

Luyben, W. L., *Process Modeling, Simulation, and Control for Chemical Engineers*, McGraw-Hill, New York (1973).  
Miller, J. A., A. M. Lopez, C. L. Smith, and P. W. Murrill, "A Comparison of Controller Tuning Techniques," *Control Engineering*, **14**, No. 12, 72 (1967).  
Murrill, P. W., *Automatic Control of Processes*, International Textbook Co., Pennsylvania (1967).  
Pemberton, T. J., "PID: The Logical Control Algorithm," *I: Control Engineering*, **19**, No. 5, 66 (1972a).

Pemberton, T. J., "PID: The Logical Control Algorithm—II," *Control Engineering*, **19**, No. 7, 61 (1972b).  
Yuwana, M., M.S. Thesis, "Controller Tuning Based on Closed-Loop Process Identification," University of California, Santa Barbara (1980).  
Ziegler, J. G. and N. B. Nichols, "Optimum Settings for Automatic Controllers," *Trans. ASME*, **64**, 759 (1942).

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# Multiple-Phase Equilibria in Hydrates from Methane, Ethane, Propane and Water Mixtures

Phase-equilibrium conditions for multicomponent hydrocarbon-water mixtures were experimentally determined, demonstrating that both structure I and structure II hydrates can form from a single mixture. Model parameters were optimized to allow prediction of the hydrate structure, and prediction of the pressure and temperature of hydrate formation for the experimental mixtures.

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## SCOPE

In the past five years, the existence of natural gas hydrates in the earth has become a subject of increasing concern since hydrates may impede the production of petroleum and natural gas from reservoirs where these crystalline structures can be formed (Holder et. al., 1976). This interest has been fueled by studies which suggest that hydrates may exist under the ocean (Stoll et. al., 1971), an occurrence which supports the possibility of vast reserves of natural gas existing in hydrate form.

In efforts to develop a generalized procedure for predicting hydrate formation in the earth, the lack of compositionally quantitative, experimental hydrate data for multicomponent mixtures is evident. In particular, no data has been presented showing that an equilibrium locus exists for structure I and structure II hydrate phases. In this paper, the ethane-propane-water and methane-ethane-propane water systems are studied

to provide a better data base for theoretically calculating hydrate dissociation pressures, and to provide experimental evidence for the existence of hydrate I-hydrate II equilibria.

For prediction of hydrate-hydrate equilibria, Parrish and Prausnitz's (1972) widely used algorithm for determining hydrate equilibrium conditions is modified by using the data obtained in this and previous studies to obtain model parameters. By optimizing the experimentally undetermined zero-point properties (the enthalpy and chemical potential differences between the unoccupied hydrate lattice and ice at 273 K and zero pressure) a more accurate predictive scheme is developed. This method enables the prediction of hydrate formation from hydrocarbon-rich liquids and vapors whenever a water-rich liquid phase co-exists.

## CONCLUSIONS AND SIGNIFICANCE

Hydrates formed from certain mixtures of ethane-propane and methane-ethane-propane may form structure I crystals under certain *P-T-x* conditions and structure II crystals under other *P-T-x* conditions. Consequently, the methane-ethane-propane-water system exhibits several quadruple and one quintuple point loci where two liquids, two solids and a vapor are all in equilibrium. Because two different hydrate structures can form in this system, hydrate formers such as ethane may exhibit unusual anti-freeze behavior.

In predicting hydrate-forming conditions for all systems consisting entirely of methane and/or ethane and/or propane, the optimal values for the zero-point thermodynamic properties

are in relatively good agreement with those expected from theoretical considerations although the zero-point enthalpic differences between the empty hydrate and ice are markedly different from those used by Parrish and Prausnitz (1972). In addition to prediction of three-phase (water rich liquid-hydrate-vapor) equilibria, this work predicts the quintuple and quadruple point loci displayed by this system. A generalization of the method used could be applied to predicting hydrate formation from multicomponent mixtures containing both hydrate-formers (butanes and lighter) and non-hydrate-formers (pentane-plus) and could be used for predicting hydrate formation in the earth.

Hammerschmidt (1934) discovered that they were the cause of plugged natural gas pipelines. These studies, while primarily focused on determining the pressure and temperature conditions at which hydrates formed, also revealed that hydrates were non-stoichiometric compounds and that the number of gas molecules per water molecule in the equilibrium hydrate phase depends upon the temperature and pressure at which the hydrates are formed.

## INTRODUCTION

Gas hydrates, which are crystalline compounds composed of water and dissolved gas, have been studied extensively since

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TABLE 1. LATTICE PROPERTIES OF STRUCTURE I AND STRUCTURE II HYDRATE

	Structure I	Structure II
Number of Large Cavities/Unit Cell	6	16
Number of Small Cavities/Unit Cell	2	8
Number of Water Molecules/Unit Cell	46	136
Large Cavity Diameter, pm	860	946
Small Cavity Diameter, pm	788	782

Much of this early work has been reviewed by Katz et al. (1959) and by Byk and Fomina (1968).

Gas hydrates generally form two structures, called structure I and structure II, with the water molecules forming a solid lattice structure having large interstitial vacancies or cavities which can be occupied by small gas molecules. Each structure has two types of cavities, one large and one small, as shown in Table 1. The gas molecules which occupy the cavities interact physically with the surrounding water molecules thereby stabilizing the structure. Not all of the available cavities need be occupied by a gas molecule, but a completely unoccupied or empty water lattice is metastable and does not exist. The structure which actually forms depends upon the molecular diameters of the gas molecules in the hydrate. In general, small molecules (such as methane or ethane) form structure I hydrate and large molecules (such as propane) form structure II. For gas mixtures the equilibrium hydrate structure depends upon the pressure, temperature and composition of the system.

In recent years, interest in gas hydrates has been stimulated by the discovery of oil and natural gas in colder climatic regions such as the North Slope of Alaska, and by the resulting implication of the existence of hydrates in the earth (Katz, 1971; Verma et al., 1975; Holder, Katz, Hand, 1976). Because of the permafrost layer, the reservoir temperature in these colder regions is relatively low when compared to pressure and temperature conditions within the earth at warmer latitudes. Since hydrate formation is favored by high pressures and low temperatures, some reservoirs in these regions actually have a hydrate phase present (Bily and Dick, 1974). Additional data supporting the hypothesis that hydrates exist within the earth has been presented by Stoll et al. (1971). In that report, acoustical evidence indicated that hydrates may exist in ocean sediments.

### Theoretical Model

The X-ray studies of Stackelberg and co-workers (Stackelberg and Muller, 1954) produced widely accepted structural models for hydrates I and II and, allowed the development of a statistical thermodynamic theory for describing the molecular interactions in hydrate crystals. The basic model, developed by van der Waals and Plateeuw (1959) enabled prediction of the hydrate dissociation pressure of any mixture of hydrate forming gases. This model assumed that no two gas molecules occupy the same lattice cavity, and that gas molecules in the lattice have the same rotational and vibrational partition functions as vapor phase molecules. In addition, the model assumes that a gas molecule interacts solely with the lattice water molecules nearest to it.

