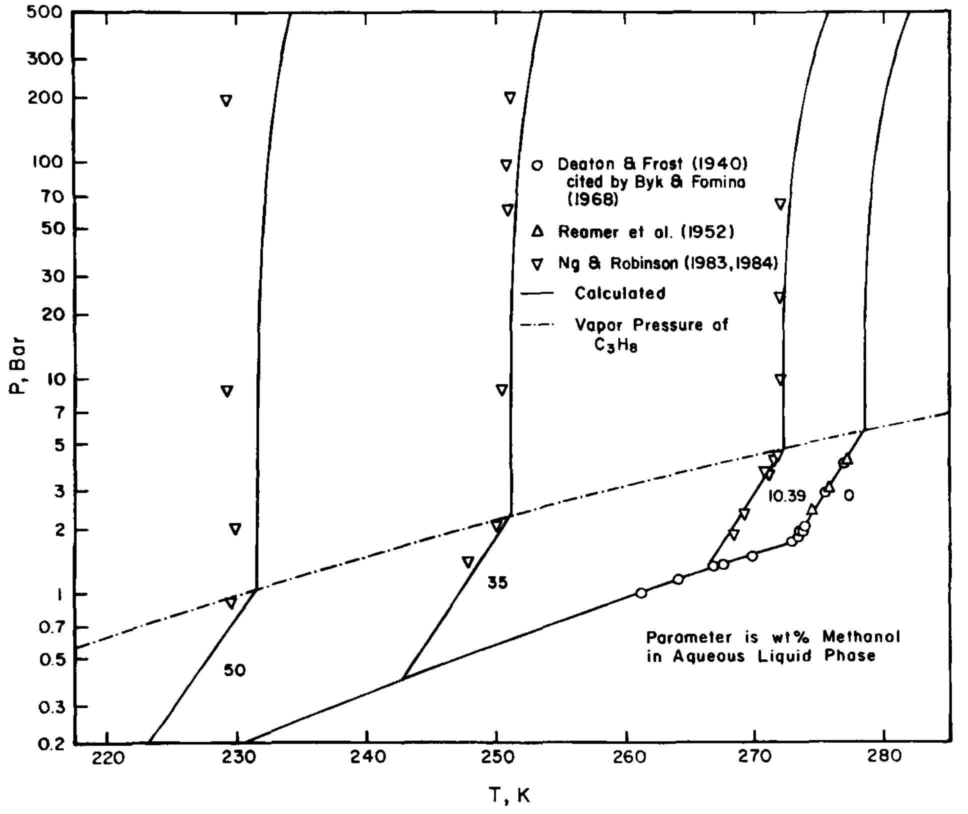

Figure 8. Inhibition of propane hydrate by methanol.

Unfortunately, this method is thermodynamically inconsistent. The thermodynamic ambiguity arises from two different methods for calculation of f_w^β. Ng and Robinson (1980) calculated $\Delta\mu_w^{\beta-H}$ based on previously determined Kihara potential parameters (Ng and Robinson, 1977). To determine these Kihara parameters, Ng and Robinson (1977) used the method of Parrish and Prausnitz (1972) for calculation of $\Delta\mu_w^{\beta-\alpha,L}$; this is thermodynamically equivalent to the assumption of a specific function for f_w^β. Based on their previously defined Kihara parameters and the hydrate/gas data of Aoyagi et al., Ng and Robinson (1980) fitted new functional forms for f_w^β for both hydrate structure types. Presumably, Ng and Robinson use their new functions for f_w^β in the hydrate/gas region of the phase diagram and the method outlined by Parrish and Prausnitz for the hydrate/gas/aqueous-liquid or ice region of the phase diagram.

Sloan et al. (1976) and Aoyagi et al. used the van der Waals-Platteeuw model for hydrate-phase fugacities and the virial equation for gas-phase fugacities. In their work, the virial equation was truncated after the third term. Applicability of their treatment was limited to the methane-water system; no attempt was made to calculate phase equilibria for other systems. Using their hydrate/gas data and previously determined Kihara and empty hydrate phase parameters, Sloan et al. and Aoyagi et al. fitted second and third virial cross-coefficients for the methane-water system. However, no comparison was given of calculated and experimental dew points for the methane-water system.

Song and Kobayashi (1982) extended the work of Aoyagi et al. by measuring the water content above the hydrate of a methane-propane gas mixture. They used the Soave modification of the Redlich-Kwong equation of state for gas-phase fugacities. They were forced to resort to pressure-dependent k_{ij} values to fit their data for the water content of a methane-propane gas mixture in equilibrium with hydrate. Unfortunately, pressure-dependent k_{ij} values lead to thermodynamic inconsistency.

