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THE EFFECT OF THE INHIBITORS
POTASSIUM CHLORIDE, CALCIUM CHLORIDE, AND METHANOL
ON CYCLOPROPANE HYDRATE FORMATION CONDITIONS

BY

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A thesis submitted to the Faculty and Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Chemical and Petroleum-Refining Engineering.

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ABSTRACT

The effect of inhibitors on hydrate formation was investigated in this work. The dissociation pressure elevation was experimentally determined in a cyclopropane-water-inhibitor system. These dissociation curves (P vs. T) were found to agree within 2 % with predicted curves obtained from a statistical thermodynamic model.

The inhibitors used were calcium chloride (CaCl_2), potassium chloride (KCl), and methanol (CH_3OH). The salt concentrations used were 0.1, 0.5, and 1.0 mole per liter. Methanol was used at concentrations of 0.5, 1.0, and 5.0 moles per liter. The temperature range of the experiments was 0-4 °C, with pressures ranging from 0 to 2000 Torr (mm Hg corrected to 0 °C). Dissociation pressures were determined at various temperatures for each inhibitor concentration after equilibrium was attained.

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INTRODUCTION

The formation of natural gas hydrates was first brought to the attention of the natural gas industry by Hammerschmidt (1) in 1934, when he determined that freezing of gas lines was not due to ice, but gas hydrates. Since that time, industry has become increasingly involved in the prevention of hydrate formation in transmission pipelines and equipment. In addition, hydrates have more recently been found to exist in great abundance in formations in the producing areas of Russia, Canada and Alaska (2,3,4). With a diminishing international supply of fossil fuel reserves, the production of the natural gas bound in hydrate form is of great interest.

The methods now widely used for combating hydrate formation are: (1) dehydration of the gas, (2) reducing pressure below hydrate formation, (3) raising temperature above hydrate formation, or (4) introducing an inhibitor (alcohol or electrolyte) into the system which will lower the temperature (or, correspondingly, raise the pressure) at which the hydrate forms. In many cases, the use of an inhibitor is the most practical method of prevention--where dehydration facilities would not be used on a year-round basis, for example, or to unplug a stoppage formed by hydrates. Industrial use of methanol and glycol is widespread. Makogon (2) reports that in 1974 the gas producing industry in Russia consumed over 60,000 tons of alcohol annually. Other effective inhibitors are the electrolytic solutions of calcium chloride and potassium chloride.

The main objective of this work is to improve upon the determination of amount of inhibitor needed to prevent hydrate formation for a given set of conditions. The method currently used within the natural gas industry employs equations empirically determined from Hammerschmidt's work (5) to calculate the amount of inhibitor (specifically, methanol) needed (21). These figures can be as much as 300 % in error (6), which can result in a substantial monetary loss. This work uses a modification of the statistical thermodynamic equation presented by Parrish and Prausnitz (7) to predict the dissociation pressure, at a given temperature, of the cyclopropane gas hydrate with various inhibitors present. The pressures were then experimentally determined, and were compared to the prediction.

Cyclopropane gas was chosen for this experiment because it forms two different structures, which are each within the experimental temperature and pressure range of this work. The inhibitors used (KCl, CaCl_2 , and CH_3OH) are the most effective, and most common ones in practical usage. The concentration levels used closely approximated industrial levels, within equipment limitations.

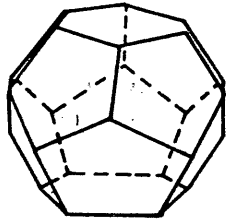
LITERATURE SURVEY

1. Nature and history of gas hydrates

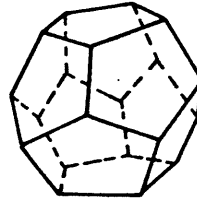
Gas hydrates are members of a group of compounds called clathrates, which are comprised of guest molecules and host molecules. The host molecules (water) form a lattice which is stabilized by the inclusion of the gas molecules. Hydrates were first reported in 1811 when Sir Humphrey Davy formed a crystalline compound from chlorine and water (8). Other investigators, working in the 1850's-1890's reported many additional hydrate forming gases, including carbon dioxide, acetylene, hydrogen sulfide, methane, ethane, and ethylene (8). It was not until the 1930's, when Hammerschmidt brought the problem of natural gas hydrates to the attention of the gas industry (1), that hydrates were generally known outside the academic community. After that publication, there was appreciable interest in the study of gas hydrates. Hammerschmidt's work was verified by a joint investigation of the U.S. Bureau of Mines and the American Gas Association under the supervision of Deaton and Frost (8). The hydrate crystal structure was determined as a result of the investigations of von Stackelberg, Claussen, Pauling, and Marsch (9,10,11,12,13). Research on hydrates in the area of statistical thermodynamics was begun in the late 1950's and early 1960's by several investigators. Among them were Van der Waals and Platteeuw (14), who derived the fundamental thermodynamic equations for hydrates. Since that time, studies have been carried out on hydrate formation conditions, water content of

gases forming hydrates, and the fundamental parameters for use in thermodynamic models. Parrish and Prausnitz, in 1972, developed a computer model to predict dissociation pressures of gas hydrates formed from gas mixtures of more than three gases (7).

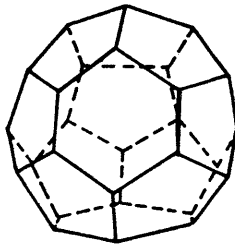
Gas hydrates can be formed by a pure gas, or mixture of gases. They are non-stoichiometric compounds in which molecules of gas are held by van der Waals forces in a metastable crystal framework of water molecules. The water molecules are held together by hydrogen bonding. Gas hydrates crystallize in one of two cubic structures, (I) or (II). The basis for the hydrate structure is the dodecahedron structure shown in figure 1 (b). In the figure each junction represents an oxygen atom which has three lines (and a fourth not shown) connected to the oxygen; two lines represent hydrogen atoms and two lines represent hydrogen bonds. One of the hydrogen bonds connects the cavity to other cavities, such that the unit cells of structure I and II are formed, as shown in figure 1 also (d and e). Not all of the cavities are the dodecahedron framework, due to packing constraints. In structure I, a tetradecahedron form is also present (figure 1a), and in structure II, a hexadecahedron (figure 1c) form occurs. Thus, in the unit cell of structure I there are 2 small and 6 large voids, and in the unit cell of structure II there are 16 small and 8 large cavities for the gas molecules to enter. The physical properties of these structures, from the data of von Stackelberg and Müller (15), are shown in Table 1. The structure formed depends upon the size and



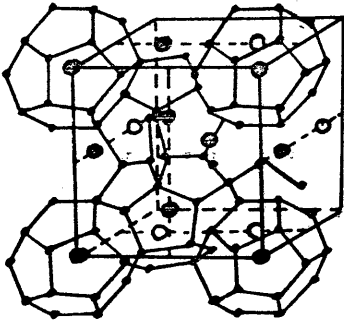
(a) Tetracahedron. (Structure I)



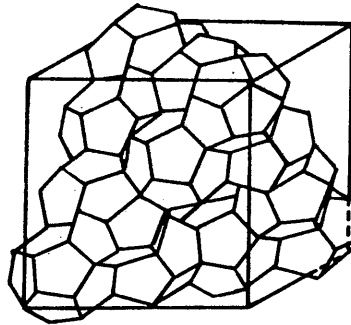
(b) Pentagonal Dodecahedron



(c) Hexadecahedron (Structure II)



(d)



(e)

Packing of dodecahedra in the hydrate unit cell of structure I (d), and structure II (e).

FIGURE 1.

TABLE 1
PHYSICAL PROPERTIES OF HYDRATE LATTICE

	Structure I	Structure II
Number of water molecules/unit cell	46	136
Number of cavities/ unit cell		
Small	2	16
Large	6	8
Cavity radius, A°		
Small	3.94	3.91
Large	4.30	4.73
Typical gases which form this structure	Methane Ethane Ethylene Cyclopropane	Propane iso-Butane n-Butane Cyclopropane

shape of the guest (gas) molecule. The cavities are normally stabilized when the ratio of molecular diameter to free cavity diameter is close to 0.65. The degree to which the cavities are filled depends upon the external pressure and temperature.

A conventional phase diagram, Figure 2, may be used to represent the behavior of a gas which forms a hydrate of only one structure and is capable of condensation to a liquid phase at the temperatures under consideration. Here, S, L and V stand for solid, liquid, and vapor, respectively. Above CE are the liquid phases of water and gas, and below FBCE are liquid water (containing a small amount of dissolved gas) and vapor (gas with water vapor). This vapor and liquid, when cooled below CB, change to solid hydrate with liquid water remaining if there is excess water. Further cooling below BG, which tilts slightly from vertical because dissolved gas and pressure lower the freezing point, causes the liquid water to change to ice. Line AB is the boundary between two solid phases and ice with a vapor phase. The curve DC is approximately vertical, and represents the equilibrium between the solid hydrate and liquid. Points B and C are quadruple points where the system is invariant with four phases present. The line BC is the most commonly measured dissociation pressure curve, and the one referred to in this work.

2. Review of work on inhibitors

The gas industry, in its efforts to prevent hydrate formation, currently employs alcohols, electrolytes and glycols as inhibitors.

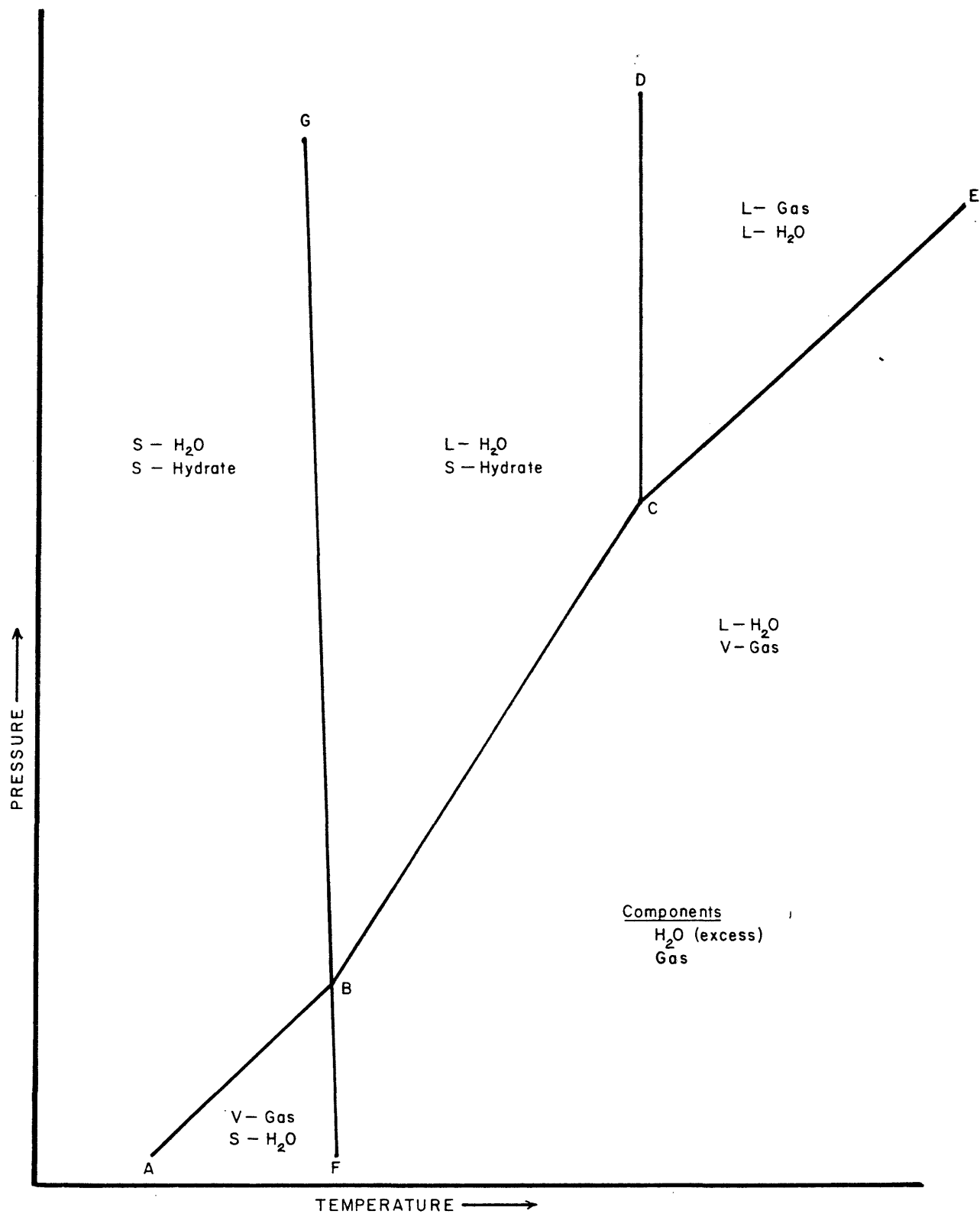


Figure 2 — Phase diagram illustrating hydrate formation.

The use of these compounds came about through experimentation, and by the practical demands which must be met. These requirements, as discussed by Makogon (2), are: (1) the substance must effectively lower the temperature of hydrate formation, (2) it must have a low freezing point, (3) it must be unreactive with natural gas flow components, (4) it must be soluble in water, (5) it must not increase the toxic properties of the gas, (6) it must have a low viscosity, and (7) it must be readily available at a reasonable cost. The selection of inhibitors is made empirically, as no quantitative analysis of the mechanism by which inhibitors prevent hydrate formation has been reported in the literature. The qualitative behavior of inhibitors in the formation process can, however, be explained. The means by which hydrates are inhibited, common to alcohol and glycol aqueous solutions, is the alteration of the structure of the water molecules themselves. By the addition of a foreign substance, either alcohol or salt, into water, the hydrogen bonding between water molecules is broken up. With salts, which completely dissociate into positive and negative ions in solution, the charges attract the dipole of the water molecule, such that water molecules cluster around individual ions. This phenomenon, known as "salting out", prevents water from forming the host lattice of the hydrate by interaction with the gas molecules. As reported by Makogon (2), this salting out

action increases with the charge, and depends on the ionic radius, indicating that a salt with maximum charge and minimum radius would be the most effective inhibitor. This structural change in the water is a possible explanation for inhibiting hydrate formation.

The experimental work on inhibitors was initiated by Hammerschmidt in 1939 (5). He reported the freezing point lowering of hydrate formation of a natural gas using from 5 to 20 weight percent of ethanol, methanol, isopropanol and ammonia. His work does not give an analysis of the natural gas, nor does it contain actual experimental data, but contains graphs obtained from more than 100 experimental determinations. Using these results, he developed a formula for the depression of the hydrate formation temperature. The formula, with a modification for dissociating compounds such as salts, uses the molecular weight and the weight percent of the antifreeze:

$$(1) \quad d = (2335 W)/(M(100-W))$$

where d = lowering of the freezing point, in $^{\circ}\text{F}$

M = molecular weight of the antifreeze, and

W = weight percent antifreeze.

His studies show that for a constant weight percent of antifreeze, the most effective compound is ammonia, followed, in order of effectiveness, by methanol, ethanol, calcium chloride, n-propanol, ammonium bicarbonate, and acetone. Hammerschmidt points out that ammonia is undesirable as an inhibitor because of the reaction it undergoes with carbon dioxide in

the presence of water to form solid carbonates, which can plug up lines.

Russell (16) and Powell (17) subsequently reported data on the inhibiting effect of the above mentioned antifreezes on natural gases. Miller and Strong (18) determined the effect on propane hydrates of acetone, methanol, ethanol and potassium hydroxide. Kobayashi (19) investigated the effect of sodium chloride and ethanol on the hydrate decomposition conditions of methane, and the effect of sodium chloride brine on the hydrate decomposition of propane. Kobayashi used the concept of chemical reaction equilibria in an attempt to calculate the inhibiting effect on hydrate dissociation pressure. He concluded that thermodynamic and vapor-liquid equilibria data are not generally available to enable calculation of hydrate dissociation by this method, and further, that his assumptions may cause serious error in the calculated pressure.