The governing equation produced by van der Waal's model predicts the chemical potential,  $\mu_H$ , of water in the hydrate lattice.

$$\mu_H = \mu_H^\beta + RT \sum_i \nu_i \ln \left( 1 - \sum_j y_{ji} \right) \quad (1)$$

where  $\mu_H^\beta$  is the "hypothetical" chemical potential of the empty lattice,  $\nu_i$  is the number of cavities of type  $i$  per lattice water molecule, and  $y_{ji}$  is the fraction of the  $i$  cavities occupied by a  $j$  mol-

ecule. This fractional occupancy is determined by a Langmuir type expression,

$$y_{ji} = \frac{C_{ji} f_j}{1 + \sum_k C_{ki} f_k} \quad (2)$$

where  $f_j$  is the fugacity of a  $j$  type gas molecule and  $C_{ji}$  is the temperature dependent Langmuir constant. If each cavity is considered to be an adsorption site, they  $y_{ji}$  gives the fraction of the cavities of type  $i$  occupied by each gas species  $j$ . As the pressure, and consequently the component fugacities, is increased, the fractional occupancies increase, but at finite pressures one hundred percent of the  $i$  type sites can never be occupied. This restriction is consistent with experimental results.

The Langmuir constant,  $C_{ji}$ , is calculated by integrating the gas-water potential interaction function over the volume of the cavity:

$$C_{ji} = \frac{4\pi}{RT} \int_{\text{volume}}^{\text{cell}} \exp(-w(r)/RT) r^2 dr \quad (3)$$

where  $r$  is the distance of an enclathrated gas molecule from the center of the cell, and  $w(r)$  is an appropriate intermolecular potential function, as discussed below. The Langmuir coefficient,  $C_{ji}$ , depends upon the cavity size, the temperature and the value of the potential function,  $w(r)$ . Clearly,  $C_{ji}$  is different for each cavity and, as a result, the fractional occupancies of the large and small cavities by any gas species will be different.

Many potential functions have been used for  $w(r)$ ; van der Waals and Plateeuw (1959) used the Lennard-Jones 12-6 potential and had mixed results in predicting hydrate dissociation pressures. McKoy and Sinanoglu (1963) tried other potential functions and found that the interaction of water with rod-like molecules, such as ethane, could be more accurately described by the Kihara line core potential. Instead of using potential parameters calculated from second virial coefficient data, Kobayashi and co-workers determined potential parameters for methane, nitrogen and argon hydrates (Marshall et al., 1964) by fitting experimental and calculated hydrate dissociation pressures. By fitting the potential parameters, accurate hydrate dissociation pressures could be predicted for the first time. Errors in predicted dissociation pressures were reduced from as much as one hundred percent to less than five percent. Parrish and Prausnitz (1972) expanded the concept of fitting hydrate parameters to develop a generalized method for predicting hydrate dissociation pressures of fifteen different gases and their mixtures. This work gave excellent results when predicting hydrate dissociation pressures of binary, gas-water mixtures and mixed results when predicting dissociation pressures of the few multi-component mixtures that have been studied. Recently, Ng and Robinson (1976) have added another adjustable parameter to this algorithm and have improved the prediction of specific multi-component dissociation pressures. This modified algorithm also predicts the conditions for hydrate formation from condensed systems.

The general value of these algorithms for predicting multi-component hydrate forming data has never been thoroughly investigated because of the sparcity of data on the hydrate forming pressures of well analyzed gas mixtures. Because of this lack of data, the multicomponent systems methane-ethane-propane-water and ethane-propane-water, were studied in the present work. The results show not only solid-gas-liquid equilibria but also solid-solid-gas-liquid equilibria for these systems and consequently indicate that the prediction of hydrate dissociation pressures of multi-component mixtures may be more complicated than previous studies have indicated.

### Experimental

The apparatus used for measuring hydrate equilibrium conditions, shown schematically in Figure 1, consisted of a glass windowed high pressure cell in which the hydrates were formed from gas and liquid mixtures. A calibrated chromel-alumel thermocouple and a high accuracy Heise gauge provided the temperature and pressure readings. The high pressure hand pump was used for injecting distilled water into the system at any pressure.

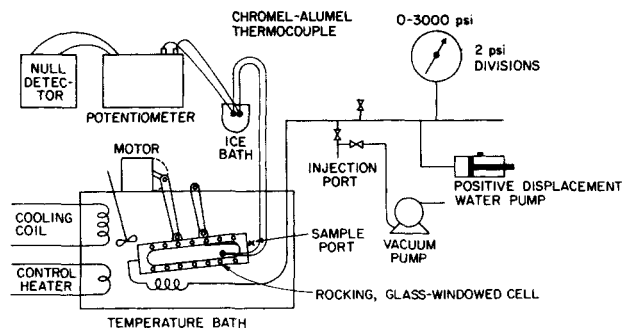


Figure 1. Experimental apparatus.

Experimental details are given elsewhere (Holder, 1976).

At the beginning of each experiment, the cell was evacuated and then charged quantitatively with water and with a gas mixture. A motor driven arm rocked the cell, causing inversion of the gas and liquid phases which allowed rapid equilibration. The temperature was then lowered until hydrates began to form. A freshly charged mixture would often have to be subcooled by 10 K before hydrate formation could be initiated, and often ice would form before the hydrates. The ice crystals provided nucleation sites for the subsequent rapid formation of hydrates. The temperature was then raised until the hydrates were, by visual observation, clearly melting. At this stage of the experiment, the temperature of the cell was cycled until only a single, minute crystal remained in the hydrate chamber. When the crystal remained stable, without significantly increasing or decreasing its size for at least 8 hours, the existing pressure and temperature were taken as the equilibrium hydrate point. Temperatures could be measured to a precision of  $\pm 0.01$  K and with an uncertainty of ( $\pm 0.05$  K) of the final hydrate temperature. Pressures could be read to 7 kPa and were accurate to better than 20 kPa. The gases used were all better than 99.5% pure.

### DISCUSSION OF EXPERIMENTAL RESULTS

The curves in Figures 2 and 3 are all labeled with a solid hydrate structure although these structures were not actually measured by X-ray or other direct means. Instead, the available information about the structures formed from ethane-water, methane-water and propane-water binary mixtures, together with some basic theoretical considerations, allow the equilibrium hydrate structure to be deduced with virtual certainty.