Figures 7–10 show the calculated inhibition effect of methanol on hydrate formation in the ethane, propane, hydrogen sulfide, and carbon dioxide-water systems. Agreement with experimental data is good. For the propane and carbon dioxide systems, slight discrepancies are due to several factors. First, for some systems Kihara parameters obtained from high-temperature data are used to calculate equilibria at lower temperatures. Second, UNIQUAC parameters based on high-temperature data are extrapolated to low temperature. UNIQUAC parameters for aqueous binaries are based on VLE and LLE data; these data must be obtained above the ice-point temperature. Some extrapolation is therefore necessary to make low-temperature calculations. Finally, binary UNIQUAC parameters are used for multicomponent systems. This scale-up approximation is probably responsible for the discrepancies in Figure 10. Since the solubility of carbon dioxide in aqueous methanol solutions is much larger than those of other hydrate-forming gases, this effect is much more pronounced in Figure 10 than in other systems.

For a methane-propane gas mixture, Figure 11 shows calculated results that are in good agreement with the data of Ng and Robinson (1983, 1984). However, agreement between calculations and other multicomponent gas-mixture data of Ng and Robinson (1984) is generally not as good as that shown in Figure 11. Generally, errors in predicted hydrate-point temperatures for multicomponent systems (at set pressure) are less than about ±5°C. A possible source of disagreement follows from the

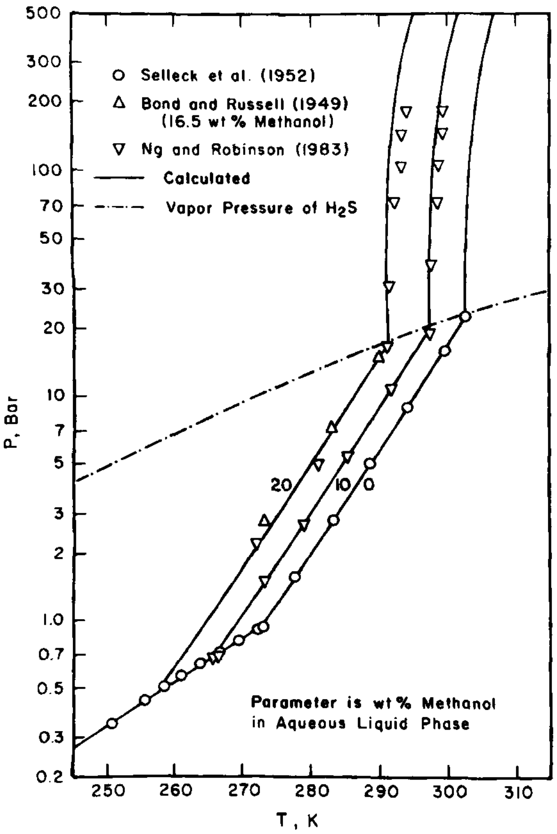

Figure 9. Inhibition of hydrogen sulfide hydrate by methanol.

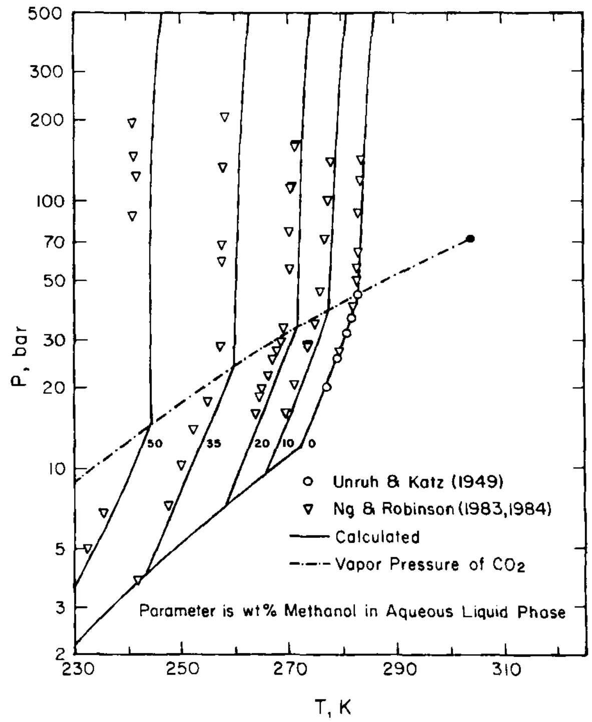

Figure 10. Inhibition of carbon dioxide hydrate by methanol.