In 1955, Pieroen reported an equation for the depression of the hydrate equilibrium temperature upon the addition of an inhibitor, or third component, as he refers to it(20). Pieroen derives his equation using the reaction equation for hydrate formation:

$A + nH_2O \rightleftharpoons A \cdot nH_2O$ where A is the hydrate forming gas, and n is the number of water molecules per mole of A in the hydrate. At equilibrium for this reaction, the following condition is met:

$$(2) \quad \mu_A + n \cdot \mu_{H_2O} = \mu_{A \cdot nH_2O}$$

Using the definition of activity, he rewrites the equation as:

$$(3) \quad n R \ln(a_{H_2O}) = (\mu_{A \cdot nH_2O} - \mu_A - n \cdot \mu_{H_2O}^{\circ})_T / T$$

He then writes a similar equation for the reaction, in the absence of the inhibitor, at temperature T_0 . By subtracting the latter equation from the former, he can write:

$$(4) \quad n R \ln(a_{H_2O} / a'_{H_2O}) = (\mu_{A \cdot nH_2O} - \mu_A - n \cdot \mu_{H_2O}^{\circ})_T / T - \\ (\mu_{A \cdot nH_2O} - \mu_A - n \cdot \mu_{H_2O}^{\circ})_{T_0} / T_0$$

where a'_{H_2O} denotes the activity of water in the absence of the third component. Using the equation:

$$(5) \quad \frac{\partial(\mu/T)}{\partial T} = -\frac{\bar{h}}{T^2}$$

where \bar{h} is the partial molar enthalpy, Piroen reduces equation (4) to the form presented as the end result in his paper:

$$(6) \quad \Delta T = - \frac{n R T_0^2}{\Delta H} x_{T.C.}$$

where ΔT is the equilibrium temperature lowering, $T_0 - T$

n is the number of moles of water per mole of hydrate

R is the gas constant

T_0 is the equilibrium temperature in the absence of the third component

ΔH is the heat of formation of one mole of hydrate from the vapor and liquid that are in equilibrium with each other at the temperature T_0 , and

$x_{T.C.}$ is the mole fraction of the third component in the water layer

To obtain this result, Pieroen made several assumptions. First, it is assumed that ΔH is independent of temperature and not affected by the presence of the inhibitor. Next, it is assumed that the activity of water does not differ from its mole fraction (that is, the activity coefficient of the water is equal to 1.0) in the solutions containing the "third component". The third assumption is that the mole fraction of third component is small enough such that :

$$(7) \quad \ln (1 - x_{T.C.}) = -x_{T.C.}$$

This relationship is exactly represented with the infinite series:

$$(8) \quad \ln (1 - x_{T.C.}) = -x_{T.C.} - \frac{1}{2} x_{T.C.}^2 - \frac{1}{3} x_{T.C.}^3 - \frac{1}{4} x_{T.C.}^4 \dots$$

The right hand side of equation (7) starts deviating significantly from the infinite series above $x_{T.C.}$ of about 0.05.

Pieroen compares his equation to Hammerschmidt's, substituting in weight percent and molecular weight of inhibitor for mole fraction, calculating ΔH from an approximate equation, and using an average value of T_0 from Hammerschmidt's graph. Converted to Celsius degrees, the equations are:

$$(6) \text{ Pieroen's-- } \Delta T = \frac{1240 W}{M(100-W)}$$

$$(1) \text{ Hammerschmidt's-- } \Delta T = \frac{1297 W}{M(100-W)}$$

where M and W have the same meaning as before. This indicates a very close agreement (4 % difference in the constant) , which is suprising considering the approximate nature of both derivations. Pieroen's theoretical equation, therefore, represents no significant improvement over the empirical equation presented by Hammerschmidt twenty years

earlier. Piroen states, in fact, that the reasonable agreement between the experimental and calculated results at concentrations up to 20 weight percent is undoubtedly due to a compensation of errors.

The procedure currently used by industry to calculate amount of methanol inhibitor required to prevent hydrate formation uses Hammerschmidt's data. The method, presented by Jacoby (21), employs a graph of freezing point lowering required vs. weight per cent methanol in liquid, which was plotted using equation (1). Hammerschmidt's data of vapor to liquid composition ratio of methanol in natural gas is then used to calculate amount needed in each phase, and injection rate per day. This procedure should apply only to the same natural gas as used by Hammerschmidt in taking this data, and also relies on the correlation of Katz (22) for the dissociation pressure for a given gravity natural gas, and given temperature. The K values for methanol used to construct Jacoby's graphs were extrapolated from 700 to 4000 psia, which is another source of error. In light of these approximations, it would be desirable for the industry to have a more exact calculational procedure for determining the required amount of inhibitor.

3. Recent work in hydrate thermodynamics

The basic statistical thermodynamic equations for gas hydrates were developed by Van der Waals and Platteeuw (14), using a model similar to the Langmuir gas adsorption model. The basic assumptions are: the gas-containing cavities are spherical, with no more than one molecule per cavity; there is no distortion of the host lattice by the encaged molecules; there is no interaction between the encaged molecules. They obtained the following expression:

$$(10) \quad \Delta \mu^H = \mu^\beta - \mu^H = -R T \sum_m V_m \ln (1 - \sum_j \theta_{mj})$$

where μ^β and μ^H are the chemical potential of the unoccupied and occupied lattice water respectively, and μ^β is a standard state potential

R is the gas constant

T is the temperature

V_m is the number of type m cavities per water molecule in the lattice, and

θ_{mj} is the fraction of type m cavities occupied by a j -type gas molecule.

This fractional occupancy is given by the formula:

$$(11) \quad \theta_{mj} = C_{mj} f_j / (1 + \sum_l C_{ml} f_l)$$

where C_{mj} is the Langmuir constant which is a function of temperature and

the potential function parameters, $C = C(T, \sigma, \epsilon, a)$. Here, σ is the molecular distance parameter, ϵ is the depth of the binary potential well, and a is the core radius of the gas molecule. Parrish and Prausnitz (7) used the Kihara potential function to describe the gas-water interaction. They present an expression for the Langmuir constant as a function of temperature:

$$(12) \quad C_{ml}(T) = (A_{ml}/T) \exp(B_{ml}/T)$$

The constants A_{ml} and B_{ml} , functions of the gas and the type cavity filled (small or large), are reported for several gases. For cyclopropane, which only fits into the large cavities, the following constants are reported:

	$A_{ml} \times 10^2$	$B_{ml} \times 10^{-3}$
Structure I	.1449	4.5796
Structure II	1.3136	4.6534

The fugacity of the gas component j , f_j in equation (11), is found by the equation:

$$(13) \quad f_j = \phi_j y_j P$$

where ϕ_j is the fugacity coefficient of the gas component,

y_j is the mole fraction in the gas phase of component j , and

P is the total pressure

For a pure gas hydrate, equation (10) can be written in terms of the Langmuir constant as:

$$(14) \quad \Delta \mu^L(T, P) = R T \sum_m \nu_m \ln(1 + C_m f) + R T \ln(x_w)$$

when liquid water which is essentially pure is present. Here, x_w is the

mole fraction of water in the liquid phase.

At equilibrium, because the chemical potential of water in the hydrate phase is equal to that in each of the other phases, the following equation can be written (when liquid water is present):

$$(15) \quad \Delta\mu^H = \Delta\mu^L = \mu^g - \mu^L$$

where μ^L is the chemical potential of water in the liquid phase.

The change of both of these chemical potential differences with temperature and pressure must be the same along the equilibrium T-P locus, and this fact enables a so called " experimental chemical potential difference " to be calculated in two steps with the use of a reference hydrate. First, the quantity $\Delta\mu^L(T, P_r)$ at the temperature T and reference hydrate dissociation pressure P_r is found as follows:

$$(16) \quad \frac{\Delta\mu^L(T, P_r)}{R T} = \frac{\Delta\mu^L(T_0, P_0)}{R T_0} - \int_{T_0}^T \frac{(\Delta h^\alpha + \Delta h^f)}{R T^2} dT + \int_{T_0}^T \frac{(\Delta v^\alpha + \Delta v^f)}{R T} \left(\frac{dP}{dT}\right) dT$$

where $\Delta\mu^L(T_0, P_0)$ is an experimentally determined chemical potential difference of a reference hydrate at the ice-point temperature, T_0 , and P_0 , the dissociation pressure of the reference hydrate at T_0 .

In equation (16), Δv^α and Δh^α are the molar difference in volume and enthalpy, respectively, between the empty hydrate lattice and ice; Δv^f and Δh^f are, respectively, the molar difference in volume and enthalpy between ice and liquid water. The reference chemical potential difference has been determined from equation (10) by Dharmawardhana (23), who measured the fractional occupancy of the large cavities of the hydrate when the gas molecules are too large to

enter the small cavities. The values used here are those reported by Parrish and Prausnitz (7), due to the fact that Dharmawardhana's figures were not yet available at the time of this investigation. In the second integral on the right hand side of equation (16), because the system is univariant, dP has been replaced by $(dP/dT) dT$, where dP/dT is the slope of the reference hydrate. Parrish (7) reports the reference hydrate pressures as a function of temperature:

$$(17) \quad \ln (P_r) = A_r + B_r/T + C_r \ln(T)$$

Constants for the various reference hydrates are given in his work.

(A_r , B_r and C_r are constants) For structure I below 0 °C, the reference hydrate is xenon, and above 0 °C is methane. For structure II, hydrates of natural gas mixtures are the reference above 0 °C, and bromochlorodifluoromethane below 0 °C. The second term in equation (16) accounts for the change in enthalpy from T_0 to T . Parrish (7) assumes the enthalpy difference between empty hydrate and water varies as the enthalpy difference between ice and water:

$$(18) \quad \Delta h = \Delta h^\alpha + \Delta h^f, \quad \text{where}$$

$$(19) \quad \Delta h^f = \Delta h_o^f + \int_{T_0}^T \Delta c_{p_w} dT, \quad \text{where}$$

Δh^α is the enthalpy difference between the empty hydrate lattice and ice,

Δh^f is the enthalpy difference between ice and liquid water at the freezing point, and

Δc_{p_w} is the difference in heat capacity between ice and water:

$$(20) \quad \Delta c_{p_w} = \Delta c_{p_w}^o - a (T - T_0)$$

The values of Δh^α have been backed out of the equation by forcing experimental dissociation pressures to fit the equation.

The second step of the procedure obtains $\Delta\mu^L$ at T and P as follows:

$$(21) \quad \Delta\mu^L(T,P) = \Delta\mu^L(T,P_r) + (\Delta v^\alpha + \Delta v^f)(P - P_r)$$

The thermodynamic properties reported by Parrish for use in these equations are shown in Table 2. Parrish presents a computational scheme for calculating the dissociation pressure at a given temperature using equations (14) and (21). This procedure, employed in this work on cyclopropane, is an iterative Newton-Raphson calculation. The properties of the gas and the structure formed are input, with an initial guess for pressure. The computer program then converges on a pressure by forcing the two equations to be equal. When the $\Delta\mu^L$ from equation (14) matches the value from equation (21), hydrates will form.

In this work, equation (14) was modified for the effect of inhibitors as follows:

$$(22) \quad \Delta\mu^L(T,P) = RT \sum_m \nu_m \ln(1 + C_m f) + RT \ln(a_w)$$

By adding inhibitors, the activity coefficient of the water, γ_w , is changed from 1.0 of pure water. The product $\gamma_w x_w$ is the activity, a_w , which was incorporated into the equation. The other difference in the equation made by adding this third component is in the gas fugacity term: the mole fraction of pure component gas decreases from 1.0 on the addition of a volatile inhibitor component

TABLE 2

THERMODYNAMIC PROPERTIES OF EMPTY HYDRATE (β -PHASE) AND
LIQUID WATER (L) RELATIVE TO ICE PHASE (α) AT 0 °C AND ZERO PRESSURE

	Structure I	Structure II
$\Delta\mu^H$, J/mole	1263.6	882.8
Δh^α , J/mole	1150.6	807.5
Δv^α , m ³ /mole x 10 ⁶	3.0	3.4
Δv^f , m ³ /mole x 10 ⁶	1.598	
Δh_o^f , J/mole	6009.5	
Δc_{p_w} , J/mol °K	38.12 - 0.1406 (T - 273.1)	

such as methanol, and the fugacity of the gas also changes.

4. Governing equations for this work

In this work, pure cyclopropane was used as the hydrate forming gas. According to the data of Hafemann and Miller (24), cyclopropane forms structure II hydrate between 0 °C and 1.46 °C, and structure I hydrate above 1.46 °C. This experiment was designed to operate in the temperature range 0 - 4 °C, to demonstrate the formation of both structures. The inhibitors used were two salts, and methanol. The salts used were calcium chloride and potassium chloride.

The activity of water in the salt solutions was calculated from the freezing point depressions. According to the derivation given by Glasstone (25), this equation is:

$$(23) \quad \ln (a_w) = - \frac{\Delta h_f}{R T_o^2} \Delta T_f$$

for reasonably dilute solutions. In equation (23),

a_w = activity of water

Δh_f = molar heat of fusion of water (6009.5 J/mole)

R = gas constant

T_o = freezing point of pure water, and

ΔT_f = depression of the freezing point of water with addition of electrolyte.

The freezing point depressions in degrees Celsius were obtained from data in the Chemical Rubber Company Handbook of Chemistry and Physics (26).

It was established through calculations that this equation would be accurate in the concentration region of these experiments (≤ 1 molar). These calculations included: (1) estimating the higher order terms in the exact form of equation (23), which showed their effect to be negligible, and (2) comparing the activity values obtained from equation (23) with those calculated using the vapor-solid equilibrium equation:

$$(24) \quad a_w^1 = \frac{P_{w(\text{ice})}^{\circ}|_{T_F}}{P_{w(\text{liq})}^{\circ}|_{T_F}}$$

Furthermore, Lewis and Randall(27)state that for freezing point depressions of up to 5 °C, equation (23) is appropriate. The highest concentration of calcium chloride used here has a value of $\Delta T_f = 6.05$ °C, very close to this upper limit.

The fugacity coefficients for cyclopropane were obtained from the Pitzer-Curl correlation for a pure gas using the virial equation, with coefficients fit to T by Abbott (28):

$$(25) \quad \frac{B P_c}{R T_c} = B^{\circ} + \omega B', \quad (26) \quad B^{\circ} = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$(27) \quad B' = 0.139 - \frac{0.172}{T_r^{4.2}}, \quad \text{and (28) } \ln \phi = \frac{B P}{R T}$$

In these equations, B is the second virial coefficient,

R = gas constant,

P_c = critical pressure

T_c = critical temperature

ω = acentric factor

T_r = reduced temperature, = T / T_c , and

ϕ = fugacity coefficient.

In the salt solutions, considering cyclopropane to be a pure gas was a reasonable assumption because of the very low vapor pressures of solutions, and corresponding very small amount of water in the vapor phase. The methanol solutions all had a vapor phase mole fraction of cyclopropane in excess of 0.99. Therefore, the water-methanol-cyclopropane gas phase interactions were thought to be insignificant, and again the cyclopropane could be treated as a pure gas. This was verified by comparing values for fugacity coefficients obtained from the Pitzer-Curl for pure cyclopropane with those obtained from the Tsonopoulos (29) correlation for polar-non-polar mixtures. The calculation proved this assumption was an excellent one, as the coefficients varied by less than 0.2 percent.

For the methanol solutions, the Wilson equation was used to calculate activity coefficients. This equation, for a binary solution, is:

$$(29) \ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right]$$

$$(30) \ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right]$$

where (31) $\Lambda_{ij} \equiv v_j^L / v_i^L \exp \left[-(\lambda_{ij} - \lambda_{ii}) / RT \right]$

The parameters used in equation (31), $\lambda_{12} - \lambda_{11}$ and $\lambda_{12} - \lambda_{22}$ were obtained from Holmes and Van Winkle (30). In these equations, v_j^L and v_i^L are the molar volumes of the two components, which were

obtained as a polynomial function of temperature. The advantage of the Wilson equation is that it uses temperature independent parameters, which allows the activity coefficient to be determined as a function of temperature. The values for activity coefficients obtained from this equation were compared with those obtained from published experimental data for the water-methanol system to verify the accuracy of the Wilson equation with the given constants. The activity coefficients from experimental data were calculated according to the relationship:

$$(32) \quad \gamma_i = \frac{\phi_i y_i P}{x_i P_i^0}$$

where ϕ_i was assumed to be 1.0, because of the low pressure (≤ 1 atm) range of the data. The vapor pressures were calculated with the Antoine equation, using constants given in Holmes and Van Winkle (30).

To use the Parrish and Prausnitz model, the mole fraction of cyclopropane in the gas phase, y_{c-c_3} had to be determined. Due to equipment limitations, i.e., lack of a gas chromatograph, a method of calculating this mole fraction indirectly was devised, using the Henry's law constant for cyclopropane in the water-methanol mixture. Therefore, an experiment was performed to determine this constant.

When a gas phase and a liquid phase are in chemical equilibrium, their fugacities are equal:

$$(33) \quad f_i^g = f_i^l$$

The gas phase fugacity is calculated as:

$$(34) \quad f_1^g = \phi_1 y_1 P \quad , \text{ where}$$

ϕ_1 = fugacity coefficient of component 1,

y_1 = vapor phase mole fraction of component 1, and

P = total pressure.