First consider the hydrate forming characteristics of the three above mentioned hydrate forming binary mixtures. Methane and ethane both form structure I hydrate although ethane apparently enters only the large cavities of structure I. Similarly, propane, which forms structure II hydrate, apparently enters only the large cavities of this structure. The molecular diameters of ethane and propane make these molecules too large to enter the small cavities

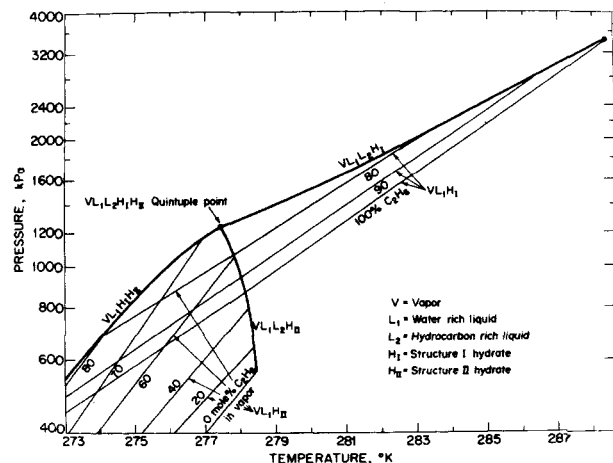


Figure 2. Overall hydrate diagram for hydrate formation from ethane-propane-water mixtures.

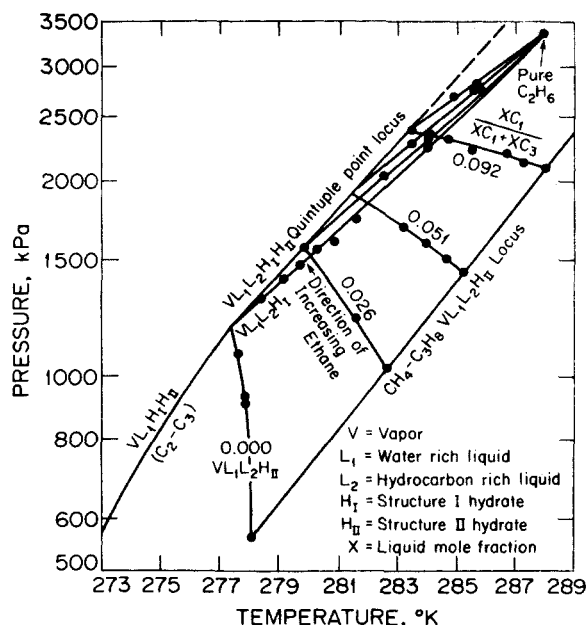


Figure 3. Pressure and temperature conditions of hydrate formation along  $VL_1L_2H$  curves of methane-ethane-propane-water mixtures.

of their respective structures. This is supported by the compositions of the hydrates. For one hundred percent occupancy of both hydrate cavities, the ratio of water molecules to gas molecules should have the values shown for complete occupancy,  $5\frac{3}{4}$  for structure I and  $5\frac{2}{3}$  for structure II, as shown in Table 6. For methane, the experimentally determined ratio is about 6, which requires that both structure I cavities be partially filled. For propane and ethane, however, the experimentally determined ratios are about 18 and 8 respectively (Ceccotti, 1966; Galloway et al., 1970). From these ratios, and from the sizes of the molecules involved, one can reasonably conclude that propane and ethane occupy only the large cavities of their respective structures.

Experiments have shown that methane-propane-water mixtures form only structure II hydrate for propane to methane ratios as low as 0.01 (and probably even lower). This phenomenon occurs because propane is too large to enter either cavity of structure I and consequently cannot contribute to the stability of this structure at all. Methane, however, can enter the small cavities of structure II hydrate and can contribute structural stabilization beyond that provided by propane. Consequently, most methane-propane mixtures form structure II hydrate when contacted with water.

In ethane-propane-water mixtures, the argument is more complex. Ethane forms structure I hydrate and cannot enter the small cavities of either structure I or II and propane forms structure II hydrate and likewise cannot enter the small cavities of either structure. Consequently, adding small amounts of ethane to a structure II forming propane-water mixture should not improve the stabilization of hydrate structure II. Instead, the ethane will act to dilute the propane mixture and cause the hydrate II dissociation pressure to rise. This is equivalent to causing the hydrate forming temperature to drop at a fixed pressure; therefore ethane should act as an antifreeze. Indeed, this is exactly what is observed experimentally as shown in Figure 4. At 690 kPa, the maximum temperature at which hydrates can exist, drops from 278.7°K to 274.6°K as the ethane mole fraction is increased from 40 to 78 percent. As the gas phase mole fraction of structure I forming ethane increases, and the mole fraction of structure II forming propane decreases, then the preference of the mixture for forming structure II hydrate also decreases. At fixed pressure, there will exist a composition where there is precisely enough ethane present to make structures I and II equally stable. At this point, both structures can exist in equilibrium. From this quadruple point up to 100% ethane, increases in the ethane mole fraction should serve to make structure I hydrate more stable and thereby raise the maximum

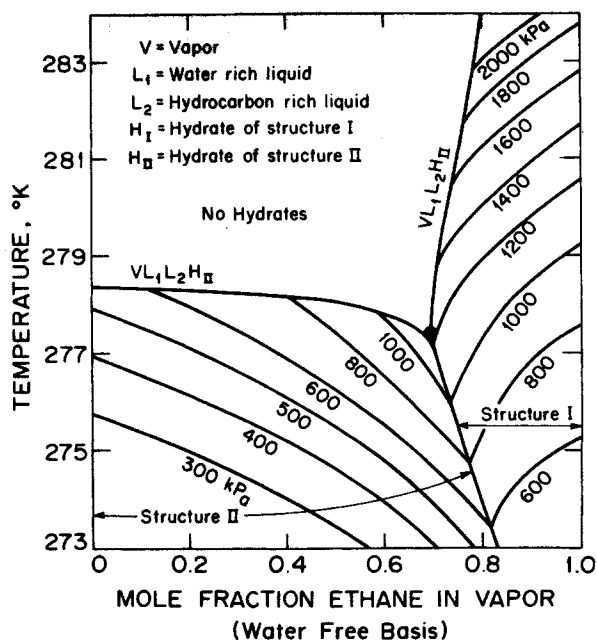


Figure 4.  $VL_1H$  hydrate isobars for the ethane-propane-water system.

hydrate forming temperature at the fixed dissociation pressure. Again, this expectation was experimentally verified; continuing along the 690 kPa isobar, the hydrate forming temperature increases to 276.7°K as the composition is increased to 100% ethane.