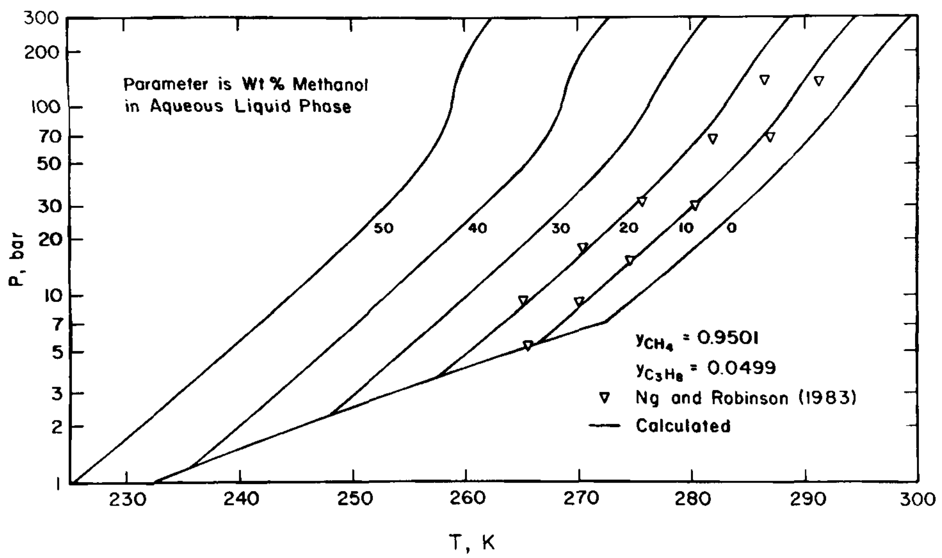

Figure 11. Inhibition of a gas mixture hydrate by methanol.

scale-up approximation: Kihara parmeters based on binary data are used to calculate multicomponent equilibria. Agreement with experiment may also improve if the van der Waals-Platteeuw model is refined as suggested by John et al. (1985); this refinement did not come to our attention until after our work was completed. John et al. note, however, that their procedure also has problems for multicomponent systems.

Disagreement between experiment and our correlation arises from several sources. The most important source of error lies with the van der Waals-Platteeuw model for hydrate-phase fugacities. Inadequacies of this model for multicomponent systems have long been recognized (Parrish and Prausnitz, 1972; Ng and Robinson, 1976). Until the recent work by John et al., only empirical corrections (Ng and Robinson, 1976) have been made to the van der Waals-Platteeuw theory. A second source of disagreement follows from the inability of UNIQUAC to describe accurately activity coefficients in multicomponent systems. Errors introduced by the assumptions implicit in UNIQUAC are carried through the calculations and result in errors in the hydrate-point temperatures.

When inadequate models are coupled with experimental data of finite accuracy, data reduction inevitably produces binary parameters that are not unique. While uncertainty in binary parameters often produces acceptable results for binary systems (because of compensation), such uncertainty may become severe for multicomponent systems.

Empirical corrections may be necessary to improve the results of this correlation for multicomponent systems; such corrections must be made with care however, as extrapolation may be unreliable.

Computational Procedure

Given a gas/water/methanol mixture of known overall composition and temperature, the phase-equilibrium computation routine calculates the hydrate-formation pressure and the relative amounts and compositions of all coexisting phases. The phase-equilibrium computation routine uses four sequentially nested, iterative calculational procedures. The first iterative routine solves for the density (Topliss, 1985) of a gas mixture at a given temperature, pressure, and composition using the equation of state. Based on this density, we calculate fugacity coefficients. *K* factors are then calculated using these fugacity coefficients with the other molecular-thermodynamic models. The second iterative procedure uses these *K* factors to perform flash calculations yielding the relative amounts and compositions of the phases: gas, aqueous liquid, and hydrocarbon liquid. Initialization of this three-phase flash routine leads to nonconvergence problems for multicomponent systems; these systems are hence not included in this work. The third iterative routine iterates around the flash routine to solve for the fraction of the total water in the ice phase. The fourth and final routine iterates around the other routines to solve for the hydrate-point pressure where the fugacity of water in the hydrate phase is equal to that in any other phase. Several special cases exist that allow simplification of this general procedure.

Amount of Methanol Needed for Inhibition

Some hydrate-inhibition applications require a method for calculating the amount of methanol needed to prevent hydrate formation at a fixed pressure, temperature, and gas composition. Since the program calculates hydrate-formation pressures at a given temperature and methanol composition, for the gas mixture of interest we must first prepare a plot similar to Figure 11. Using these graphical data, we prepare a crossplot giving hydrate-formation temperature as a function of methanol concentration for the isobars of interest. Figure 12 shows several isobars for the gas mixture of Figure 11. Figure 12 is similar to the freezing-point-depression diagram shown in Figure 3. Figure 12 enables us to obtain the desired methanol composition. To illustrate, let us assume that we have a gas mixture of the composition of Figures 11 and 12, saturated with water at 20 bar (2 MPa) and 300 K. We now wish to compress this gas to 50 bar (5 MPa) and then cool it to 270 K without hydrate formation. By performing a flash calculation, we find that the initial gas contains 1.889×10^{-3} mol frac. water. Using Figure 12, we find that to prevent hydrate formation at 270 K and 50 bar, we require 0.336 wt. frac. (0.221 mol frac.) methanol in the aqueous-liquid phase. Assuming that all of the water in the initial gas