The liquid phase fugacity is calculated by means of a standard state fugacity:

$$(35) \quad f_1^l = x_1 f_1^o \gamma$$

This standard state fugacity, f_1^o , is the fugacity of component 1 at the same temperature and pressure as the mixture, and can be chosen from one of two standard states, the Lewis and Randall, or the Henry's law. As x_1 , the mole fraction of component 1 in the liquid phase, approaches 0.0, the fugacity calculated by using Henry's law approaches the real solution behavior and γ becomes 1.0. Henry's law is the standard state used in this work, since the mole fraction of cyclopropane in the liquid phase is very close to zero. Henry's law is written as:

$$(36) \quad \lim_{x_1 \rightarrow 0} \frac{f_1}{x_1} = k_1$$

where k_1 is known as the Henry's law constant. Applying the phase equilibrium equation gives:

$$(37) \quad \phi_1 y_1 P = k_1 x_1 \quad \text{for } x_1 \rightarrow 0$$

In the low pressure region (≤ 1 atm) where the gas is ideal, $\phi_1 \approx 1.0$,

and:

$$(38) \quad P_1 = k_1 x_1 \quad , \quad \text{or} \quad k_1 = P_1 / x_1$$

This Henry's constant is a function of the mixture, and dependent on

concentration and temperature, but not on pressure. Many times the constant k_1 is inverted in solubility measurements to give:

$$(39) \quad x_1 = k_1' P_1, \text{ where } k_1' = 1/k_1$$

The inverted Henry's constant, k_1' , was used in this work.

The method for determining the solubility of cyclopropane in the aqueous solutions of potassium chloride was reported by Zerpa (31) in a prior investigation. A measured volume of gas is brought in contact with a measured quantity of gas-free liquid. Equilibrium is established by leaving the system for several hours, and hastened by agitation. The remaining gas molecules are then calculated from final volume, pressure and temperature measurements. The difference between initial and final number of gas moles gives the solubility. This experiment was conducted in the temperature and methanol concentration ranges of interest for the hydrate experiment.

The results of the Henry's constant determination, a correlation for $k_1' = k_1'(T, c)$ was used in a flash calculation to determine mole fractions of components in both phases. The equilibrium K values for methanol and water were determined using the activity coefficients from the Wilson equation:

$$(40) \quad K_1 = y_1 / x_1 = (P_1^0 \gamma_1) / P$$

The fugacity coefficients were assumed to be 1.0 for the flash calculation. This calculation was relatively insensitive to ϕ_1 , as a value of $\phi_1 = 0.6$ changed the resultant mole fraction by only 0.2 percent. The vapor pressures, again, were calculated from the Antoine equation.

These vapor pressures were compared with some tabulated data values as a check, with results accurate to within 0.2%. The equilibrium K value for cyclopropane was calculated from the inverted Henry's law constant as follows:

$$(41) \quad K_{c-c_3} = \frac{y_{c-c_3}}{x_{c-c_3}} = \frac{1.0}{k_{c-c_3} \cdot P}$$

A computer program was written to perform the flash calculation by converging on the ratio of V/L, number of moles in vapor per number of moles in liquid. The procedure was to input the number of moles of each component, T and P, and an initial V/L guess. Equilibrium K values were then calculated, as above, and then vapor moles of each component were calculated from the equation:

$$(42) \quad l_i = \frac{f_i}{1 + K_i V/L}$$

where l_i = number of liquid moles of component i

f_i = number of feed moles of component i

A new V/L ratio was then calculated using the summation of l_i 's, L, as follows:

$$(43) \quad V = F - L$$

By finding a hydrate dissociation pressure from the Parrish and Prausnitz computer model for the methanol-water-cyclopropane system, with an initial guess of $y_{c-c_3} = 1.0$, and plugging this into the flash calculation to calculate the value for y_{c-c_3} , and then returning this value to the hydrate dissociation program, convergence

was rapidly obtained for the equilibrium dissociation pressure.

EXPERIMENTAL EQUIPMENT

The experimental system consists of an equilibrium cell, a temperature control and measuring system, a pressure measuring system, tubing and valves connecting the gas bottle to the equilibrium cell, an ultrasonic agitation system, and a vacuum line. Figure 1 is a schematic diagram of the apparatus.

The equilibrium cell, where the cyclopropane and the water solutions were brought into contact with each other, is a cylinder made of bearing bronze alloy, with dimensions of 5 inches long by 2 inches inside diameter. The top and bottom blind-flange plates are made of stainless steel. Both plates are removable, and attached with six $3/8$ " bolts. Rubber "O-ring" gaskets were used on the bottom and a flat rubber gasket was used on the top for seals. Two sightglass windows, $1/4$ inch plexiglas with teflon gasket seals, were bolted on opposite sides of the cell and allowed visual observation of hydrate formation. The ultrasonic transducer, which agitated liquid in the cell, was bolted to the outside of the lower plate and covered with an aluminum cover.

A platinum resistance thermometer was connected to the upper plate of the cell by an Omegalock compression fitting. The gas inlet line, of $1/4$ " copper tubing, was affixed to the top plate with a Swagelok fitting, and was connected with the rest of the system by a quick-disconnect 5" above the top plate. The cell was supported atop a plexiglas box by three $4\frac{1}{2}$ " aluminum legs held by the bottom

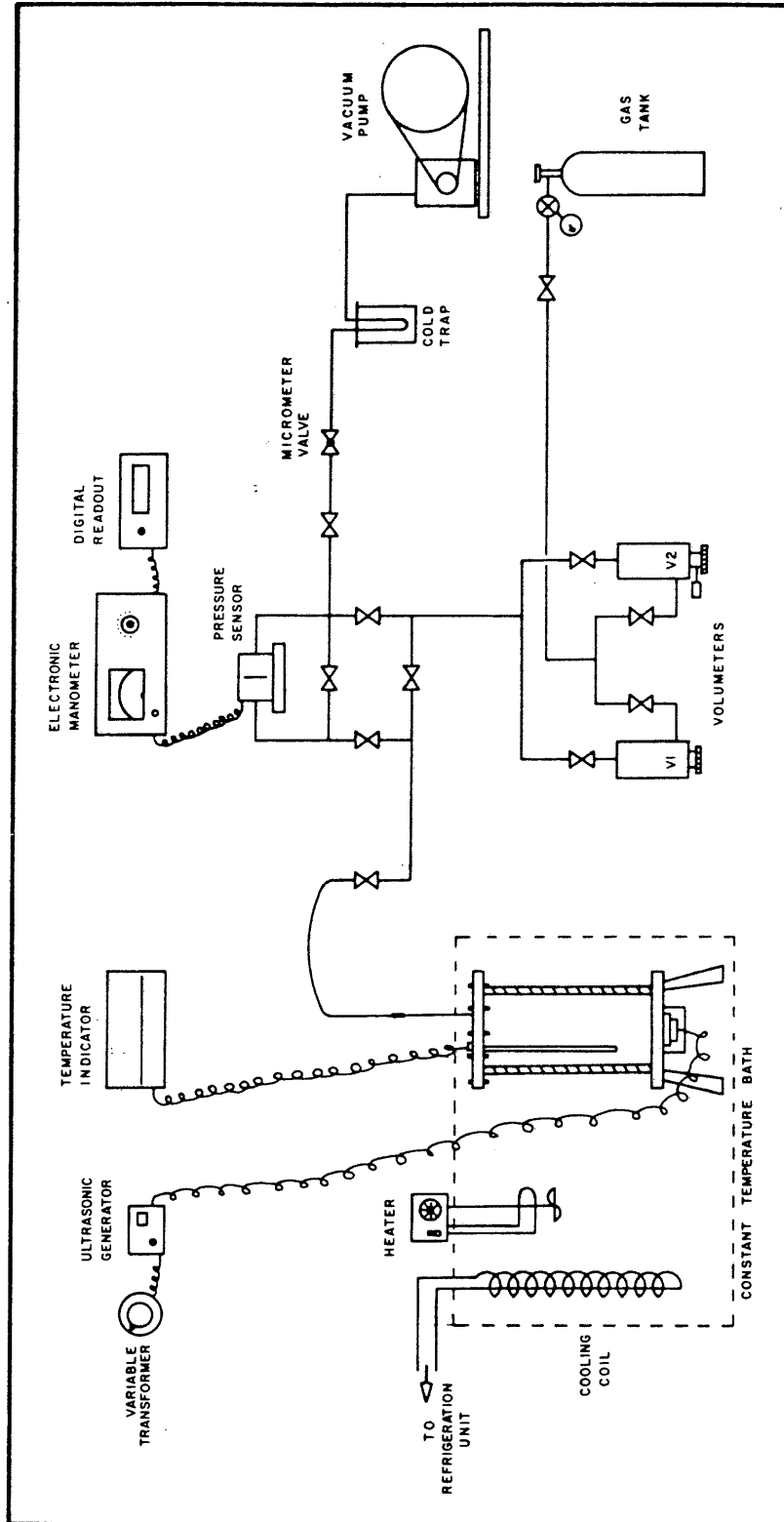


FIGURE 3 — EXPERIMENTAL APPARATUS

flange bolts.

The tubing throughout the entire apparatus is $\frac{1}{4}$ " copper refrigeration tube. All of the valves, with the exception of the two valves at the volumeter inlet, are $\frac{1}{4}$ " Nupro B 4-H bellows seal valves. The fittings are brass Swagelok fittings.

The pressure was measured by a Barocel differential pressure sensor, and the signal from the electric manometer was fed to a digital readout. The sensor works by means of a sealed metal diaphragm which changes position, and capacitance, with a change in differential pressure. The range of the sensor is from 0 to 2000 mm Hg, with a resolution of 0.001 mm Hg on the most sensitive scale. The accuracy is cited by the vendor as $\pm 0.25\%$ of reading in addition to $\pm 0.02\%$ of operating scale. The sensor was calibrated in the pressure range of 0 to 1500 mm Hg against a Mercury manometer with gradations of 0.1 mm Hg in an earlier work (31). As a check of these calibrations, the vapor pressure of pure water was read at several temperatures between 0 and 10 °C, and agreed with published values to within 1.5%.

The right hand side of the pressure sensor was connected, through a cold trap, to a vacuum pump. The cold trap used liquid nitrogen to prevent condensable vapor from going into the pump, and also to prevent diffusion of the pump oil into the system. The pump is a Welch-Duo-Seal vacuum pump, rated at 1.5×10^{-2} mm Hg absolute pressure. The discharge of the vacuum pump was vented outside the building.

The system was charged with gas from the gas cylinder through

a pressure regulator, an assembly of valves and tubing, and through two volumeters. The cyclopropane, obtained from Matheson Gas Co., was analyzed by that company as follows:

Carbon dioxide	< 1 ppm
Air	< 50 ppm
Propylene	< 1230 ppm
Allene	< 100 ppm
Cyclopropane	= balance

The regulator measures pressure downstream of the cylinder, since cyclopropane is a liquid in the cylinder, and the bottle would show a constant pressure, the vapor pressure of cyclopropane, until all liquid was gone. A Matheson pressure needle valve was used to control gas flow to the system. The gas admitted to the system was measured with two Volumeters. These Volumeters are cylinders with moveable pistons, and have a precisely calibrated volume (see Figure 2). The Volumeters are cited by the vendor as accurate to $\pm 0.15\%$.

The temperature in the cell was measured with a $6\frac{1}{2}$ " long platinum resistance thermometer. The output was fed into a digital readout. The temperature range of this equipment was from -23 to $+80$ °C with an accuracy of ± 0.02 °C. The readout was sensitive to ± 0.005 °C. The thermometer was calibrated in an earlier work (31) against a platinum thermometer traceable to the National Bureau of Standards.

The temperature was controlled to within ± 0.02 °C in a temperature bath containing Dow-Corning 200 Silicon fluid. This fluid is a good dielectric, has a freezing point of -40 °F and a viscosity of 5 centistokes at

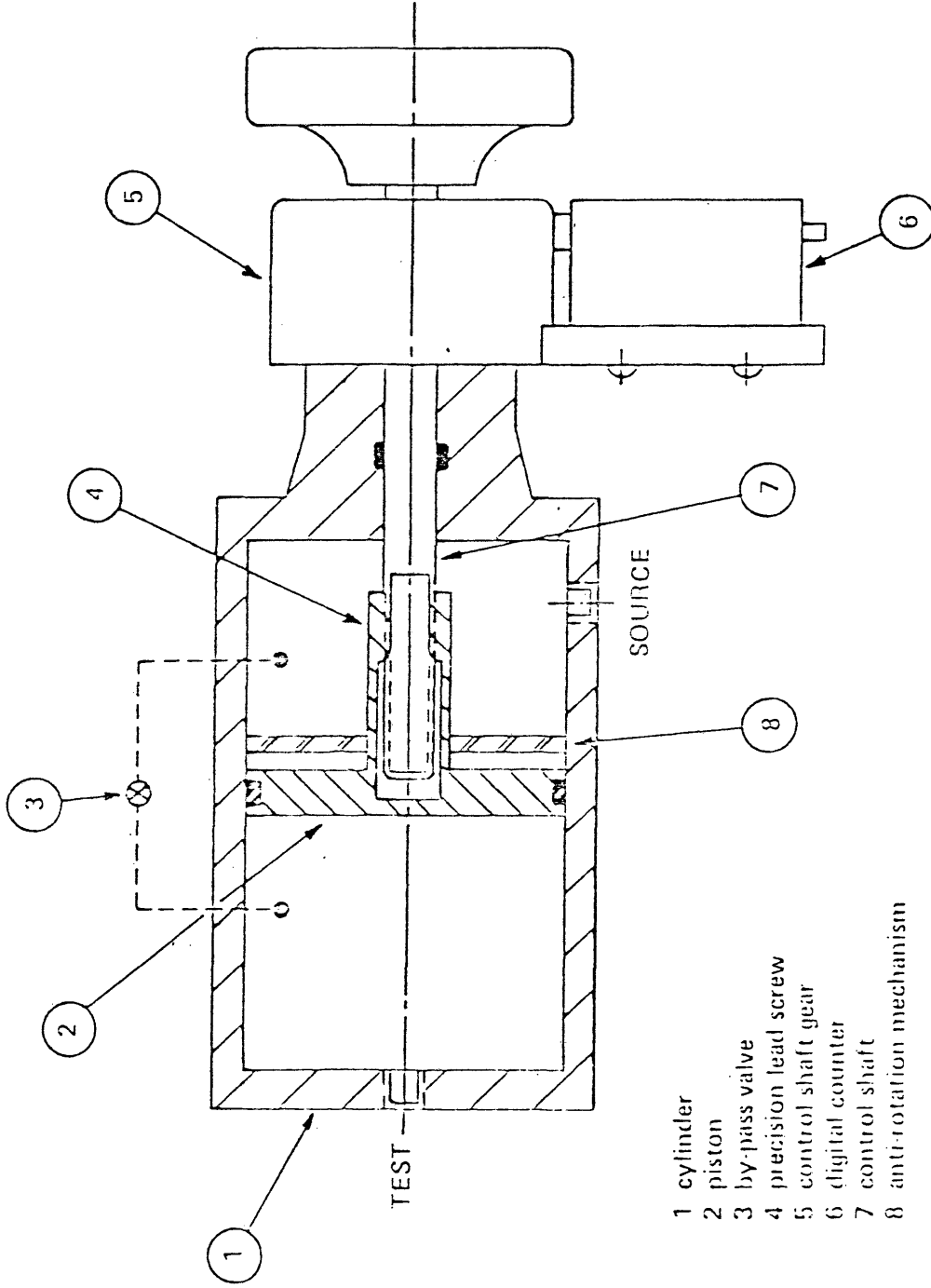


FIGURE 4 - VOLUMETRIC VOLUMETER. SCHEMATIC DIAGRAM

0 °C. The bath, with dimensions 13" long, 7½" wide, and 17" high, is made of ½" plexiglas. The outer wall is insulated with 1" Armoflex foam. The bath temperature was controlled by both a refrigerator and a heater-circulator. The refrigerator is a Blue M hermetic refrigerator with ½ hp compressor and a 3500 Btu/hr removal capacity. The refrigerant, freon-12, flows through a 16" high stainless steel coil within the bath. The heater is a Thermomix circulator which has a 10 l/min capacity pump and supplies heat from a 750 watt heater. With both units operating, the temperature of the bath can be controlled to within 0.02 °C at 0°C.

The ultrasonic system is composed of an ultrasonic transducer attached to the lower plate of the equilibrium cell and connected to an ultrasonic generator with a waterproof coaxial cable. The cable within the bath was inside copper tubing so it was completely isolated from the bath fluid. The generator is a solid state module which operates from a 120 V, 60 Hz electrical outlet, regulated by an external variable autotransformer.