TABLE 2. VAPOR-WATER RICH LIQUID-HYDRATE THREE PHASE EQUILIBRIUM DATA FOR THE ETHANE-PROPANE-WATER SYSTEM

Temperature (K)	Pressure (kPa $\times 10^{-2}$ )		Structure
	Expt.	Smoothed	
<i>72% Propane (Vapor Composition)</i>			
277.9	6.6	6.6	II
276.9	5.3	5.2	II
276.5	4.6	4.7	II
<i>55.7% Propane</i>			
275.9	5.0	5.0	II
276.4	5.7	5.7	II
276.7	6.1	6.0	II
277.0	6.5	6.5	II
277.4	7.2	7.2	II
<i>54.1% Propane</i>			
275.8	5.0	4.9	II
276.4	5.9	5.8	II
277.0	6.6	6.6	II
277.6	7.7	7.7	II
278.0	8.5	8.5	II
<i>34.2% Propane</i>			
273.9	4.4	4.3	II
274.2	4.7	4.7	II
275.1	5.9	6.1	II
275.8	6.9	7.2	II
276.2	8.3	8.2	II
276.3	8.5	8.3	II
276.5	8.7	8.8	II
277.6	10.6	11.4*	II
<i>32.2% Propane</i>			
275.6	7.5	7.5	II
276.1	8.7	8.6	II
277.1	11.4	11.2 (11.4)**	II (I)
277.2	11.6	11.4 (11.6)**	I
277.9	12.2	12.2 (12.3)**	I
278.6	13.0	13.2*	I
279.4	14.3	14.2*	I
280.4	15.6	15.6*	I
280.6	16.1	15.9*	I
281.1	16.3	16.5*	I

TABLE II (continued)

Temperature (K)	Pressure (kPa $\times 10^{-2}$ )		Structure
	Expt.	Smoothed	
<i>27.1% Propane</i>			
273.4	4.9	4.8	II
273.9	5.4	5.4	II
274.3	6.1	6.0	II
274.6	6.0	6.6	II
275.3	7.7	7.9	II
275.6	8.7	8.6	II
275.8	9.2	9.1	II
<i>26.0% Propane</i>			
274.5	6.3	6.5	II
274.7	6.9	6.8	II
275.2	7.9	7.9	II
276.4	9.4	9.4	I
277.1	10.2	10.3	I
277.7	11.2	11.1	I
<i>18.6% Propane</i>			
273.1	5.4	5.4	II
273.8	6.4	6.3 (6.4)**	II (I)
273.8	6.4	6.3 (6.6)**	II (I)
274.3	6.6	6.8	I
274.7	7.1	7.2	I
276.8	9.4	9.3	I
278.9	12.1	12.1	I
279.6	13.0	13.0	I
<i>15% Propane</i>			
275.7	7.4	7.3	I
277.2	9.0	9.0	I
280.6	13.7	14.0	I
<i>14.3% Propane</i>			
279.7	11.9	12.1	I
280.2	13.0	13.0	I
282.1	16.7	17.0	I
283.2	20.3	20.2*	I
283.3	20.2	20.3*	I
<i>0% Propane</i>			
278.8	9.5	9.5	I
280.2	11.4	11.4	I
282.0	14.5	14.5	I
281.1	12.8	12.8	I
286.0	25.1	24.6	I
286.5	26.0	26.1	I
288.2	33.6	32.5	I

\* Hydrocarbon Rich Liquid may have been present.

\*\* Possible superheated hydrate existed at these points; parenthetical values represent the smoothed pressure if the alternative hydrate structure had been present.

Additional evidence to support the structural conclusions is given by the slopes of the hydrate curves on a plot of logarithm of pressure versus temperature (Figure 2). Since a gas phase is present, the enthalpy of hydrate formation along the  $VL_1H_1$  and  $VL_1H_2$  loci are given by a modification of the Clapeyron equation,

TABLE 3. LIQUID WATER-LIQUID HYDROCARBON-HYDRATE THREE PHASE EQUILIBRIUM DATA FOR THE ETHANE-PROPANE-WATER SYSTEM

Mole Fraction Ethane (Water Free)	Temperature (K)	Pressure (kPa $\times 10^{-2}$ )
0.168*	278.1	9.1
0.168	278.1	14.4
0.168	278.2	15.5
0.168	278.3	25.6
0.168	278.6	27.9
0.435*	279.9	14.7
0.435	279.9	23.0
0.435	280.2	51.8
0.435	280.6	65.5
0.689*	284.3	22.3
0.689	284.3	29.0
0.689	284.4	55.8
0.689	284.5	72.8

\*  $VL_1L_2H$  Quadruple Point.

TABLE 4. VAPOR-WATER RICH LIQUID-HYDROCARBON RICH LIQUID-HYDRATE ( $VL_1L_2H$ ) EQUILIBRIUM DATA FOR THE METHANE-ETHANE-PROPANE-WATER SYSTEM. COMPOSITIONS ARE FOR THE  $L_2$  PHASE.

Mole Fraction Ethane	Temperature (K)	Pressure (kPa $\times 10^{-2}$ )	Hydrate Structure
$x_{c1}/(x_{c1} + x_{c3}) = 0.0^{**}$			
0.168	278.1	9.0	II
—*	278.1	9.7	II
0.280	277.8	10.8	II
—	278.2	7.0	II
0.435	279.9	14.8	I
0.523	281.8	17.4	I
0.689	284.3	22.3	I
—	278.6	13.0	I
—	279.4	14.3	I
—	280.4	15.6	I
—	280.6	16.1	I
—	281.1	16.3	I
1.000	288.3	33.3	I
$x_{c1}/(x_{c1} + x_{c3}) = 0.0255$			
0.000	282.8	10.3	II
0.189	281.7	12.4	II
0.314	280.1	15.8	II
0.517	282.8	20.2	I
0.716	284.8	23.2	I
0.799	286.1	27.3	I
1.000	288.3	33.3	I
$x_{c1}/(x_{c1} + x_{c3}) = 0.051$			
0.082	284.9	15.0	II
0.181	284.2	16.1	II
0.231	283.5	16.8	II
0.549	283.7	21.8	I
0.726	285.7	27.3	I
1.000	288.3	33.3	I
$x_{c1}/(x_{c1} + x_{c3}) = 0.092$			
0.054	287.4	21.2	II
0.148	286.9	21.7	II
0.212	285.7	22.1	II
0.365	284.9	22.8	II
0.506	283.8	23.8	I
0.616	285.1	25.7	I
0.677	285.9	28.2	I
1.000	288.3	33.3	I

\* The composition was not measured at these points.  
\*\*  $c_1$  is methane;  $c_2$  is ethane;  $c_3$  is propane.

$$\frac{d \ln P}{dT} = \frac{\Delta H}{zRT^2} \quad (4)$$

where  $\Delta H$  is the enthalpy of formation per mole of hydrated gas,  $R$  is the gas constant and  $z$  is the compressibility factor. Here,  $\Delta H$

TABLE 5. A COMPARISON OF THE DIAMETERS OF METHANE, ETHANE AND PROPANE TO THE FREE DIAMETER OF THE CAVITIES IN STRUCTURE I AND STRUCTURE II HYDRATE

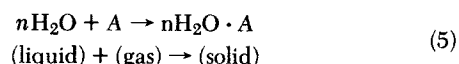
Molecule	Hydrate Structure	Hydrate Cavity	$R = \frac{\text{Molecular Diameter}}{\text{Free Cavity Diameter}}$
CH <sub>4</sub>	I	Large	0.575*
	I	Small	0.649*
	II	Large	0.504
C <sub>2</sub> H <sub>6</sub>	II	Small	0.659
	I	Large	0.652*
	I	Small	0.737
C <sub>3</sub> H <sub>8</sub>	II	Large	0.571
	II	Small	0.748
	I	Large	0.741
	I	Small	0.837
	II	Large	0.649*
	II	Small	0.849

\* These cavities are occupied in the hydrate which occurs from a binary mixture of the indicated alkane and water as determined by hydrate numbers of the crystals and assuming that the molecular diameter of water is 250 pm.

