The difference between $(E_{MV})/(E_{OG})_{b=0}$ and $(E_{MV})/(E_{OG})_{b=1}$ can then be obtained from Figures 9 and 10 and the value of $(E_{MV})/(E_{OG})_{b=1}$ evaluated. Figure 11 shows a plot of E_{MV}/E_{OG} against λE_{OG} showing where the maximum difference occurs. Figure 8 shows a plot of E_{MV}/E_{OG} against the Peclet number for various values of b. For constant values of E_{OG}, the froth velocity and the dispersion coefficient then Figure 8 is effectively a plot of E_{MV} against Z the plate length. Increases in Z would be expected to cause an increase in E_{MV} but increasing Z would also increase the hydraulic gradient across the plate causing a non-uniform vapor distribution. The effect of the non-uniform vapor distribution would increase b from zero towards 1 as Z increased. A curve could be drawn on Figure 8 starting at $b = 0$ for small values of Z then moving towards $b = 1$ for large values of Z. It could be possible for a maximum to occur in this curve.

CONCLUSION

The ratio of the Murphree plate efficiency to the point or local efficiency has been extended from the uniform vapor distribution as described in the AIChE bubble-tray design manual to a linear vapor distribution. Except for the perfectly mixed plate and the plug flow of liquid there is a reduction in the Murphree plate efficiency. The magnitude of the reduction can be readily evaluated by the use of Figures 7 to 10. The maximum reduction occurs when the liquid mixing is intermediate between the extreme cases of plug flow and perfectly mixed.

NOTATION

a = constant
b = dimensionless vapor gradient
B = vapor gradient
E_{OG} = point plate efficiency
E_{MV} = Murphree vapor plate efficiency
L = liquid flow rate
N = Peclet number
v = dimensionless vapor flow rate
V = vapor flow rate
w = dimensionless distance
x = liquid composition
x^* = equilibrium liquid composition
X = dimensionless liquid composition
y = vapor composition
y^* = equilibrium vapor composition
z = distance along the plate
Z = distance to the weir
λ = defined by $m(V_{av} Z)/L$

Subscripts

av = average
n = plate or step n
T = total
z = at point

LITERATURE CITED

1. AIChE Bubble-tray design manual (1958).
2. Bolles, W.L., *Petrol. Proc.*, **11**, 109 (1956).
3. Cicalese, J. J., et al. *Petrol. Ref.*, **26**, 495 (1947).
4. Davies, J. A., *Ind. Eng. Chem.*, 39, 774 (1947).
5. Kemp, H.S., and C. Pyle, *Chem. Eng. Progr.* **45**, 435 (1949).
6. Lockhart, F. J., and C. W. Leggett, *Adv. Petrol. Ref.*, **1**, 278 (1958).
7. Gerster, J.A., et al., Univ. Delaware, Section 11, Final rept. (1958).

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The Fluid Hydrates of Methylene Chloride and Chloroform: Their Phase Equilibria and Behavior as Influenced by Hexane

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Thermodynamic properties pertaining to phase equilibria in the binary-fluid hydrate systems, methylene chloride-water and chloroform-water, and the ternary hydrate system, methylene chloride-chloroform-water, were measured. Total vapor pressure data were recorded as a function of temperature over a range of —3 to +10°C. Quadruple locus measurements of the ternary four-phase equilibrium, L_1-L_2-H-G, and isobaric studies of the ternary system chloroform-methylene chloride-water, support the existence of a solid solution hydrate between methylene chloride and chloroform. The addition of the nonhydrate former, hexane, to the methylene chloride-water system lowered the isobaric critical decomposition temperature of the hydrate.

Gas or fluid hydrates are a specific type of crystalline clathrate or cage-like compound wherein the hydrated molecules are enclosed in a rigid lattice of water molecules. The water molecules are usually referred to as the *host* and the hydrated molecule as the *guest*. Hydrated molecules are most commonly either gases such as methane or argon, or volatile liquids such as methylene chloride or chloroform. The entrapped guest molecules stabilize the otherwise metastable host lattice. There are no chemical bonds between the water molecules and the hydrated molecules; stabilization occurs by forces similar to intermolecular forces in dense gases and liquids.

By using X-ray techniques Von Stackelberg (*25*) and Claussen (*6*) characterized hydrates into two major crystalline structures which they labelled I and II. A specific framework will retain only those molecules that fit the dimensions of the void spaces available. In a structure II hydrate, slightly distorted regular pentagonal dodecahedrons composed of water molecules assemble to form a modified cubic lattice with a lattice constant of approximately 17.3Å. The unit cell consists of 136 water molecules having two characteristic types of void spaces:

1. 16 small voids of 4.8 Å.diameter.