EXPERIMENTAL PROCEDURE

1. Hydrate experiment

The equilibrium cell was first cleaned and dried, and the tubing lines were completely evacuated. The salt solutions were made up by putting a weighed amount of the salt in a 250 ml volumetric flask and filling with twice-distilled water. All chemicals used were commercially available reagent grade. For the methanol solutions, methanol was pipetted using a 5, 10, or 50 ml pipet into the 250 ml volumetric flask (for 0.5, 1.0 and 5.0 M solutions, respectively), and the flask was filled with water. About 75 ml of the solution was then poured into the cell, and the top plate was attached. For the methanol runs, the amount of liquid used in the cell was weighed for use in the flash calculations. The cell was then placed in the bath, and cooled down. Then the cell was slowly and carefully evacuated with the vacuum pump, using the micrometer valve as a throttle. During the methanol hydrate runs, the liquid was frozen in order not to pull off the very volatile methanol. This method of degassing produced good results, as the cold trap weighings showed a loss of about 0.1 ml of solution. When the cell and all connecting tubing had been thoroughly evacuated, cyclopropane was admitted to the system through the volumeters. The pressure admitted was estimated to be slightly higher than the expected hydrate formation pressure, as the system required supersaturation to form hydrates, similar to "seeding" required to form crystals. This initial pressure was recorded when forming

hydrates with methanol solutions for use in calculating number of gas moles in the feed for the flash calculation. The ultrasonic generator was then turned on for good mixing. After the hydrates had formed, a process requiring roughly five hours, the ultrasonic agitation was stopped, because temperature control to 0.02°C was not possible with the ultrasonic generator on. The system was allowed to reach equilibrium, and then pressure and temperature were recorded. Then the temperature control was set to a different temperature for the next data point.

2. Henry's law constant experiment

The methanol solution was made up as before, and put in the clean, dry cell. Approximately 200 ml of solution were weighed and used in these experiments. The top plate of the cell was then put on, and the cell was cooled down. The system was evacuated, as before. The vapor pressure of the solution was then measured. Then cyclopropane gas was admitted to the system, with the inlet valve to the cell closed. This gas pressure, and ambient temperature, were recorded for calculating initial number of gas moles in the system. The ultrasonic generator was turned on, the inlet valve opened, and gas began dissolving in solution. Pressure was recorded at $\frac{1}{2}$ hour intervals until no noticeable change was observed. After about 4 hours (7 hours without agitation), the system reached equilibrium. The final pressure, temperature, and ambient temperature were recorded for calculating

the final number of gas moles in the system. The system was then disconnected and prepared for a new run.

EXPERIMENTAL RESULTS

The Henry's law constant determinations were made at three concentrations-- 0.0, 1.0, and 5.0 mole/liter methanol. The experimental data for this experiment is given in Table 3 and the primary data is presented in Appendix A. These results are presented graphically in Figure 3. The lines drawn through the points were generated from a fit of the data. These regression constants are given in the discussion section. The pure water points served as a check of the data presented by Zerpa (32) for the inverted Henry's constant of cyclopropane in pure water. Therefore, a third data point was not necessary, as the two taken agreed well with previous results.

The hydrate experiments were conducted in the temperature range of 0 - 4 °C. Four data points were taken at each concentration of inhibitor. The results are presented in Figures 4, 5 and 6 for the KCl, CaCl₂ and CH₃OH solutions respectively. The solid lines were generated from the computer program MUO.FOR (MUO2.FOR was used for methanol) which can be found in Appendix B, along with the primary data for this experiment.

TABLE 3

EXPERIMENTAL VALUES OF INVERTED HENRY'S CONSTANTS

Run #	Temperature (°C)	Concentration (molarity)	$k_1' \times 10^6$ (<u>mol. fract.</u>) kPa	$\ln k_1'$
1	0.050	0.000	5.444	-12.121
2	3.690	0.000	4.681	-12.272
3	-0.296	0.988	6.258	-11.982
4	2.450	0.988	5.704	-12.074
5	5.232	0.988	5.045	-12.197
6	0.133	4.938	10.242	-11.489
7	3.150	4.938	9.013	-11.617
8	4.990	4.938	8.285	-11.701

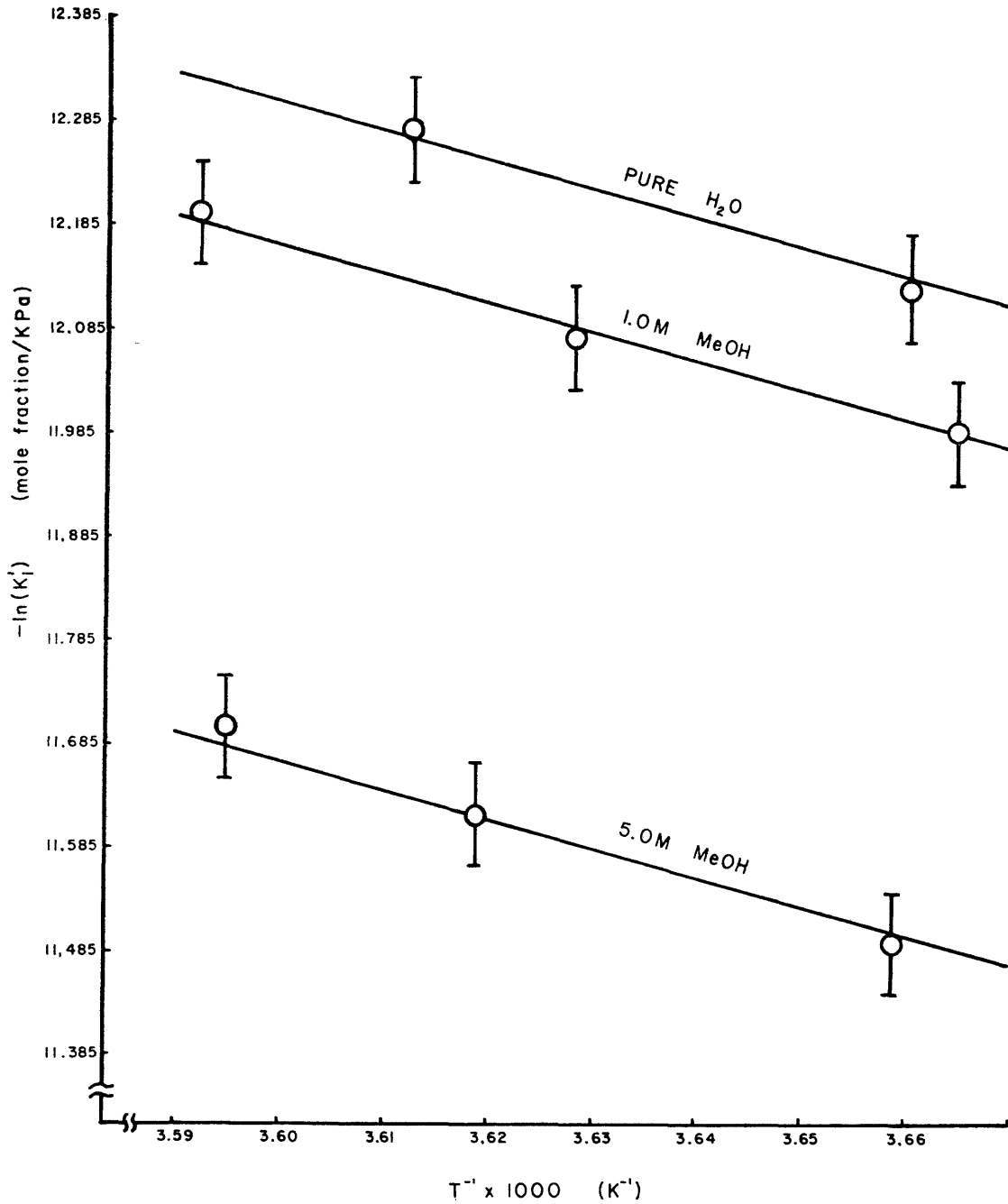


FIGURE 5 — Inverted Henry's constants of cyclopropane in methanol solutions as a function of temperature.

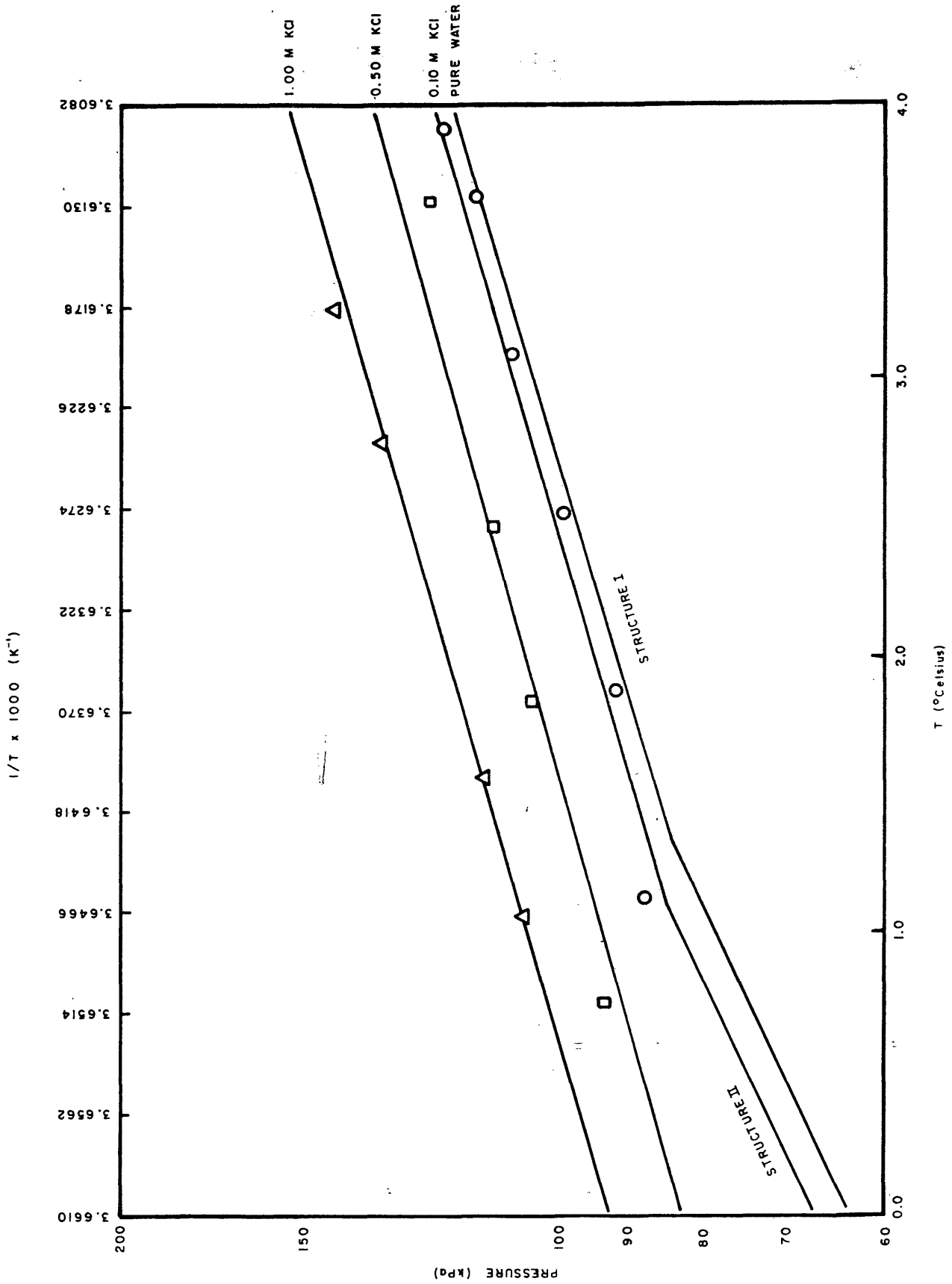


FIGURE 6 - Dissociation pressure curve for cyclopropane hydrate with KCl inhibitor.

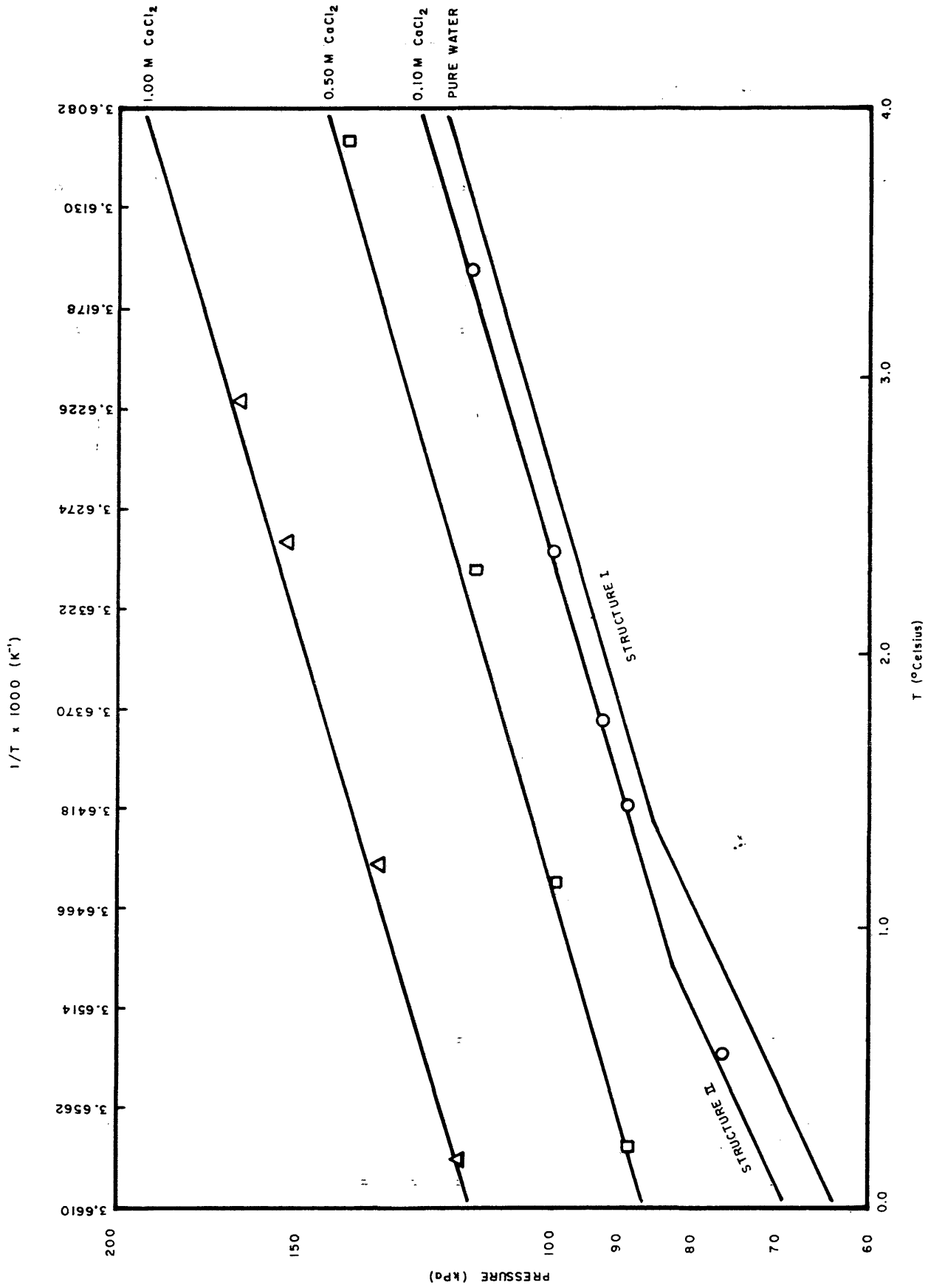


FIGURE 7 — Dissociation pressure curve for cyclopropane hydrate with CaCl₂ inhibitor.