TABLE 6. RATIOS OF WATER MOLECULES/GAS MOLECULES FOR COMPLETE AND PARTIAL OCCUPANCY OF HYDRATE STRUCTURES

	Structure I	Structure II
Complete Occupancy	5-3/4	5-2/3
Only Large Cavities Occupied	7-2/3	17

is the enthalpy change for the following equation.



In this transformation,  $n$  water molecules are combined with each gas molecule,  $A$ , which can be methane, ethane, or propane. Because the ratio of water molecules to gas molecules,  $n$ , is not sensitive to pressure and because propane does not enter structure I hydrate, the enthalpy change due to the formation of structure I hydrate from ethane-propane mixtures is nearly independent of the mole fraction of ethane in the water free gas phase. Thus, all structure I hydrate forming mixture should have the same slope as the  $VL_1H_I$  curves of ethane. Examination of Figure 2 shows that this is the case. Similar arguments can be made to show that structure II forming mixtures should have nearly the same slope as the  $VL_1H_{II}$  curve of propane. Again this is verified by Figure 2.

For methane-ethane-propane water mixtures similar arguments can be made to support the above structural conclusions. Figure 5 shows the "antifreeze" effect that ethane has on structure II hydrate and shows the existence of a five phase  $VL_1L_2H_IH_{II}$  locus for this system.

The effect of methane on the equilibrium structure in the four component system is small. Table 5 shows the ratio,  $r$ , of the Kihara molecular diameters of methane, ethane and propane to the free cavity diameter for each of the cavities in structure I and structure II hydrate. The free cavity diameter, as used here, is just the cavity diameter (Table 1) less the diameter of a water molecule. The water molecule's diameter is subtracted to account for the protrusion of the lattice water molecules into the hydrate cage from both sides of the cavity.

This table indicates that the hydrate is stabilized when the value of  $r$  is about 0.65. Because of similar values of  $r$  for the small cavities of both structures, methane can stabilize each structure equally well. Consequently, the primary compositional influences on the hydrate structure are the relative amounts of ethane and propane. This statement is also supported by data for the methane-pro-

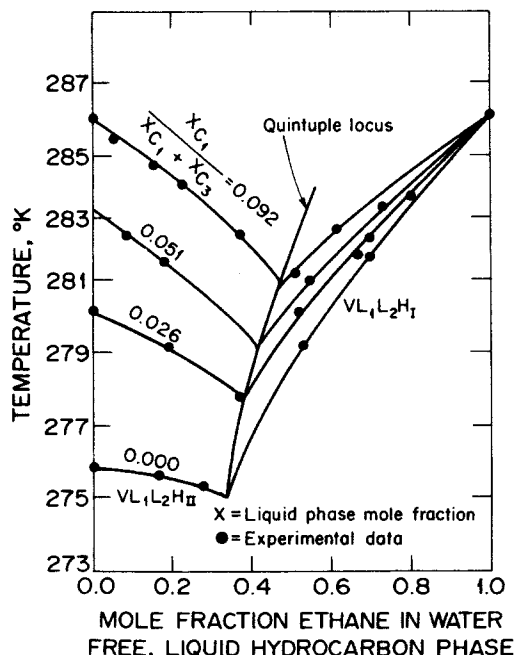


Figure 5. Effect of ethane on  $VL_1L_2H$  temperature for methane-ethane-propane-water mixtures.

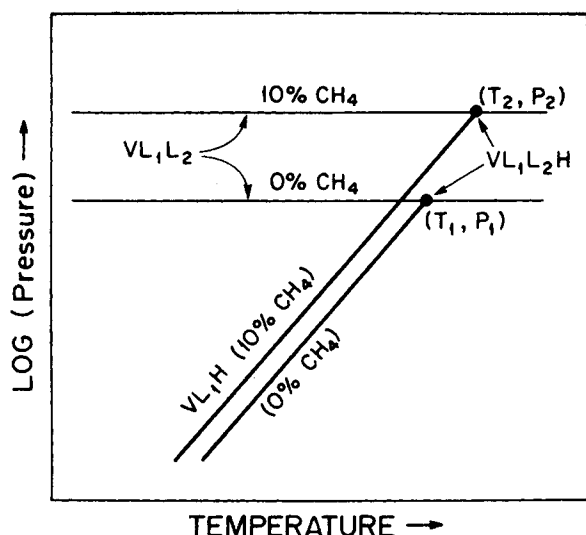


Figure 6. Schematic  $P$ - $T$  diagram showing the effect of methane on the  $VL_1L_2H$  temperature and pressure in the quaternary system.

pane-water system where only a small amount of propane (much less than 1%) is needed to enable methane to stabilize structure II hydrate, even though pure methane will form only structure I hydrate.

It should be noted, however, that even though the addition of methane to ethane-propane liquids causes a large increase in the vapor pressure of such liquids, the addition of methane causes only a small rise in the hydrate dissociation pressure because methane increases the stabilization of the hydrate. The combined effects, shown in Figure 6, show why methane generally causes a rise in both the temperature and pressure at the  $VL_1L_2H$  hydrate point.

#### Prediction of Hydrate Dissociation Pressures

An algorithm for predicting hydrate-gas-water equilibria was developed and used for predicting equilibria in mixtures containing a methane-ethane-propane gas phase and a liquid water phase. In addition to predicting  $VL_1H$  equilibria, the program can be used to predict equilibria with an additional liquid phase ( $VL_1L_2H$ ), an additional solid phase ( $VL_1H_1H_{II}$ ) or both ( $VL_1L_2H_1H_{II}$ ). The ability to predict these quadruple and quintuple point loci is obtained through a modification of the approach described by Parrish and Prausnitz (1972).

To obtain the best possible agreement between experimental and calculated dissociation pressures, the three Kihara parameters for each gas were adjusted individually using a Golden Section search for the optimal values. These three parameters are the molecular diameter,  $\sigma$ , the potential well depth,  $\epsilon$ , and the core radius,  $a$ . In addition to these individual gas parameters, three system properties, were also calculated. These properties are the differences in en-

TABLE 7. KIHARA PARAMETERS FOR THE INTERACTION OF METHANE, ETHANE AND PROPANE WITH WATER, PARAMETERS ARE FOUND BY A LEAST SQUARES FIT BETWEEN CALCULATED AND EXPERIMENTAL DISSOCIATION PRESSURES. PARENTHEetical VALUES ARE CALCULATED USING VISCOSITY AND SECOND VIRIAL COEFFICIENT DATA AND ASSUMING  $\sigma_{H_2O} = 250$  pm.