2. 8 larger voids of 6.9 Å. diameter.

For pure structure II hydrates, the enclosed guest (M) molecules are able to be present only in the larger void spaces, resulting in a formula of $M \cdot 17\ H_2O$ for the ideal hydrate.

Von Stackelberg (*25*) has measured the lattice constants of methylene chloride at 17.31 Å. and that of chloroform hydrate at 17.30 Å. This indicates that both methylene chloride and chloroform form structure II hydrates.

When crystallizing real hydrates from solution, the composition is affected by the concentration of the guest component at the site of crystal growth (*15*). Most hydrated compounds are relatively insoluble in water (for example, methylene chloride 2% by weight at 20°C.; chloroform 1% by weight at 20°C.) Since hydrates appear to show interfacial growth between the crystalline hydrate phase and the water-rich phase, increased solubility in water should result in higher rates of hydrate formation (*2*). Because of this limiting factor, hydrates do not always form in constant mole ratios between the two components. This nonstoichiometric property has been verified by Scheffer and Meyer (*24*) and Glew (*11* to *13*).

Investigators have long been concerned with the properties of hydrates. Faraday (*8*), de Forcrand (*9*), Roozeboom (*23*), and Davy (*7*) synthesized hydrates with a variety of compounds including bromine, chlorine, methyl chloride, and hydrogen sulfide. Katz and co-workers (*3* to *5*, *17*) and Olds, et al. (*18*) have been interested in phase equilibrium diagrams of a number of hydrates. More recently, Barduhn (*2*), Banks, et al. (*1*), Reamer, Selleck, and Sage (*21*), Otto and Robinson (*19*), and Roberts, et al. (*22*) have investigated several hydrate systems. Katz, et al. (*3*, *4*) proposed the existence of solid solution hydrates in a ternary system where two hydrate-formers such as methane and propane were present with water. Van der Waals and Platteeuw (*26*) and Reamer, Selleck, and Sage (*21*) have supported the existence of a solid solution hydrate in other systems.

Phase equilibria in hydrate systems are usually studied with reference to the Gibbs Phase Rule:

$$F = C + 2 - P \tag{1}$$

For the specific case of a binary system:

$$F = 4 - P \tag{2}$$

When four phases are present in equilibrium the system becomes invariant. This condition is usually labelled the quadruple point or critical decomposition point. If three phases are present, a monovariant system results and a line will exist in the projected total vapor pressure-temperature plane.

Monovariant equilibrium studies are of interest because Clausius-Clapeyron relationships can be developed. Gilmont (*10*) presents a determinant solution for the derivative of total pressure (p) with respect to temperature (T) for an N component system. For the case of isothermal, monovariant equilibrium the following equation results:

$$\frac{dp}{dT} = \frac{\Delta H_a}{T\,\Delta V_a} \tag{3}$$

Van der Waals and Platteeuw (*27*) defended the validity of the Clapeyron equation as applied to clathrate systems. Barduhn (*2*), and Pieroen and Korvezee (*14*) made suggestions concerning its use.

By making the following assumptions for a binary, three phase, monovariant system:

1. All phases pure and do not change in composition
2. Ideal gas phase present.
3. Gas phase specific volume >>> liquid or solid phase specific volume.

a simplified expression for Equation (3) is given by:

$$\frac{d \ln p}{d(1/T)} = \frac{-\Delta H_a}{R} \tag{4}$$

which is the familiar form of the Clapeyron equation. After integrating Equation (4) a linear relationship results between ln p and $1/T$ providing ΔH_a does not change appreciably with temperature or pressure. Data presented in this manner facilitate calculation of reaction enthalpies.