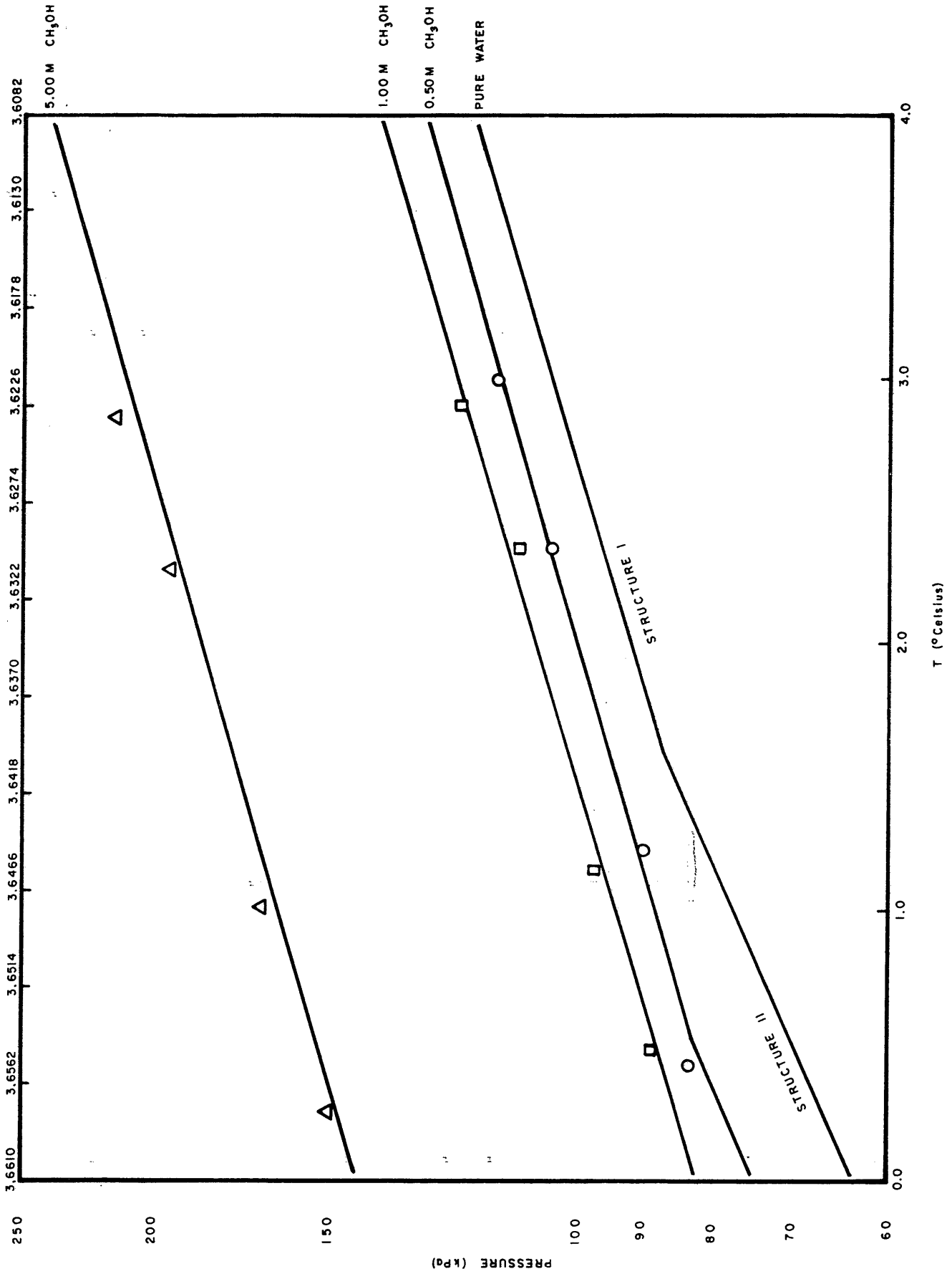


FIGURE 8 — Dissociation pressure curve for cyclopropane hydrate with CH₃OH inhibitor.

DISCUSSION

The results of the Henry's constant experiment show that the solubility of cyclopropane as a function of temperature and concentration in water-methanol systems behaves in a regular manner. The data taken for the pure water system agreed within 2 % with that of Zerpa et al. (32) and Hafemann and Miller (24), whose experimental error was estimated to be less than 2 %. These data were used in a stepwise multiple linear regression program, and the following equation for the inverted Henry's constant resulted:

$$(44) \quad \ln k_{c-c_3}' = -22.94619 + 2957.0636/T + (35.0309/T)(\text{conc.})$$

where concentration of methanol is in mole/liter, k' is in mole fraction per kPa, and T is in K. The maximum deviation of any of the data from this equation is ± 0.14 %.

The lines predicted by this equation are plotted in Figure 3 along with the experimental data. The solubility of cyclopropane decreases with increasing temperature and increases with increasing methanol concentration. This concentration effect on solubility is the reverse of that in the case of salt solutions (32). This effect can be explained by the intermolecular forces involved. Salts are completely dissociated into ions in an aqueous solution, and the ions cluster around the dipole of the water molecules. These strong ionic forces prevent a non-polar gas from dissolving in solution. Methanol will hydrogen bond with the water in solution, (the

OH^- of methanol and the H^+ dipole of water attract each other) which leaves a CH_3^- group free. The non-polarity, or similarity, of this methyl group to cyclopropane, allows the gas to dissolve more easily than in pure water.

An error analysis for this experiment is located in Appendix A. The Henry's inverted constant is accurate within $\pm 5.0\%$ according to this analysis.

The flash calculations of the methanol-water-cyclopropane system using the results of the Henry's law constant showed very little methanol in the vapor phase. The vapor phase mole fraction was between 0.992 and 0.994 for all runs. This had a very small effect ($< 2\%$) on the hydrate dissociation pressure calculated.

The results of the hydrate experiments, shown in Figures 4, 5, and 6 show the data agree very well with the computer predictions. The maximum error in dissociation pressures was between 2 and 3%. The addition of the inhibitor to pure water shifts the quadruple point, the point at which structure II no longer forms, and structure I forms. This shift is in the direction of decreasing temperature, the same direction as the dissociation temperature for a given pressure. The quadruple point was found by the intersection of the P-T curves for the two structures. Hafemann and Miller (24), whose data agreed with the computer-predicted values for pure water and cyclopropane, report this quadruple point temperature is 1.46°C . It was noted in this study that the activity coefficient of water has a very strong effect on the predicted dissociation pressures. Since

the term $R T \ln(a_w)$ in equation (22) is the only significant change made by the inhibitor, any error made in a_w , or γ_w , is magnified in the error in predicted pressure. From calculations of the change of activity and change of pressure with increasing concentrations of inhibitor, this amplification of percentage error is approximately eightfold--that is, a 1 % error in activity coefficient would result in a predicted pressure which was 8 % in error. This implies that the Wilson equation for methanol, and the freezing point depression equation for the activity of salts, provided activity coefficients accurate to within 0.40 % in order for the experimental hydrate dissociation pressures to be within 3 % of the predicted values.

To further test the computer model, the data presented by Kobayashi (19) for 15 weight percent ethanol solutions with pure methane were compared to predictions using a modification of the MUC2.FOR program. The Wilson equation was again used to calculate the activity coefficient of water, and the vapor phase was assumed to be pure methane, since no gas phase mole fractions were reported. The results of T vs. P_{diss} are tabulated in Table 4. The effect of the activity coefficient on the calculated pressure is demonstrated in Table 5 where activity coefficients backed out of the computer model using Kobayashi's data are compared with those calculated from the Wilson equation. For ethanol as well as methanol, the Wilson equation gives extremely accurate values for the activity coefficient of water. As seen from Table 5, the Wilson equation

TABLE 4

COMPARISON OF CALCULATED WITH EXPERIMENTAL DISSOCIATION PRESSURES FOR
METHANE HYDRATE USING KOBAYASHI'S DATA FOR METHANE - 15 % ETHANOL

T (K)	P (experimental) (kPa)	P (predicted, this study) (kPa)	ΔP (exp.-pred.) (%)	P (predicted, Hammerschmidt) (kPa)	ΔP (exp.-pred.) (%)
273.26	3378	3702	- 9.6	4344	- 28.6
277.21	5468	5543	- 1.4	6826	- 24.8
279.43	7060	7005	+ 0.8	9308	- 31.8
281.09	8356	8481	- 1.5	10687	- 27.9
284.71	13665	13259	+ 3.0	15858	- 16.0

TABLE 5COMPARISON OF γ_{H_2O} FROM KOBAYASHI'S DATA

T (K)	$\gamma_{\text{experimental}}$	γ_{VanLaar}	γ_{Margules}	γ_{Wilson}	$\Delta \gamma$ (exp.-Wilson) (%)
273.26	.9637	.9429	.9407	.9502	+ 1.40
277.21	.9518	"	"	.9500	+ 0.19
279.43	.9491	"	"	.9500	- 0.09
281.09	.9499	"	"	.9499	0.00
284.71	.9454	"	"	.9498	- 0.47

fits the experimental data much better than the van Laar or the Margules equations.

Also shown in Table 4 are the dissociation pressures predicted by Hammerschmidt's equation. These results are shown in graphical form in Figure 7. The method used here gives an average of eight times the accuracy of the Hammerschmidt equation. As mentioned in the literature survey section, the industrial method of calculating the amount of methanol needed uses not only the equation (1) given by Hammerschmidt, but also his vapor-liquid equilibria data. The procedure is to first determine from equation (1) the weight percent methanol needed in the liquid phase. Then, the K values developed from Hammerschmidt's work are used to determine the amount of methanol in the gas phase which is in equilibrium with that in the liquid phase. From the flow rate of the gas and liquid dropout rate, the amount of methanol needed can then be calculated on a daily basis. Since Hammerschmidt gave no vapor liquid equilibria data for ethanol, this method was not used here. The only calculation used in the Hammerschmidt prediction presented in Table 4 and Figure 7 was equation (1).

In general, Hammerschmidt's method is a conservative prediction of the amount of methanol needed, that is, the prediction results in more methanol being used than is necessary. The amount of methanol needed in the gas phase, as seen in the calculations of Jacoby (21), is usually much more than the amount needed in the liquid phase. Therefore it would appear that Hammerschmidt's vapor-liquid equilibrium

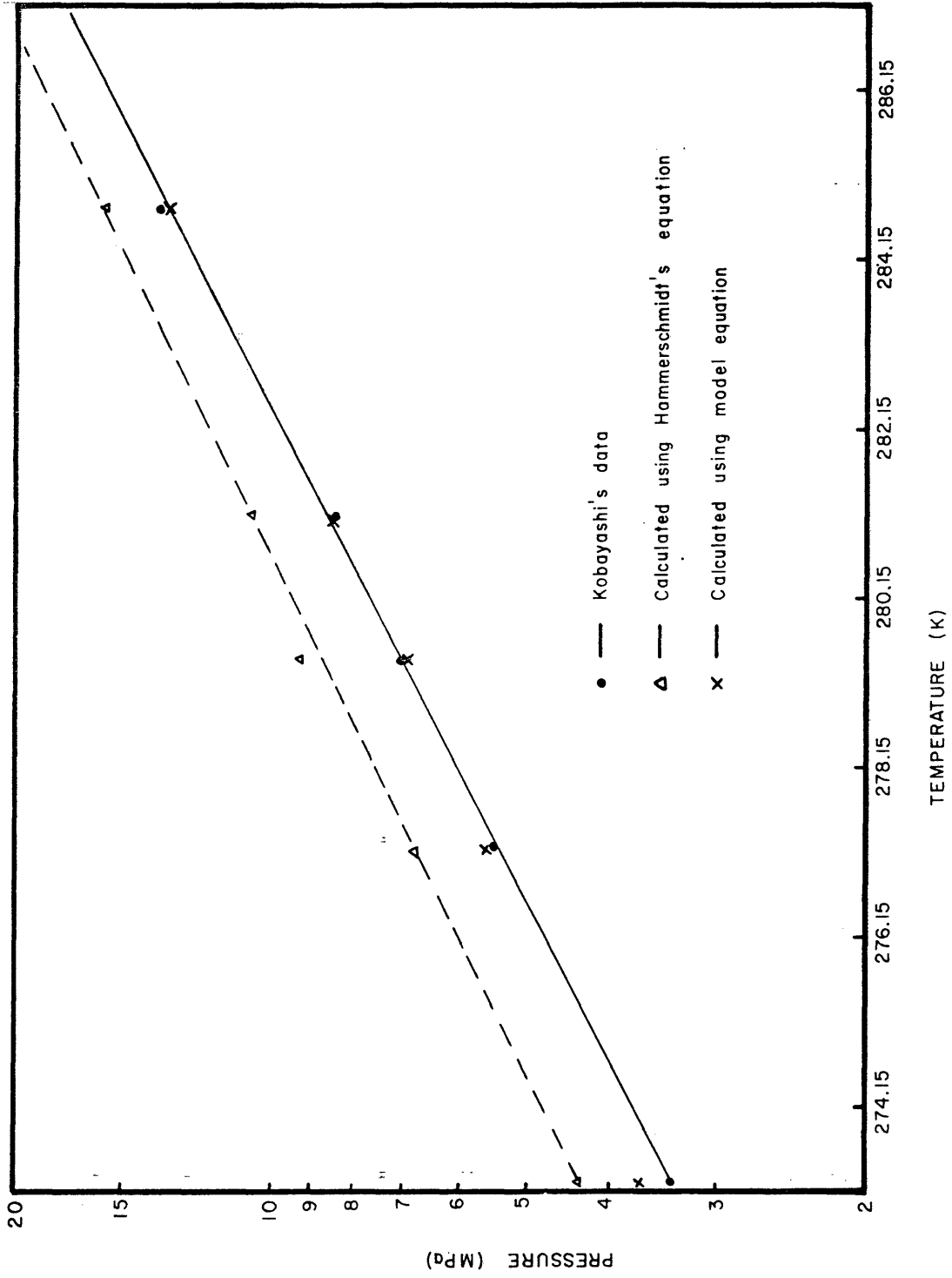


FIGURE 9 — Dissociation pressure curve for methane hydrate with 15 weight percent ethanol.

data could be the source of the error in this method of prediction. As no other such data is available in the literature, this suspicion can not be investigated until further data is taken. No data on the solubility of methane or natural gas in water-methanol or water-ethanol solutions is available.

In order to use the computer algorithm of Parrish and Prausnitz which has been modified in this study, more vapor liquid equilibrium data than is currently available is needed. In equation (13), the y_1 , mole fraction of the hydrate forming gas in the gas phase must be determined. Practical considerations require a convenient method of calculating this from solubility data. By studying the solubility of gases (methane and natural gases) in water-inhibitor solutions, a Henry's law constant for the gas could be determined. Then, as in this study, a flash calculation would provide mole fractions of all components. This gas phase mole fraction of inhibitor, when multiplied by the gas flow rate, would give the amount of inhibitor needed in the vapor phase, and when added to the liquid phase requirement, would give the total requirement of inhibitor on a daily basis.

The computer algorithm used here could be modified for use by industry such that by entering the temperature at which protection is needed (the coldest line temperature experienced), the line pressure and gas flow rate, the amount of inhibitor needed is determined by the program. That is, a flash calculation using solubility data and the Wilson equation for equilibrium K values could be included in the computer program to simplify the procedure.

CONCLUSIONS

1. The modified Parrish and Prausnitz equation accurately predicted hydrate dissociation pressures for the inhibitor-water-cyclopropane systems studied.
2. The only significant inhibiting effect in the calculations was seen in the term $R T \ln(a_w)$, as the mole fraction of methanol in the vapor phase was very small.
3. The equation is extremely sensitive to the activity coefficient of water. For the experimental range studied here, the Wilson equation for methanol in water, and the freezing point depression equation for salts in water, provide accurate values for this activity.
4. The model equation used also provided accurate pressure predictions when compared with the published data of Kobayashi for pure methane with ethanol as the inhibitor. The predictions were an average of eight times more accurate than the predictions using the Hammerschmidt equation.

RECOMMENDATIONS

In order for the results of this study to be useful in industrial calculations, more solubility data is needed. It is therefore recommended that solubilities of methane and natural gases in water-inhibitor (ethanol, methanol, etc.) systems be experimentally determined, and Henry's law constants be correlated as a function of concentration and temperature for these systems. These correlations could then be used in a computer program algorithm to directly determine the amount of inhibitor needed to prevent hydrate formation for a given set of conditions.