Parameter	Unit	Methane	Ethane	Propane
$\sigma$	pm	318.8 (300.3)	315.5 (323.9)	332.0 (351.0)
$\epsilon/k$	K	150.73 (150.7)	174.77 (204.0)	209.02 (219.7)
$a$	pm	033.3 (038.3)	055.8 (056.5)	064.6 (065.0)

TABLE 8. OPTIMIZED THERMODYNAMIC PROPERTIES FOR STRUCTURE I AND STRUCTURE II HYDRATES AT 273.16 K AND 0 PRESSURE

Variables	Opt. value (This work)	Literature Values
$\Delta h_{w,I}$ (J/mol)	-5627	-6008, <sup>c</sup> -4857 <sup>a</sup>
$\Delta h_{w,II}$ (J/mol)	-6008	-6008, <sup>c</sup> -5213, <sup>b</sup> -5201 <sup>a</sup>
$\Delta \mu_{w,I}$ (J/mol)	1155	1264, <sup>a</sup> 699, <sup>c</sup> 732, <sup>d</sup> 900 <sup>d</sup>
$\Delta \mu_{w,II}$ (J/mol)	—*	883 <sup>a</sup>
$\Delta v_{w,I}$ (cc/mol)	—*	4.60 <sup>a</sup>
$\Delta v_{w,II}$ (cc/mol)	—*	5.00 <sup>a</sup>

\* Parrish and Prausnitz (1972).

<sup>b</sup> Child (1964).

<sup>c</sup> van der Waals and Platteeuw (1959).

<sup>d</sup> Estimated from hydrate number of ethane from Galloway et al. (1970).

\* The literature values for these properties have been directly derived from experimental data.

thalpy,  $\Delta h_{w,I}$  and  $\Delta h_{w,II}$ , between the unoccupied hydrate lattices and ice at 0°C and zero pressure, and the difference in chemical potential  $\Delta \mu_{w,I}$ , at the same conditions. A least squares fit between experimental and calculated dissociation pressures was the criterion for selecting the final values for the Kihara parameters and the system properties.

Parrish and Prausnitz (1972) fitted the Kihara parameters,  $\sigma$  and  $\epsilon$ , for ethane, methane and propane by forcing agreement between the experimental and calculated  $VL_1H$  dissociation pressures of the binary gas-water mixtures. Excellent fits between calculated and experimental pressures were obtained for these binary mixtures since most  $VL_1H$  data are linear on logarithm of pressure versus temperature plots and not difficult to fit with two parameters. However, when these values are used to predict dissociation pressures of multicomponent mixtures, accuracy is decreased, although still fair in many cases.

In this study, the three spherical core Kihara parameters describing the interaction between each enclathrated gas molecule and the water molecules of the cage were fitted to binary and ternary hydrate data, resulting in the values shown in Table 7. For comparison, values calculated using pure gas component Kihara parameters deduced from viscosity and second virial coefficient data, values for water of  $\sigma_{H_2O} = 250$  pm (estimated from water's van der Waals radius),  $(\epsilon/k)_{H_2O} = 97.8$  K (from  $\epsilon_{mix}$  of methane) and  $a_{H_2O} =$  (McKoy and Sinanoglu, 1963) and the mixing rules:

$$\begin{aligned} \sigma_{mix} &= \frac{1}{2}(\sigma_{H_2O} + \sigma_{gas}) \\ \epsilon_{mix} &= (\epsilon_{H_2O} \cdot \epsilon_{gas})^{1/2} \\ a_{mix} &= \frac{1}{2}(a_{H_2O} + a_{gas}) \end{aligned} \quad (6)$$

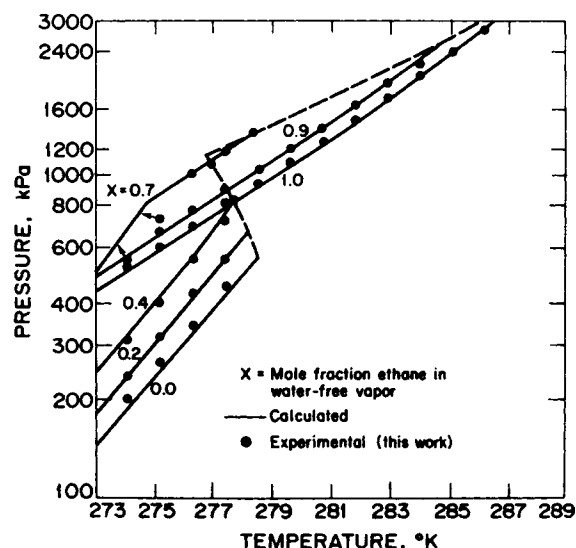


Figure 7. Comparison of experimental and calculated dissociation pressures of  $VL_1H$  hydrate curves of ethane-propane-water mixtures.

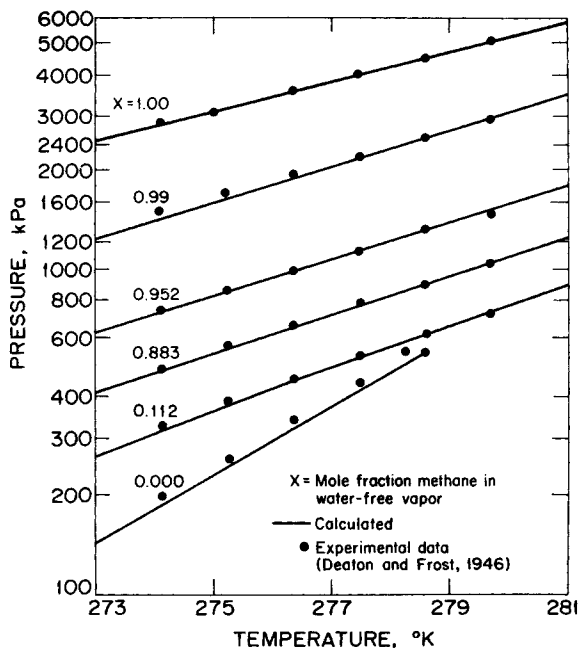


Figure 8. Comparison of experimental and calculated dissociation pressures of  $VL_1H$  hydrate curves of methane-propane-water mixtures.

are shown in parentheses. Dissociation pressures were found to be insensitive to values of the core radius,  $a$ , and this third adjustable parameter could be eliminated in future studies. The justification for fitting the Kihara parameters rather than using those from viscosity or second virial coefficient is purely pragmatic; it increases the accuracy of prediction.