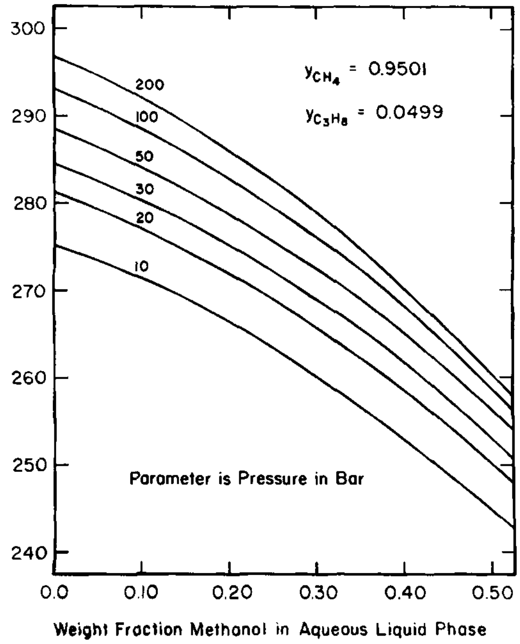

Figure 12. Hydrate-point depression by methanol for a gas mixture.

and all of the added methanol condense into the liquid phase, we must add at least 4.184 × 10^{-4} mol of methanol per mole of inlet gas.

Acknowledgment

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Notation

a = Kihara hard-core parameter for component j
$a(T)$ = Redlich-Kwong constant
B_{ii} = second virial coefficient of component i
b = Redlich-Kwong constant
$C_{mj}(T)$ = Langmuir adsorption constant for component j on cavity type m
f = fugacity
f_w^α = fugacity of water in ice phase
f_i^o = reference state fugacity for pure liquid i
f_w^β = fugacity of water in the hypothetical empty-hydrate lattice
f_w^H = fugacity of water in the hydrate phase
H_{ij} = Henry's constant for component i in liquid j
Δh_w^{fus} = enthalpy of fusion of water
$\Delta h_w^{\beta-\alpha}$ = enthalpy difference between empty hydrate lattice and ice
k = Boltzmann's constant
k_{ij} = binary parameter for Redlich-Kwong $a(T)_M$
P = pressure (absolute)
P_i^{sat} = vapor pressure of component i
R = gas constant
r = radial distance in hydrate cavity
T = temperature (absolute)
T_t = triple-point temperature of water
υ_w^α = molar volume of ice
$\bar{\upsilon}^\infty$ = partial molar volume at infinite dilution
$\Delta\upsilon_w^{\beta-\alpha}$ = difference in volume between empty hydrate lattice and ice
$\Delta\upsilon_w^{fus}$ = change in volume of water upon fusion
x = liquid phase mole fraction
y = gas phase mole fraction

Greek letters

γ = activity coefficient
ϵ = Kihara energy parameter
ν_m = number of cavities of type m per water molecule in hydrate
μ_w^α = chemical potential of water in ice phase
μ_w^β = chemical potential of water in empty hydrate lattice
μ_w^H = chemical potential of water in hydrate phase
$\Delta\mu_w^o$ = standard-state chemical potential difference between hydrate and ice
$\Delta\mu_w^{\beta-H}$ = difference in chemical potential of water between empty and filled hydrate lattice
$\Delta\mu_w^{\beta-\alpha}$ = difference in chemical potential of water between empty hydrate lattice and ice
$\Delta\mu_w^{\beta-L}$ = difference in chemical potential of water between empty hydrate lattice and pure liquid water
ρ = molar density
σ = Kihara size parameter
ϕ = fugacity coefficient
$\omega_{mj}(r)$ = cavity potential function for component j in cavity type m

Superscripts

α = ice phase
β = hypothetical empty hydrate lattice phase
$\beta - \alpha$ = difference between empty hydrate lattice and ice
$\beta - H$ = difference between empty and filled hydrate lattices
$\beta - L$ = difference between empty hydrate lattice and pure liquid water
G = gas phase
$H1$ = hydrate structure I phase
$H2$ = hydrate structure II phase
$L - \alpha$ = difference between liquid and ice
$L1$ = aqueous liquid phase
$L2$ = natural gas liquid phase
sat = saturation conditions
o = standard state
(0) = reference term in perturbation expansion
(1) = first term in perturbation expansion
(2) = second term in perturbation expansion
(3) = third term in perturbation expansion

Subscripts

i, j = component
M = mixture
m = cavity type
w = water

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