NOMENCLATURE

- A-- hydrate forming gas (used in Pieroen formula)
- a_w, a_{H_2O} -- activity of water
- B--second virial coefficient
- C_{mj} -- Langmuir constant for type m cavities in gas component j
- f_i -- feed moles of component i
- f_j -- fugacity of component j
- ΔH -- heat of formation of one mole of $A \cdot nH_2O$ at T_0
- Δh^f -- heat of fusion of water per mole
- Δh^α --molar enthalpy difference between empty hydrate lattice and ice
- \bar{h} -- partial molar enthalpy
- K_i -- equilibrium K value (y_i/x_i) for component i
- k_i' -- inverted Henry's constant for component i
- k_i -- Henry's constant for component i
- l_i -- liquid moles of component i
- n_i -- initial number of gas moles
- n_f -- final number of gas moles
- Δn_g -- difference in gas moles = $n_i - n_f$
- n_{soln} -- number of moles of solution
- P_i^0 -- vapor pressure of component i
- P_i -- partial pressure of component i
- P_c -- critical pressure
- P_f -- final equilibrium pressure
- P_r -- reduced pressure = P/P_c ; hydrate reference pressure

P_t -- total initial pressure

R -- universal gas constant

T -- temperature

T_{a1} -- initial ambient temperature

T_{a2} -- final ambient temperature

T_c -- critical temperature

T_o -- ice point temperature

T_r -- reduced temperature = T/T_c

V_v -- volume of vapor space in cell to quick disconnect

V_t -- volume of volumetrics and lines to cell inlet valve

$V_{t'}$ -- volume of volumetrics and lines to quick disconnect

V/L -- vapor to liquid mole ratio

Δv^{Δ} -- molar difference in volume between empty hydrate lattice and ice

Δv^f -- molar difference in volume between ice and liquid water

x_i -- liquid mole fraction of component i

y_i -- vapor mole fraction of component i

z -- compressibility factor

Greek letters

γ_i -- activity coefficient of component i

ϕ_i -- fugacity coefficient of component i

μ^{β} -- chemical potential of water in the empty hydrate lattice

μ^H -- chemical potential of water in the filled hydrate lattice

μ^L -- chemical potential of pure liquid water

$$\Delta\mu^H \approx \mu^\beta - \mu^H$$

$$\Delta\mu^L \approx \mu^\beta - \mu^L$$

ν_m -- number of cavities of type m per water molecule in the lattice

ω -- acentric factor

APPENDICES

APPENDIX A-- Henry's law constant experiment data reduction

1. Sample calculation

$$k_i' = x_i / P_i$$

$$x_i = \Delta n_g / (n_{\text{soln}} + \Delta n_g)$$

$$\Delta n_g = n_i - n_f$$

Run #3. 1.0 Molar methanol solution at -0.296°C

$$P^0 = 6.00 \text{ mm Hg}$$

$$T = 272.85 \text{ K}$$

$$T_{a1} = 300.25 \text{ K}$$

$$P_t = 798.2 \text{ mm Hg}$$

$$V_t = 508.46 \text{ cm}^3$$

$$P_f = 518.9 \text{ mm Hg}$$

$$V_v = 87.53 \text{ cm}^3$$

$$T_{a2} = 302.05 \text{ K}$$

$$V_{t'} = 526.71 \text{ cm}^3$$

initial moles of gas charged:

$$n_i = P_t V_t / (R T_{a1} z_1)$$

$$z = 1 + \frac{B P_c}{R T_c} \frac{P_r}{T_r}$$

Pitzer-Curl equation for B, using the Abbott correlation to T:

$$\frac{B P_c}{R T_c} = 0.083 - 0.422 / T_r^{1.6} + \omega (0.139 - 0.172 / T_r^{4.2})$$

for cyclopropane: $T_c = 397.8 \text{ K}$

$$P_c = 54.23 \text{ atm}$$

$$\omega = 0.1270$$

$$z_1: T_r = T_{a1} / T_c = 0.7548 \quad P_r = P_t / P_c = 0.01937$$

$$\frac{B_1 P_c}{R T_c} = -0.63247, \quad z_1 = 1 + (-0.63247)(.01937 / .7548) = 0.984$$

$$n_1 = \frac{(798.2/760) (508.46)}{(82.056) (300.25) (.98377)} = 0.02203$$

moles of solution, n_{soln} :

weight of solution used = 207.72 g

(10 ml CH_3OH in 250 ml solution)

10 ml x 0.7914 g/ml = 7.914 g CH_3OH

240 ml x 0.9975 g/ml = 239.40 g H_2O

247.314 g solution

wt % CH_3OH = 7.914 / 247.314 = 3.20 %

wt % H_2O = 239.40 / 247.314 = 96.80 %

moles CH_3OH = $\frac{(207.72 \times .032) \text{ g}}{32.04 \text{ g/mole}}$ = 0.207 moles

moles H_2O = $\frac{(207.72 \times 0.968) \text{ g}}{18.016 \text{ g/mole}}$ = $\frac{11.161 \text{ moles}}{11.368 = n_{\text{soln}}}$

final moles of gas at equilibrium:

(assuming methanol diffuses through the entire system)

$$n_f = \frac{(P_f - P^0)}{R} \left[\frac{V_v}{T z_2} + \frac{V_{t'}}{T_{a2} z_3} \right]$$

using the same procedure as before to find z_2 and z_3 :

$$z_2 = 0.98590, \quad z_3 = 0.98977$$

$$n_f = \frac{(518.9 - 6.0)/760}{82.056} \left[\frac{87.53}{(272.85)(.98590)} + \frac{526.71}{(302.05)(.98977)} \right]$$

$$n_f = 0.01717$$

$$\Delta n_g = n_i - n_f = 0.02203 - 0.01717 = 0.00486$$

$$x_i = \frac{\Delta n_g}{n_{\text{soln}} + \Delta n_g} = \frac{0.00486}{11.368 + 0.00486} = 4.280 \times 10^{-4}$$

$$k_i' = x_i / P_i = (4.280 \times 10^{-4} / 512.9) = 8.344 \times 10^{-7}$$

(mole fraction / mm Hg)

A computer program was written to perform this calculation. A print out of this program (HLAW2.FOR) is on the following page.

```

      TY HLA W2, FOR
      [7:52:29]
00100      5      READ(4,10)PT,TA1,VT,PV,VV,T,PF,VT1,TA2,AWAT
00150
00200      10     IF<PT.EQ.0>GO TO 15
00300          FORMAT(10F)
00400          R=82.056
00500          CALL VIRIAL<PT,TA1,Z1>
00600          PI=PF-PV
00700          CALL VIRIAL<PI,T,Z2>
00800          CALL VIRIAL<PI,TA2,Z3>
00900          AMOLI=(PT*VT)/(760.*R*TA1*Z1)
01000          AMOLF=(PI*VV)/(760.*R*T*Z2)+(PI*VT1)/(760.*R*TA2
01100          1*Z3)
01200          DELMOL=AMOLI-AMOLF
01300          X=DELMOL/(AWAT+DELMOL)
01400          AKPR=X/PI
01500          WRITE(4,20)Z1,Z2,Z3,AMOLI,AMOLF,X,AKPR
01600          GO TO 5
01700          20     FORMAT(6F,E13.5)
01800          15     STOP
01900          END
02000          SUBROUTINE VIRIAL<P,T,Z>
02100          PR=P/(760.*54.23)
02200          TR=T/397.8
02300          BPRO=.083-.422/(TR**1.6)+.127*(.139-.172/(TR**4.2))
02400          Z=1+(BPRO*PR)/TR
          RETURN
          END

```

2. Auxiliary calculations

V_t = volume of volumetrics and volume of lines to inlet valve
of cell

$V_{t'}$ = volume of volumetrics and volume of lines to quick-disconnect
of cell

V_v = volume of vapor space in cell up to quick-disconnect

a. volume of volumetrics was determined by helium expansion from the volumeters to an initially evacuated cylinder of known volume. $V_{\text{volumeter}} = 196.08$ ml

b. volume of the cell was found by water displacement:

$$V_{\text{cell}} = 293.52 \text{ g} / .997 \text{ g/ml} = 294.40 \text{ ml}$$

c. volume of tubing from volumeters up to cell inlet valve was found by changing the volume of the volumeter with the piston, and noting the pressure change:

$$V_2 / V_1 = P_1 / P_2$$

$$\Delta V = V_1 - V_2$$

$$V_1 = \Delta V / (1 - P_1/P_2)$$

example: $P_1 = 766.3$ mm Hg $P_2 = 840.1$ mm Hg

$$\Delta V = 40.980 \text{ cm}^3$$

$$V_1 = 40.980 / (1 - 766.3/840.1) = 466.7 \text{ cm}^3$$

where V_1 = volume of tubing + volume of
volumetrics

$$\text{volume of volumetrics} = 392.16 \text{ cm}^3$$

the piston was initially at 2000 counts,

or volume of 40.980 cm^3

$$\text{therefore, } V_{\text{tubing}} = 466.47 - 392.16 \\ + 40.980 = 115.29 \text{ cm}^3$$

An average of 7 such runs gave a value of

$$V_{\text{tubing to valve}} = 116.30 \text{ cm}^3$$

d. volume of tubing from valve to disconnect was calculated in the same manner as (c) above, and an average of 5 runs gave a value of $V = 18.25 \text{ cm}^3$

e. volume of tubing from disconnect to cell, by calculations from tubing diameter and length: $V = 3.11 \text{ cm}^3$

$$V_t = (a) + (c) = 392.16 + 116.30 = 508.46 \text{ cm}^3$$

$$V_{t'} = (a) + (c) + (d) = 508.46 + 18.25 = 526.71 \text{ cm}^3$$

$$V_v = (b) + (e) - (\text{volume of liquid used in run}) = 297.51 - v_{\text{liq}}$$

e.g., run #3: weight soln = 207.72 g

$$\text{" H}_2\text{O} = .968 \times 207.72 = 201.07 \text{ g}$$

$$\text{" CH}_3\text{OH} = .032 \times 207.72 = 6.65$$

$$\text{volume H}_2\text{O} = 201.07 \text{ g} / .9975 \text{ g/ml} = 201.58 \text{ ml}$$

$$\text{volume CH}_3\text{OH} = 6.65 \text{ g} / .7914 = \underline{8.40}$$

209.98 ml

$$V_v = 297.51 - 209.98 = 87.53 \text{ cm}^3$$

3. Primary data for Henry's law constant experiment

TABLE A-1

Run #	1	2	3	4	5	6	7	8
conc. (M)	0.0	0.0	0.988	0.988	0.988	4.938	4.938	4.938
P ^o (mm Hg)	4.50	5.06	6.00	7.40	8.94	11.52	13.84	15.58
T _{a1} (K)	297.25	299.85	300.25	297.95	298.45	300.65	301.45	302.85
n _{soln}	11.267	10.722	11.368	11.068	10.843	10.517	10.089	10.150
V _t (cm ³)	508.46	508.46	508.46	508.46	508.46	508.46	508.46	508.46
V _v (cm ³)	93.49	104.34	87.53	93.07	97.24	83.88	92.53	91.34
V _{t'} (cm ³)	526.71	526.71	526.71	526.71	526.71	526.71	526.71	526.71
T (K)	273.20	276.84	272.85	275.60	278.38	273.28	276.30	278.14
P _t (mm Hg)	393.8	627.9	798.2	805.4	808.0	799.1	793.1	801.1
P _f (mm Hg)	255.30	418.0	518.9	533.3	613.8	474.0	491.2	506.6
T _{a2} (K)	297.15	299.15	302.05	297.45	294.75	301.45	303.45	305.05

4. Error analysis for Henry's law constant experiment

The accuracy of the experiment was determined by performing a Monte Carlo type error analysis. This kind of error analysis determines with what confidence the experimental error will fall within certain limits. By simulating random experimental numbers on the computer, the probability function of the calculated dependent variable can be plotted--that is, a distribution of number of simulated experimental values vs. the calculated dependent variable will result, which is centered about the experimentally determined dependent variable. In this case, the Henry's law constant is the dependent variable, and the error involved in the experiment is determined from the range of the constant calculated with the simulated variables.

Using the mean and the standard deviation of each variable used to calculate the Henry's constant, random numbers were generated for these independent variables with a program in the CSM lexicon written by Professor Charles Baer. These random numbers were then used to calculate the dependent variable, the Henry's law constant. A modification of the H_{LAW2}.FOR computer program incorporated the random number generator subroutine, so that the mean and standard deviation of each variable was read in, and a loop was performed 1000 times to generate 1000 Henry's law inverted constants. A sort program was then used to arrange these values in ascending order and to count the number of times the k_1 ' values, the inverted Henry's law constant, fell within certain intervals. These data were then plotted--Henry's law inverted constant vs. number of times that value was generated.

A normal distribution around the experimental Henry's constant resulted. A confidence interval of 99.5 % was determined by area calculations, and the error represented by this confidence limit is ± 5.0 %. The confidence level indicates that, in this case, the TRUE value of k_1' has a 99.5 % chance of being within ± 5.0 % of the reported value. On the following pages are the data used for this determination, the programs used (HLAW3.FOR and SORT.FOR), and the graph of inverted Henry's constant vs. number of occurrences.

Data for Henry's constant error analysis from Run # 2 -- 5.0 M CH₃OH

<u>Variable</u>	<u>Mean</u>	<u>Standard Deviation</u>
P _t	799.1 mm Hg	1.0 mm Hg
T _{a1}	300.65 K	0.2 K
V _t	508.46 cm ³	1.85 cm ³
P ^o	11.52 mm Hg	0.15 mm Hg
V _v	83.88 cm ³	0.30 cm ³
T	273.28 K	0.22 K
P _f	473.95 mm Hg	1.0 mm Hg
V _t	526.71 cm ³	1.85 cm ³
T _{a2}	301.45 K	0.2 K
n _{soln}	10.517	0.01

$$\text{standard deviation} = \sqrt{\frac{\sum (x_i - \bar{x})^2}{(n - 1)}}$$

where n = number of determinations

\bar{x} = mean of value

$$k_1' (\text{run \# 2}) = 1.366 \times 10^{-6} \text{ (mole fraction / mm Hg)}$$

for the 99.5 % confidence limit bars:

$$1.296 \times 10^{-6} < k_1' < 1.431 \times 10^{-6}$$

Therefore, $k_1' = 1.366 \times 10^{-6} \pm 5.0 \%$

TY HLA3.FOR
[7:53:13]

```

00100      READ(4,10)PTM,TA1M,VTM,PVM,UVM,TM,PFM,VT1M,TA2M,AWATM
00150      READ(4,10)PTVAR,TA1VAR,VTVAR,PVVAR,UVVAR,TVAR,PFVAR
00175      1,VT1VAR,TA2VAR,AWATV
00180      DO 100 N=1,1000      -
00200      10      FORMAT(10F)
00300      R=82.056
00301      PT=RNORM(PTM,PTVAR)
00302      TA1=RNORM(TA1M,TA1VAR)
00303      VT=RNORM(VTM,VTVAR)
00304      PV=RNORM(PVM,PVVAR)
00305      UV=RNORM(UVM,UVVAR)
00306      T=RNORM(TM,TVAR)
00307      PF=RNORM(PFM,PFVAR)
00308      VT1=RNORM(VT1M,VT1VAR)
00309      TA2=RNORM(TA2M,TA2VAR)
00310      AWAT=RNORM(AWATM,AWATV)
00400      CALL VIRIAL(PT,TA1,Z1)
00500      PI=PF-PV
00600      CALL VIRIAL(PI,T,Z2)
00700      CALL VIRIAL(PI,TA2,Z3)
00800      AMOLI=(PT*VT)/(760.*R*TA1*Z1)
00900      AMOLF=(PI*UV)/(760.*R*T*Z2)+(PI*VT1)/(760.*R*TA2
01000      1*Z3)
01100      DELMOL=AMOLI-AMOLF
01200      X=DELMOL/(AWAT+DELMOL)
01300      AKPR=X/PI
01400      100      WRITE(1,20)AKPR
01500      20      FORMAT(E9,3)
01600      STOP
01700      END
01800      SUBROUTINE VIRIAL(P,T,Z)
01900      PR=P/(760.*54.23)
02000      TR=T/397.8
02100      BPRO=,083-,422/(TR**1,6)+,127*(,139-,172/(TR**4,2))
02200      Z=1+(BPRO*PR)/TR
02300      RETURN
02400      END

```

TY SORT.FOR
[7:54:09]

```

00100      DIMENSION ITEM(1000),NEXT(1000)
00150      DIMENSION AKPR(1000)
00200      N=1000
00300      DO 10 KK=1,N
00400      READ(1,20)ITEM(KK)
00500      20  FORMAT(E9,3)
00600      10  CONTINUE
00700      CALL SORTA(ITEM,N,INIT,NEXT)
00800      K=INIT
00900      5   WRITE(2,30)ITEM(K)
01000      30  FORMAT(E9,3)
01100      K=NEXT(K)
01200      IF(K.NE.0)GO TO 5
01300      NN=N
01350      REWIND 02
01400      N=1
01600      READ(2,100)AKPR(N)
01810      BAKPR=AKPR(N)
01820      DO 40 K=2,1000
01830      READ(2,100)AKPR(K)
01900      100  FORMAT(E9,3)
02000      IF(BAKPR.LT,AKPR(K))GO TO 50
02100      N=N+1
02200      IF(K.EQ,NN)GO TO 50
02300      GO TO 40
02400      50  WRITE(3,60)BAKPR,N
02500      IF(K.EQ,NN)STOP
02600      60  FORMAT(E9,3,I)
02700      BAKPR=AKPR(K)
02800      N=1
02900      IF(K.EQ,NN)WRITE(2,60)BAKPR,N
03000      40  CONTINUE
03100      STOP
03200      END