The three system properties,  $\Delta h_{w,I}$  (0°C, 0 kPa),  $\Delta h_{w,II}$  (0°C, 0 kPa) and  $\Delta\mu_{w,I}$  (0°C, 0 kPa) are the same regardless of the gas mixture that is present. They are analogous to standard state enthalpies and free energies in that they are the reference points for calculating the change in properties of the hydrate phase with temperature and pressure. These three properties are adjusted to force agreement between experimental and calculated dissociation pressures. Values are used to calculate the chemical potential of the hydrate at any temperature  $T$  from the following equation:

$$\frac{\Delta\mu_w(T,P)}{RT} = \frac{\Delta v_w(P - P_R)}{RT} + \frac{\Delta\mu_w(T_o,0)}{RT_o} + \frac{\Delta v_w(P_R)}{RT_o} + \int_{T_o}^T \left( \frac{\Delta h_w}{RT^2} + \frac{\Delta v_w}{RT} \left( \frac{dP}{dT} \right)_R \right) dT - \ln x_w \quad (7)$$

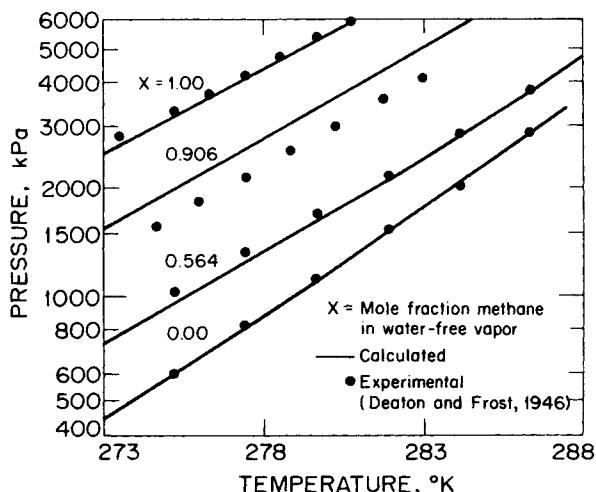


Figure 9. Comparison of experimental and calculated dissociation pressures of  $VL_1H$  hydrate curves of methane-ethane-water mixtures.

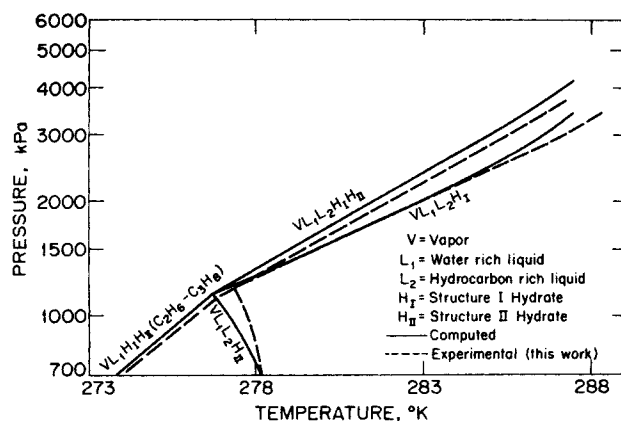


Figure 10. Comparison of experimental and calculated dissociation pressures of  $VL_1L_2H$ ,  $VL_1H_1H_{II}$  and  $VL_1L_2H_1H_{II}$  hydrate curves of methane-ethane-propane-water mixtures.

where  $T_o$  is the ice-point temperature 273 K,  $\Delta\mu_w$  is the difference of chemical potential between the unoccupied hydrate and water;  $\Delta v_w$  and  $\Delta h_w$  are the corresponding volume and enthalpy changes respectively;  $P_R$  is the experimentally determined dissociation pressure of a reference hydrate; and  $(dP/dT)_R$  is the temperature dependent slope of that reference hydrate. The quantities  $\Delta\mu_w(T_o,0)$ ,  $\Delta h_w(T_o)$  and  $\Delta v_w$  are given in Table 8. In these equations,  $\Delta h_w$  is assumed to vary with temperature according to the following equation:

$$\Delta h_w(T) = \Delta h_w(T_o) + \int_{T_o}^T \Delta C_{p_w} dT \quad (8)$$

where  $\Delta C_{p_w}$  is  $-38.1 + 0.14(T - T_o)$  J/mol/K (Parrish and Prausnitz, 1972).  $x_w$  is the mole fraction water in the water rich liquid phase. At any temperature, the equilibrium dissociation pressure is calculated by finding the pressure at which  $\Delta\mu_w$  from Eq. 7, is equal to  $\mu_H^g - \mu_H$  from Eq. 1. Note that structural consistency must be maintained when using Eqs. 7 and 8.

Examination of Table 7 shows that a wide range of values exist in the literature for the properties which were optimized. The values suggested by Child (1964), however, appear to be based upon a modification of equation 1 and may be inconsistent with the generally accepted theory. Van der Waals suggested that ice and hydrate have the same enthalpy ( $\Delta h_w = -6,008$  J/mol) since hydrate and ice structures have similar molecular arrangements and bonds. The optimized value for  $\Delta\mu_{w,I}$  is close to that used by Parrish and Prausnitz (1972) and is reasonable in comparison with  $\Delta\mu_{w,II}$  which has the experimentally determined value of 883 J/mol.

In optimizing these parameters, several starting values were used including the theoretical values and the values suggested by Parrish and Prausnitz (1972) but in each case the same optimal values were obtained. If the model is adjusted to allow ethane to enter all the hydrate cavities instead of just the large ones, the calculated dissociation pressures are poor, even after optimization of the various parameters. The final values chosen give the best fit between experimental and calculated dissociation pressures. The results, shown in Figures 7-10, are generally good, although the experimental methane-ethane-water data of Deaton and Frost (1949) with 90.6% methane in the water free vapor do not agree well with the calculated results. Also, the ethane-propane water data with 70% ethane does not agree well with the calculated values for structure II forming hydrate although the fit for this mixture is good in the temperature range that forms structure I hydrate. In methane-ethane mixtures, the ethane stabilizes structure I to a greater extent than methane, so that in both of these cases where the error is large, the concentration of gas which stabilizes the hydrate to the greater extent is small, thus magnifying any error caused by an incorrectly measured composition.

A comparison of the accuracy of the computed results to those obtained using the Kihara parameters of Parrish and Prausnitz

TABLE 9. COMPARISON OF CALCULATED AND EXPERIMENTAL VAPOR-LIQUID WATER-HYDRATE DISSOCIATION PRESSURES FOR METHANE-ETHANE-PROPANE-WATER VAPORS

Vapor Composition (Mol Fractions)	Temperature (K)	Pressure, Expt.	(kPa $\times 10^{-2}$ ) Calc.
	279.8	12.5	13.0
CH <sub>4</sub> - 0.174	280.5	13.9	14.4
C <sub>2</sub> H <sub>6</sub> - 0.705	281.4	15.9	16.3
C <sub>3</sub> H <sub>8</sub> - 0.121	282.2	17.8	18.0
	284.0	21.7	23.2
	281.4	17.2	17.9
CH <sub>4</sub> - 0.364	282.5	20.1	20.7
C <sub>2</sub> H <sub>6</sub> - 0.541	283.8	23.4	24.3
C <sub>3</sub> H <sub>8</sub> - 0.095	285.0	27.6	28.8
	275.8*	9.2	9.9
CH <sub>4</sub> - 0.454	280.8	16.8	18.1
C <sub>2</sub> H <sub>6</sub> - 0.457	282.1	18.8	21.3
C <sub>3</sub> H <sub>8</sub> - 0.089	285.2	27.6	31.2

\* Structure II hydrate formed (based upon calculated results). Other values are Structure I hydrate.