```

H LAW ERROR ANALYSIS

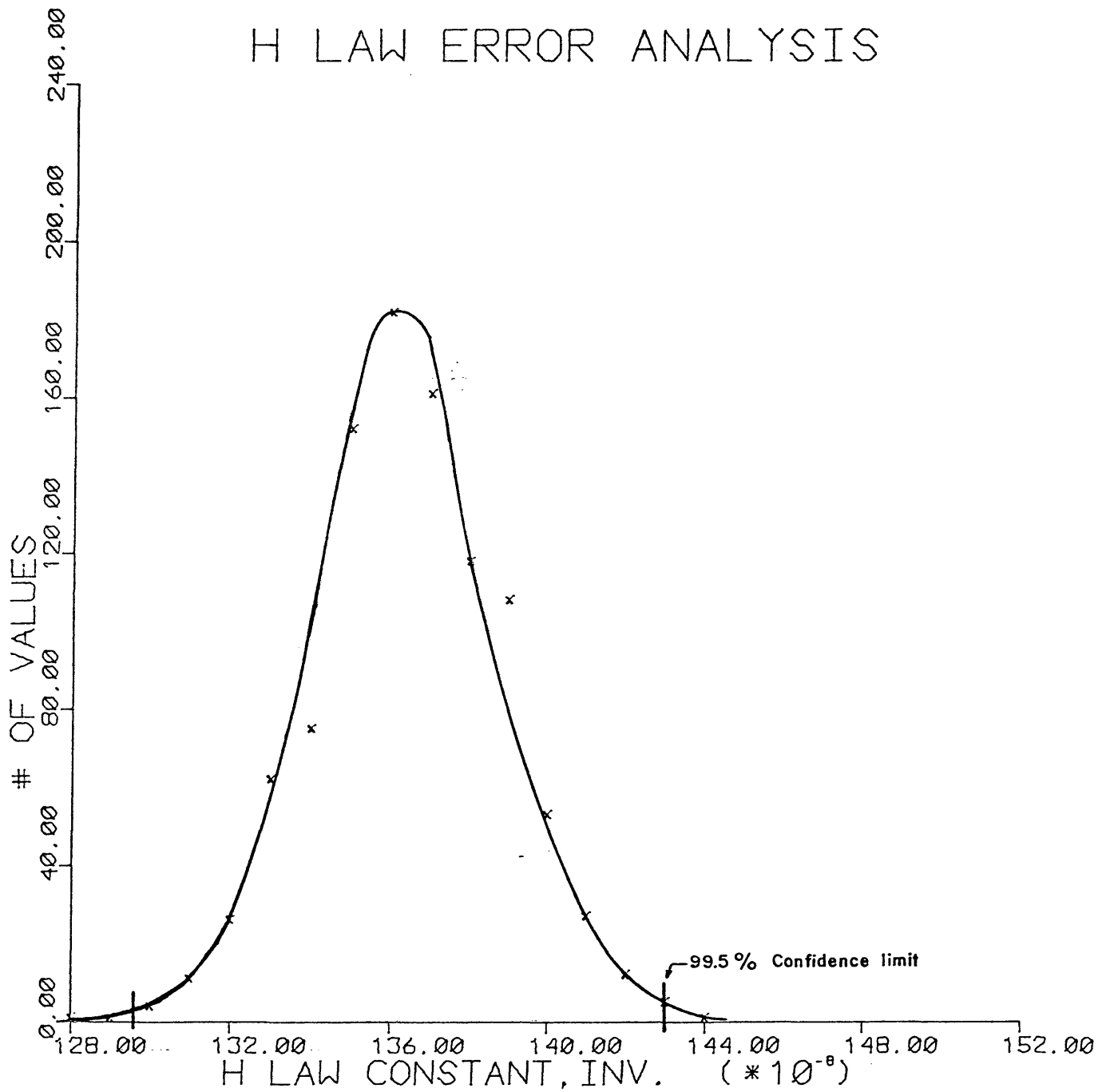


Figure 10

APPENDIX B-- Hydrate experiments data reduction

1. Check of the Wilson parameters for the binary water-methanol system

The activity coefficients for water and methanol calculated from the Wilson equation were compared with those calculated from experimental data (33,34), according to the following equation:

$$\phi_i = \frac{y_i P}{x_i P_i^0}$$

These data were obtained at pressures lower than 1 atmosphere, so that $\phi_i \approx 1.0$.

The results are shown in Table B-1 for 6 data points. Here, "Me" stands for methanol, and "w" for water, and "exp" means experimentally determined, while "Wil" stands for that calculated using the Wilson equation.

TABLE B-1

COMPARISON OF γ VALUES

T (C)	P (mm Hg)	x_{Me}	y_{Me}	$\gamma_{m, exp.}$	$\gamma_{m, Wil.}$	$\Delta\% \frac{\gamma}{exp-Wil.}$	$\gamma_{Me., exp.}$	$\gamma_{Me., Wil.}$	$\Delta\% \frac{\gamma}{exp-Wil.}$
92.3	760	.050	.284	.9988	1.004	-0.5	2.124	2.132	-0.4
71.1	760	.600	.828	1.333	1.457	-0.1	1.083	1.076	+0.7
82.9	760	.182	.552	1.043	1.045	-0.2	1.556	1.595	-2.5
81.6	760	.200	.586	1.038	1.054	-1.5	1.573	1.549	+1.5
75.5	760	.400	.724	1.184	1.172	+1.1	1.2073	1.217	-0.8
40.1	200	.600	.862	1.2427	1.383	-11.2	1.081	1.092	-1.1

2. Flash calculation -- sample calculation

"1" refers to component 1, methanol

"2" refers to component 2, water

"3" refers to component 3, cyclopropane

$$K_1 = y_1 / x_1 = \gamma_1 P_1^{\circ} / P$$

$$K_2 = y_2 / x_2 = \gamma_2 P_2^{\circ} / P$$

$$K_3 = y_3 / x_3 = (k_i' P)^{-1} = 1 / (\exp(-24.579 + 2851.80/t + 34.555 \times \text{conc}/T) \times P)$$

where concentration is in molarity

Example: 0.50 M CH₃OH, T = 273.59 K, P = 624.0 mm Hg, x₁ = 0.0091

$$\log_{10} P^{\circ} \text{ (mm Hg)} = A - \frac{B}{(C + T)} \quad T \text{ in K}$$

	A	B	C
water	7.96681	1668.21	228.0
methanol	7.87863	1473.11	230.0

at T = 0.44 °C, P₁[°] = 30.62 mm Hg

P₂[°] = 4.62 "

γ values from the Wilson equation:

$$v_1^1 = 39.563 \text{ cc/gmol}$$

$$v_2^1 = 18.055 \text{ "}$$

$$\lambda_{12} - \lambda_{11} = 205.30 \text{ cal/gmol}$$

$$\lambda_{12} - \lambda_{22} = 482.16 \text{ "}$$

$$\Lambda_{12} = v_2^1 / v_1^1 \exp \left[- (\lambda_{12} - \lambda_{11}) / R T \right]$$

$$\Lambda_{21} = v_1^1 / v_2^1 \exp \left[- (\lambda_{12} - \lambda_{22}) / R T \right]$$

$$\Lambda_{12} = \frac{18.055}{39.563} \exp \frac{-205.30}{(1.987)(273.59)} = 0.31282$$

$$\Lambda_{21} = 0.90261$$

$$\ln \gamma_1 = - \ln (x_1 + \Lambda_{12} x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right]$$

$$\ln \gamma_2 = - \ln (x_2 + \Lambda_{21} x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right]$$

$$x_1 = 0.0091$$

$$x_2 = 0.9909$$

$$\ln \gamma_1 = - \ln (0.0091 + (0.31282)(0.9909)) + 0.9909 \left[\frac{0.31282}{(0.0091 + (0.31282)(0.9909))} - \frac{0.90261}{((0.90261)(0.0091) + 0.9909)} \right]$$

$$\gamma_1 = 3.3825$$

$$\gamma_2 = 1.00019$$

$$K_1 = (3.3825)(3.0622)/624.0 = 0.1660$$

$$K_2 = (1.00019)(4.615)/624.0 = 7.40 \times 10^{-3}$$

$$K_3 = ((7.589 \times 10^{-7})(624))^{-1} = 2112.6$$

Let initial V/L guess be 0.01

Component	K value	$1 + KV/L$	$f_i = \text{feed}$ moles	$l_i = \text{liquid}$ moles = $\frac{f_i}{1 + KV/L}$
1	0.1660	1.0017	0.050	0.0499
2	7.34×10^{-3}	1.0001	5.541	5.5406
3	2112.6	22.126	0.059	0.0026
			5.650	5.5932

$(V/L)_{\text{new}} = (5.650 - 5.5932) / 5.5932 = 0.0102$, therefore V/L_{new}

is very close to that assumed.

$$y_i = (f_i - l_i) / v$$

$$y_3 = (0.059 - 0.0026) / .0568 = 0.9930$$

The computer program, FLASH.FOR, converges V/L to within 0.00004.

This program, along with a flow chart, is listed on the following pages.

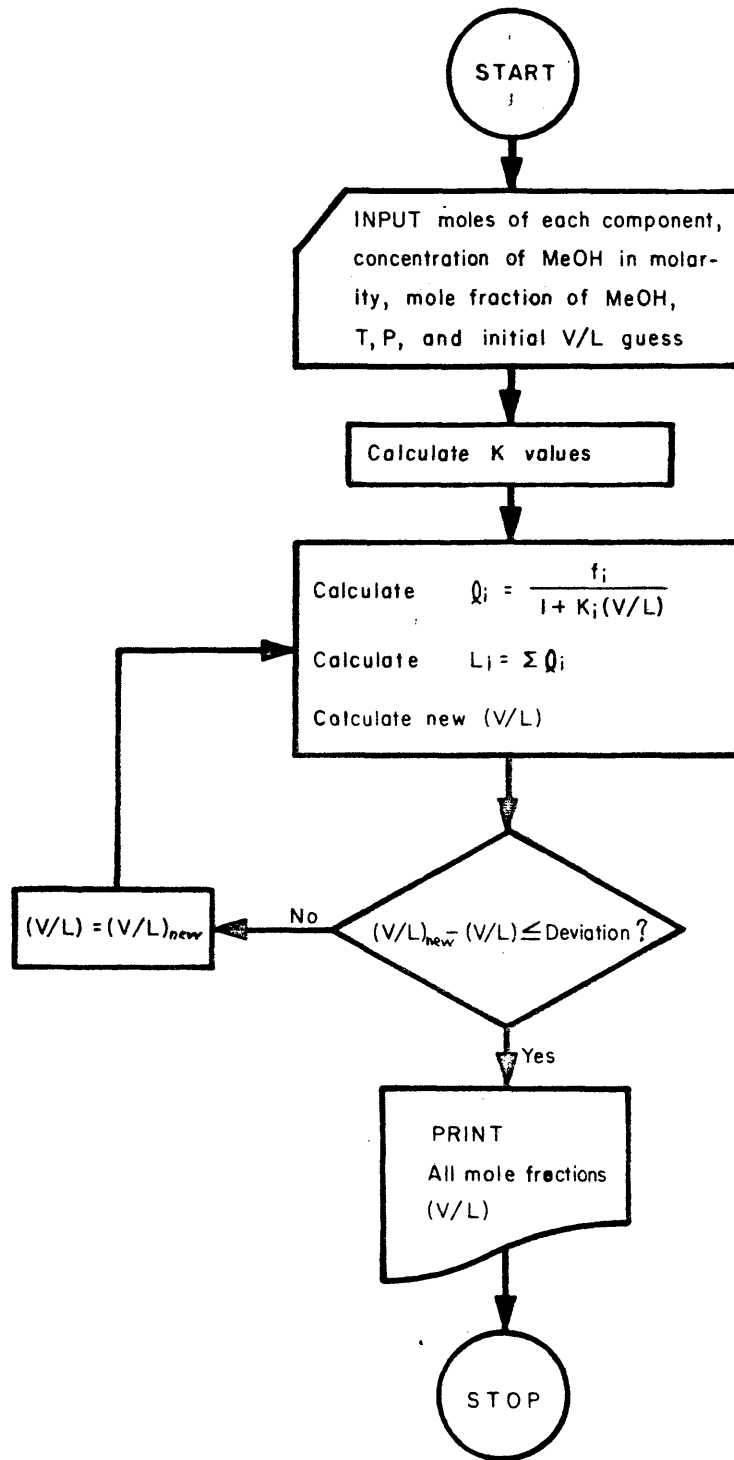


FIGURE II — Flow chart for FLASH.FOR

TY FLASH, FOR
[7:58:16]

```

00100 40      WRITE(4,1)
00200 1       FORMAT(' INPUT MOLES OF MEQH, H2O, AND C-C3, CONC IN M
00300          READ(4,2)AMOL1,AMOL2,AMOL3,CONC
00350          IF(AMOL1.EQ.0)GO TO 60
00400 2       FORMAT(4G)
00500          WRITE(4,3)
00600 3       FORMAT(' INPUT X1, MOL FRACT OF MEQH ')
00700          READ(4,4)X1
00800 4       FORMAT(1G)
00900          WRITE(4,5)
01000 5       FORMAT(' INPUT T IN DEG K, P IN MM HG ')
01100          READ(4,6)T,P
01200 6       FORMAT(2G)
01300          WRITE(4,7)
01400 7       FORMAT(' INPUT INITIAL V/L GUESS ')
01500          READ(4,4)RAT
01600          X2=1.0-X1
01700          VLH2=22.8815-.0364*T+6.856E-05*T**2
01800          VLME=64.517-.1972*T+3.874E-04*T**2
01900          DEL12=VLH2/VLME*EXP(-205.3/(1.987*T))
02000          DEL21=VLME/VLH2*EXP(-482.16/(1.987*T))
02100          GAMM2=EXP(-ALOG(X2+DEL21*X1)-X1*(DEL12/(X1+DEL12*
02200          1X2)-DEL21/(DEL21*X1+X2)))
02300          GAMM1=EXP(-ALOG(X1+DEL12*X2)+X2*(DEL12/(X1+DEL12*
02400          1X2)-DEL21/(DEL21*X1+X2)))
02500          TC=T-273.15
02600          PV1=10**((7.87863-1473.11/(230.+TC))
02700          PV2=10**((7.96681-1668.21/(228.+TC))
02800          AK1=(GAMM1*PV1)/P
02900          AK2=(GAMM2*PV2)/P*.6
03000          AK3=1.0/(P*EXP(-24.57863+2851.8029/T+34.55521*CONC/T))
03100          N=1
03200 30      A=1.0+AK1*RAT
03300          B=1.0+AK2*RAT
03400          C=1.0+AK3*RAT
03500          AL=AMOL1/A
03600          BL=AMOL2/B
03700          CL=AMOL3/C
03800          TOTL=AL+BL+CL
03900          AMOLT=AMOL1+AMOL2+AMOL3
04000          RATNEW=(AMOLT-TOTL)/TOTL
04002          X1=AL/TOTL
04004          X2=BL/TOTL
04006          X3=CL/TOTL
04008          Y1=(AMOL1-AL)/(AMOLT-TOTL)
04010          Y2=(AMOL2-BL)/(AMOLT-TOTL)

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```
04012      Y3=(AMOL3-CL)/(AMOLT-TOTL)
04100      IF((RATNEW-RAT).GT,.00004)GO TO 10
04200      GO TO 20
04300      10  RAT=RATNEW
04400      N=N+1
04500      IF(N.GT.100)GO TO 50
04600      GO TO 30
04700      20  WRITE(4,8)AK1,AK2,AK3,RATNEW,Y1,Y2,Y3,X1,X2,X3
04800      8   FORMAT(' K1=   ,K2=   ,K3=   ,Q/L=   '//,4G.//' Y1=
04900      1,Y2=   ,Y3=   ,X1=   ,X2=   ,X3=   '//,6G)
05000      GO TO 40.
05100      50  WRITE(4,9)
05200      9   FORMAT(' SOLUTION DID NOT CONVERGE ')
05250      GO TO 40
05300      60  STOP
05400      END
```

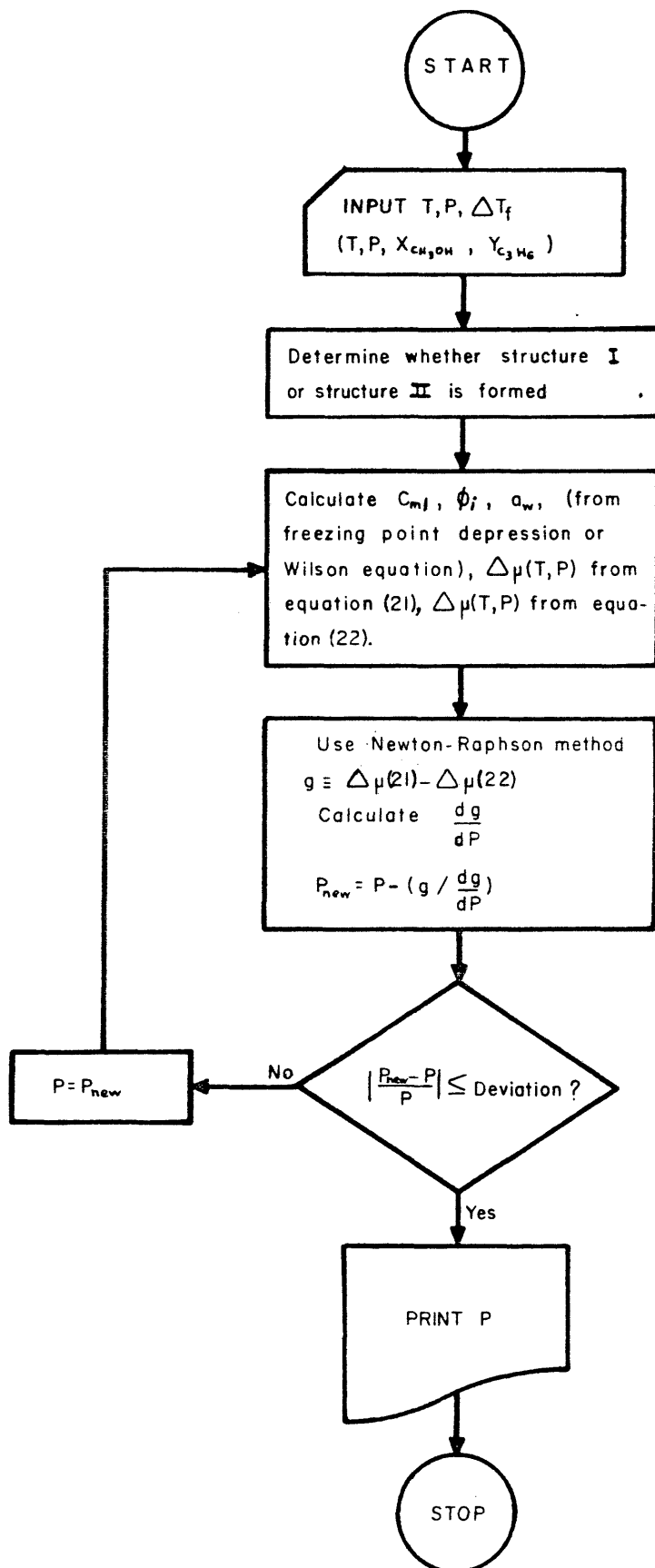


FIGURE 12 — Flow chart for MUO.FOR (and MUO2.FOR)

TY MUO.FOR

[7:55:01]

```

      PR(X)=EXP(AR+BR/X+CR*ALOG(X))
5     READ(4,10)T,P,DTF
C     INPUT T IN DEG K, P IN MM HG, DTF IN DEG K
      VINT=0.0
      VINT1=0.0
      VINT2=0.0
      IF(T.EQ.0)GO TO .50
10    FORMAT(3F)
      P=P/760.
      IF(T.LT.274.61)GO TO .20
C     CALCULATE STRUCTURE I PROPERTIES
      V=6./46.
      AML=.001449
      BML=4579.6
      GO TO .30
C     CALCULATE STRUCTURE II PROPERTIES
20    V=8./136.
      AML=.013136
      BML=4653.4
30    CML=AML/T*EXP(BML/T)
C     CALCULATE FUGACITY USING PITZER-CURL CORRELATION
      TC=397.8
      TR=T/TC
      W=.127
      PC=54.23
      R=82.056
      B=(.093-.422/(TR**1.6)+W*(.139-.172/(TR**4.2)))*
      1R*TC/PC
      PHI=EXP((P*B)/(R*T))
C     CALCULATE LN OF ACTIVITY
      A=(-1436.3*DTF)/(1.997*273.15**2)
      IF(T.LT.274.61)GO TO .60
C     CALCULATE STRUCTURE I PROPERTIES
      AR=-1212.2
      BR=44344.0
      CR=187.719
      DV=4.598
      DH=275.66
      DM=302.01
      GO TO .70
C     CALCULATE STRUCTURE II PROPERTIES
60    AR=-1023.14
      BR=34984.3
      CR=159.923
      DV=4.998
      DH=193.

```



```

DM=211.
70 TO=273.15
C CALCULATE MUO/RTO AT P0,TO
DMUO=(DM+DV*PR(TO)*.0242152)/(1.987*TO)
C CALCULATE ENTHALPY INTEGRAL
HINT=(1./1.987)*(DH*(1./T-1./TO)+2616.398*(1./T-
11./TO)+20.6166*ALOG(T/TO)-.021163*(T-TO))
C CALCULATE VOLUME INTEGRAL
N=ABS(273.15-T)
DO 40 I=1,N+1
DT=1.
TI=TI+DT
IF(I.EQ.1)TI=TO
DFRDT=((-BR/TI+CR)/TI)*PR(TI)
VINT1=(DFRDT/TI)*(DV/82.056)
-----
VINT=.5*(VINT1+VINT2)+DT*VINT
VINT2=VINT1
40 CONTINUE
DMPR=(DMUO+HINT+VINT)*1.987*T
DO 100 MM=1,10
DMU1=1.987*T*(V*ALOG(1.+CML*PHI*P)+A)
DMU2=DMPR+DV*.0242152*(P-PR(T))
G=DMU2-DMU1
DG=DV*.0242152-1.987*T*V*CML*PHI/(1+CML*PHI*P)
PNEW=P-G/DG
DEV=ABS((PNEW-P)/P)
IF(DEV.LT..001)GO TO 200
IF(PNEW.LT.0)PNEW=0.5*P
P=PNEW
100 PI=P*760.
IF(DEV.GT..001)GO TO 300
200 WRITE(4,250)DEV,DMU1,DMU2,PI,MM
250 FORMAT(1X,F12.5,5X,F12.5,5X,F12.5,5X,F6.1,5X,I2)
GO TO 5
300 WRITE(4,350)DEV,DMU1,DMU2,PI
350 FORMAT(1X,' PROBLEM DID NOT CONVERGE '/1X,F12.5,
15X,F12.5,5X,F12.5,5X,F6.1)
GO TO 5
50 STOP
END

```

```

TY MU02, FOR
C7:56:33]
      FR(X)=EXP(AR+BR/X+CR*ALOG(X))
5      WRITE(4,15)
15     FORMAT(' INPUT T IN K DEG, P IN MMHG, X1--MOL FRA
          1CTION OF MEOH, Y--MOL FRACTION OF C-C3 ')
          READ(4,10)T,P,X1,Y
C      INPUT T IN DEG K, P IN MM HG, X MEOH, Y C-C3
          VINT=0.0
          VINT1=0.0
          VINT2=0.0
          IF(T.EQ.0)GO TO 50
10     FORMAT(4F)
          X2=1.0-X1
          P=P/760.
          IF(T.LT.274.61)GO TO 20
C      CALCULATE STRUCTURE I PROPERTIES
          V=6./46.
          AML=.001449
          BML=4579.6
          GO TO 30
C      CALCULATE STRUCTURE II PROPERTIES
20     V=8./136.
          AML=.013136
          BML=4653.4
30     CML=AML/T*EXP(BML/T)
C      CALCULATE FUGACITY USING PITZER-CURL CORRELATION
          TC=397.8
          TR=T/TC
          W=.127
          PC=54.23
          R=82.056
          B=(.083-.422/(TR**1.6)+W*(.139-.172/(TR**4.2)))*
          1R*TC/PC
          PHI=EXP((P*B)/(R*T))
C      CALCULATE ACTIVITY
          VLH2=22.8815-.0364*T+6.856E-05*T**2
          VLME=64.517-.1972*T+3.874E-04*T**2
          DEL12=VLH2/VLME*EXP(-205.3/(1.987*T))
          DEL21=VLME/VLH2*EXP(-482.16/(1.987*T))
          GAMM=EXP(-ALOG(X2+DEL21*X1)-X1*(DEL12/(X1+DEL12*X
          12)-DEL21/(DEL21*X1+X2)))
          A=X2*GAMM
          IF(T.LT.274.61)GO TO 60
C      CALCULATE STRUCTURE I PROPERTIES
          AR=-1212.2
          BR=44344.0
          CR=187.719
          DV=4.598
          DH=275.66

```

```

DM=302.01
GO TO 70
C   CALCULATE STRUCTURE II PROPERTIES
60  AR=-1023.14
    BR=34984.3
    CR=159.923
    DV=4.998
    DH=193.
    DM=211.
70  TO=273.15
C   CALCULATE MUO/RTO AT PO,TO
    DMUO=(DM+DV*PR(TO)*.0242152)/(1.987*TO)
C   CALCULATE ENTHALPY INTEGRAL
    HINT=(1./1.987)*(DH*(1./T-1./TO)+2616.398*(1./T-
11./TO)+20.6166*ALOG(T/TO)-.021163*(T-TO))
C   CALCULATE VOLUME INTEGRAL
    N=ABS(273.15-T)
    DO 40 I=1,N+1
    DT=1.
    TI=TI+DT
    IF(I.EQ.1)TI=TO
    DFRDT=(-BR/TI+CR)/TI*PR(TI)
    VINT1=(DFRDT/TI)*(DV/82.056)
    VINT=.5*(VINT1+VINT2)+DT*VINT
    VINT2=VINT1
40  CONTINUE
    DMPR=(DMUO+HINT+VINT)*1.987*T
    DO 100 MM=1,10
    DMU1=1.987*T*(V*ALOG(1.+CML*PHI*P*Y)+ALOG(A))
    DMU2=DMPR+DV*.0242152*(P-PR(T))
    G=DMU2-DMU1
    DG=DV*.0242152-1.987*T*V*CML*PHI*Y/(1+CML*PHI*P*Y)
    PNEW=P-G/DG
    DEV=ABS((PNEW-P)/P)
    IF(DEV.LT..001)GO TO 200
    IF(PNEW.LT.0)PNEW=0.5*P
    P=PNEW
100  PI=P*760.
    IF(DEV.GT..001)GO TO 300
200  WRITE(4,250)DEV,DMU1,DMU2,PI,MM
250  FORMAT(1X,F12.5,5X,F12.5,5X,F12.5,5X,F6.1,5X,I2)
    GO TO 5
300  WRITE(4,350)DEV,DMU1,DMU2,PI
350  FORMAT(1X,' PROBLEM DID NOT CONVERGE '/1X,F12.5,
15X,F12.5,5X,F12.5,5X,F6.1)
    GO TO 5
50  STOP
    END

```

4. Primary data for hydrate experiments

KCl-water solutions:TABLE B-2

Concentration (mol/l)	T (°C)	Dissociation P (mm Hg)	ΔT_f (°C)
0.10	1.130	659.8	0.340
0.10	1.880	689.8	0.340
0.10	2.520	745.0	0.340
0.10	3.085	807.0	0.340
0.10	3.660	855.9	0.340
0.10	3.900	909.1	0.340
0.50	0.755	699.9	1.690
0.50	1.830	787.2	1.690
0.50	2.460	833.2	1.690
0.50	3.715	947.9	1.690
1.00	1.070	799.9	3.410
1.00	1.570	845.1	3.410
1.00	2.770	997.0	3.410
1.00	3.270	1079.4	3.410

CaCl₂-water solutions:TABLE B-3

Concentration (mol/l)	T (°C)	Dissociation P (mm Hg)	ΔT_f (°C)
0.10	0.560	571.1	0.440
0.10	1.430	664.7	0.440
0.10	1.760	690.8	0.440
0.10	2.380	747.1	0.440
0.10	3.390	857.1	0.440
0.50	0.215	663.0	2.460
0.50	1.170	744.1	2.460
0.50	2.310	850.3	2.460
0.50	3.870	1041.4	2.460
1.00	0.180	869.9	6.050
1.00	1.245	984.6	6.050
1.00	2.400	1150.6	6.050
1.00	2.935	1235.4	6.050

CH₃OH-water solutions:

TABLE B-4

Concentration (mol/l)	T (°C)	Dissociation P (mm Hg)	CH ₃ OH (moles)	H ₂ O (moles)	C ₃ H ₆ (moles)
0.50	0.440	624.0	.050	5.541	.0586
0.50	1.225	674.7	.050	5.541	.0586
0.50	2.365	781.7	.050	5.541	.0586
0.50	2.995	853.9	.050	5.541	.0586
1.00	0.485	666.1	.090	4.871	.0589
1.00	1.160	731.5	.090	4.871	.0589
1.00	2.355	823.4	.090	4.871	.0589
1.00	2.900	912.2	.090	4.871	.0589
5.00	0.260	1132.5	.499	4.475	.0709
5.00	1.025	1259.3	.499	4.475	.0709
5.00	2.285	1475.0	.499	4.475	.0709
5.00	2.860	1625.1	.499	4.475	.0709

LITERATURE CITED

1. Hammerschmidt, E.G., Ind. & Eng. Chem., 26, 8, p.851
2. Makogon, Yu F., "Hydrates of Natural Gases", manuscript, translated by W.J. Cieslewicz (Moscow, 1974)
3. Bily, C. and Dick, W.L., Bull. of Canadian Pet. Geol, 22, 3, p. 340-352 (1974)
4. Holder, G.D., Katz, D.L. & Hand, J.H., Am. Assoc. of Pet. Geol. Bull., 60, 6, p.981-994 (1976)
5. Hammerschmidt, E.G., Proceedings A.G.A., Tulsa, 1939, printed in Oil and Gas Jour., 37, 52, p. 68 (1939)
6. Personal correspondence, W.R. Parrish
7. Parrish, W.R. and Prausnitz, J.M., Ind. Eng. Chem, Process Des. Develop., 11, 1, p.26 (1972)
8. Deaton, W.M. and Frost, E.M., "Gas hydrates and their relation to the operation of natural-gas pipe lines", Monograph No. 8, U.S. Bureau of Mines (1946)
9. von Stackelberg, M. and Müller, H.G., J. Chem. Phys., 19, 1319 (1951)
10. von Stackelberg, M. and Müller, H.G., Naturwiss., 39, 20 (1952)
11. Claussen, W.F., J. Chem. Phys., 19, 259 (1951)
12. Claussen, W.F., J. Chem. Phys., 19, 1425 (1951)
13. Pauling, L. and Marsch, R.E., Proc. Nat. Acad. Sci. U.S., 38, 112 (1952)
14. van der Waals, J.H. and Platteeuw, J.C., Advan. Chem. Phys., 2, 41 (1959)
15. von Stackelberg, M. and Müller, H.G., Z. Elektrochem., 58, 25 (1954)
16. Russell, J.T., Am. Gas Journal, 146, 22, 6 (1937)
17. Powell, J.S., Jr., Proc. California Nat. Gas. Assoc., September meeting, p. 7-12 (1939)
18. Miller, B. and Strong, E.R., Proceedings A.G.A., p. 80-94 (1945)

19. Kobayashi, R., Withrow, H.J., Williams, G.B., and Katz, D.L., Proceedings N.G.A.A (1951)
20. Pieroen, A.P., Rec. Trav. Chim., 74, 995 (1955)
21. Jacoby, R.H., Stanolind Oil and Gas Co., Tulsa, Ok., Gas Hydrate Control Conference, May 5-6, 1953
22. Katz, D.L., A.I.M.E. Trans., 160, p.140 (1945)
23. Dharmawardhana, P.B., PhD. Thesis, Colorado School of Mines (in progress)
24. Hafemann, D.R. and Miller, S.L., J. of Phys. Chem., 73, 5, p. 1392-1397 (1969)
25. Glasstone, Samuel, Textbook of Physical Chemistry, Van Nostrand Inc. (New York, 1946)
26. CRC Handbook of Chemistry and Physics, Chemical Rubber Company, 51st edition, 1970-71
27. Lewis, G.N. and Randall, M., Thermodynamics, rev. by Pitzer, K.S. and Brewer, L., (McGraw-Hill, 1961)
28. Smith, J.M. and Van Ness, H.C., Introduction to Chemical Engineering Thermodynamics, 3rd edition, Ch. 3 and 7, McGraw-Hill (1975)
29. Tsonopoulos, C., A.I.Ch.E. Journal, 20, 2, p.263-272 (1974)
30. Holmes, M.J. and van Winkle, M., Ind. and Eng. Chem, 62, 1, p. 21-31 (1970)
31. Zerpa, Carlos, "An apparatus for the measurement of hydrate properties and the measurement of cyclopropane solubility in KCl solutions", Thesis #1975, Colorado School of Mines, 1977
32. Zerpa, C., Dharmawardhana, P.B., Parrish, W.R. & Sloan, E.D., J. of Chem. and Eng. Data, 24, 1, P.26 (1979)
33. Othmer, D.F. and Benenati, R.F., Ind. Eng. Chem., 37, 299 (1945)
34. Chu, J.C. et al., Vapor-liquid equilibrium data, J.W. Edwards, p.420-425, (Ann Arbor, 1956)