(1972) shows that the parameters from this work give a more accurate prediction over the indicated temperature range.

#### Calculation of Dissociation Pressures of Multicomponent Mixtures

Ultimately, this model must be able to predict hydrate dissociation pressures of multicomponent mixtures. A prediction was attempted for the quaternary methane-ethane-propane-water systems, with the results shown in Table 9. The average error for all three mixtures is 5.6% indicating that the procedure is generalizable. The mixture containing the most methane produced the largest relative error. This is expected since this mixture has dissociation pressures nearer to structure I—structure II equilibrium conditions where errors tend to be largest.

In Figure 10, calculated hydrate curves for several quadruple loci and for the methane-ethane-propane-water quintuple point locus are compared to experimental results. The general shape of the calculated curves is in excellent agreement with the experimental curves which all lie to the right of the calculated curves. Errors in these curves could partially be attributed to the errors in calculating vapor-liquid equilibria and to the fact that the effect of water was ignored in vapor-liquid equilibria calculations (but not in hydrate-liquid equilibrium calculations).

Overall, the program allows calculation of the hydrate curves of methane-ethane-propane mixtures with good accuracy. This program could be extended to include multicomponent mixtures whose Kihara parameters have been determined.

#### LITERATURE CITED

- Bily, C., and J. W. L. Dick, "Naturally Occurring Gas Hydrates in the MacKenzie Delta, N. W. T.," *Bull. Can. Pet. Geo.*, **22**(3), 340 (1974).  
 Byk, S. Sh., and V. I. Fomina, "Gas Hydrates," *Russian Chemical Reviews*, **37**(6), 469 (1968).  
 Cecotti, P. J., "Crystallization of Gas Hydrates from the Vapor Phase," *Ind. Eng. Chem. Fund.*, **5**(1), 106 (1966).  
 Child, W. C., Jr., "Thermodynamic Functions for Metastable Ice Structures I and II," *J. Phys. Chem.*, **68**(7), 1834 (1964).  
 Deaton, W. M. and E. M. Frost, "Gas Hydrates and Their Relationship to the Operation of Natural Gas Pipelines," *U.S. Bur. of Mines Monograph*, **8** (1946).  
 Galloway, T. J., W. Ruzka, P. S. Chappellear, and R. Kobayashi, "Experimental Measurement of Hydrate Numbers for Methane and Ethane and Comparison with Theoretical Values," *Ind. Eng. Chem. Fund.*, **9**(2), 237 (1970).  
 Hammerschmidt, E.G., "Formation of Gas Hydrates in Natural Gas Transmission Lines," *Ind. Eng. Chem.*, **26**, 851 (1934).  
 Holder, G.D., "Multi-Phase Equilibria in Methane-Ethane-Propane Hydrate Forming Systems," Ph.D. Thesis, University of Michigan, Ann Arbor (1976).  
 Holder, G. D., D. L. Katz, and J. H. Hand, "Hydrate Formation in Sub-surface Environments," *AAPG Bull.*, **60**(6), 981 (1976).

- Katz, D. L., D. Cornell, R. Kobayashi, F. H. Poettman, J. A. Vary, J. R. Elenbass, and C. F. Weinaug, "Handbook of Natural Gas Engineering," McGraw-Hill, New York (1959).  
 Katz, D. L., "Depths to which Frozen Gas Fields (Gas Hydrates) May Be Expected," *J. Pet. Tech.*, **23**, 419 (1971).  
 Marshall, D. R., S. Saito, and R. Kobayashi, "Hydrates at High Pressures: Part I, Methane-Water, Argon-Water and Nitrogen-Water Systems," *AIChE J.*, **10**(2), 202 (1964).  
 McKoy, V., and O. Sinanoglu, "Theory of Dissociation Pressures of Some Gas Hydrates," *J. Chem. Phys.*, **38**, 2946 (1963).  
 Ng, H. J., and D. B. Robinson, "The Measurement and Prediction of Hydrate Formation in Liquid Hydrocarbon-Water Systems," *Ind. Eng. Chem. Fund.*, **15**(4), 293 (1976).  
 Parrish, W. R., and J. M. Prausnitz, "Dissociation Pressures of Gas Hydrates Formed by Gas Mixtures," *Ind. Eng. Chem. Proc. Des. Dev.*, **11**, 26 (1972).  
 Stackelberg, M. Von and H. R. Muller, "Tests Gashydrate II," *Zeit. Electrochem.*, **58**, 25 (1954).  
 Stoll, R. O., J. Ewing, and G. M. Bryan, "Anomalous Wave Velocities in Sediments Containing Gas Hydrates," *J. Geo. Res.*, **76**(8), 2090 (1971).  
 van der Waals, J. H., and J. C. Platteeuw, "Clathrate Solutions," *Adv. Chem. Phys.*, **2**(1) (1959).  
 Verma, V. J., D. L. Katz, J. H. Hand, and G. D. Holder, "Denuding Hydrocarbon Liquids of Natural Gas Constituents by Hydrate Formation," *J. Pet. Tech.*, **27**, 223 (1975).

#### NOTATION

- $a$  = Kihara core radius, pm  
 $\Delta C_{pw}$  = difference in heat capacity between hydrate lattice and liquid water, J/mol/K  
 $C_{ji}$  = Langmuir constant for component  $j$  in cavity  $i$ , kPa<sup>-1</sup>  
 $\Delta h_w$  = difference in enthalpy between hydrate lattice and water, J/mol  
 $H$  = hydrate phase  
 $\Delta H$  = change in enthalpy for hydrate formation, J/mol  
 $L_1, L_2$  = water rich and hydrocarbon rich liquid phases, respectively  
 $P$  = pressure, kPa  
 $r$  = radial cavity position, pm  
 $R$  = gas constant, J/mol/K  
 $T$  = temperature, K  
 $T_o$  = zero-point temperature (273.16 K)  
 $\Delta v_w$  = difference in molar volume between empty hydrate lattice and water, cc/mol  
 $V$  = vapor phase  
 $w$  = spherically symmetric cell potential,  $J$   
 $y_{ji}$  = fraction of cavities of type  $i$  occupied by a  $j$  molecule

#### Greek Letters

- $\epsilon$  = depth of Kihara spherical core potential well,  $J$   
 $\sigma$  = Kihara distance parameter, pm  
 $\nu_i$  = number of cavities of type  $i$  per water molecule in hydrate  
 $\Delta \mu_w$  = difference in chemical potential between hydrate lattice and water, J/mol

#### Subscripts

- $H$  = indicates hydrate phase  
 $I, II$  = indicates Structure I and Structure II hydrate respectively  
 $R$  = indicates reference hydrate  $VL_1H$  pressure-temperature point or curve  
 $W$  = indicates water phase

#### Superscripts

- $\beta$  = indicates empty hydrate lattice phase

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