Van der Waals and Platteeuw (*26*), by use of statistical mechanics, predicted thermodynamic properties of several simple clathrates. Their mathematical model is analogous to Langmuir's isotherm for ideal localized adsorption. By developing a partition function and relating it to the thermodynamic variables of the system, they developed relationships between the vapor pressure, chemical potential, composition, and temperature. Evaluation of thermodynamic properties from these equations depends on calculating what Van der Waals refers to as the *cell partition function.* He and his associates have used the Lennard-Jones and Devonshire 6-12 potential energy function to estimate the partition function and consequently predict several thermodynamic properties. For example, they predicted dissociation pressures for the three-phase, *H-I-G*, system at 273°K. to within 10% of the observed values for argon, krypton, and xenon as the enclosed molecules. However, for larger hydrocarbon molecules the predictions were much poorer: ethylene showed a 1,000% difference between experimental and theoretical values, and ethane 500%. These large deviations reflect the inadequacy of the 6-12 potential in describing molecules that are nonspherical, and hindered in rotation in the cavities. Recently, Nagata and Kobayashi (*16*) utilized the Kihara potential model to predict dissociation pressures for the nitrogen-water and the methane-water systems and found reasonable agreement with experimental values. However, no completely satisfactory potential model exists to describe the behavior of larger, more complex molecules such as ethylene, methylene chloride, and chloroform.

Additional information on clathrates is available from the complete reviews of Van der Waals and Platteeuw (*26*), and Mandelcorn (*15*).

EXPERIMENTAL APPARATUS

Equilibrium Cell for Vapor Pressure Measurements

Phase equilibrium was obtained in a cell consisting of a 4 in., thermally-annealed, borosilicate glass pipe cap and a 3/8 in. brass plate cover which was clamped by an epoxy coated standard carbon-steel flange fitting. This is similar to the original design proposed by Barduhn (*2*). A Teflon gasket, 1/4 in. in thickness, was used between the brass plate and the glass cap as a seal for vacuum and pressure service. To minimize leaks a uniform pressure was applied on the gasket by six equally spaced 1/4 in. brass machine bolts. Teflon was selected as the gasket material and a high vacuum silicone lubricant as a sealer because of their inertness to chlorinated hydrocarbons. The problem of maintaining a tight seal with Teflon was minimized by frequent uniform tightening of the bolts. The vessel was designed to withstand pressures up to 2 atm. Leakage was less than 0.05 mm. Hg/hr. at an absolute pressure of 10 mm. Hg.

Liquid samples were introduced and removed from the cell with a 10 cc. hypodermic syringe. The syringe was fitted with a 9 in. stainless steel needle to allow sampling of a specific liquid phase if two or more immiscible phases were present. Entrance to the vessel under vacuum or pressure was attained by passing the needle through a silicone rubber septum mounted in the brass plate.

A Beckman Differential Thermometer, accurate to 0.01°C., was placed in an opening in the center of the brass plate with its mercury well approximately 1 in. from the cell bottom. A standard —35 to +25°C. mercury thermometer accurate to 0.05°C. was placed in the vessel through another opening in the plate.

A Teflon coated 2 in. magnet was used for agitation. The magnet, located in the equilibrium cell, was driven by a water-operated, submersible, rotating magnet. Vortex formation was negligible, and the stirrer was run at maximum speed.

Thermal Arrest (TA) Cell for Isobaric Studies

Hydrate decomposition temperatures were measured in a 250 ml. round-bottomed flask with a 6 in. long glass tube extension from a ground glass joint at the neck. A supported Beckman Differential Thermometer with its mercury well located in the center of the flask about 1 in. from the bottom fit tightly into the glass tube so evaporation losses were minimized. The liquid and solid phases received adequate mixing (from the Teflon coated magnet as before) while vortex formation was reduced by the presence of the immersed part of the thermometer.

Pressure Measurement and Temperature Control

Mercury manometers, 900 mm. in length, were used for vapor pressure measurements to a tolerance of ± 0.5 mm. Hg. A piezoelectric transducer was used to check results, but its accuracy was only ± 1 mm. Hg. Glass capillary and temperature corrections were utilized for the manometers. The atmospheric pressure was measured to an accuracy of 0.02 mm. Hg., well within the tolerance of the manometers.

Since all of the hydrates studied exist at temperatures below ambient, a refrigeration unit was necessary. Several equipment arrangements were tested, and a secondary equilibrium bath used in conjunction with a primary cooling bath gave best results. A temperature control of ± 2°C. was obtained in the primary bath, while a control of ± 0.01°C. was reached in the secondary bath.

EXPERIMENTAL PROCEDURE

Vapor Pressure Measurements

Vapor pressure equilibrium was established between existing phases by maintaining a constant temperature (± 0.01°C.) and good agitation. Air and other volatile impurities were removed from the cell prior to equilibration to insure measurement of the true total vapor pressure. When only liquid and vapor phases were present, approximately 3 hr. were necessary for equilibration; with one solid phase present, 6 to 12 hr. were required. Temperature, vapor pressure, and the number and character of the phases were recorded in the data.

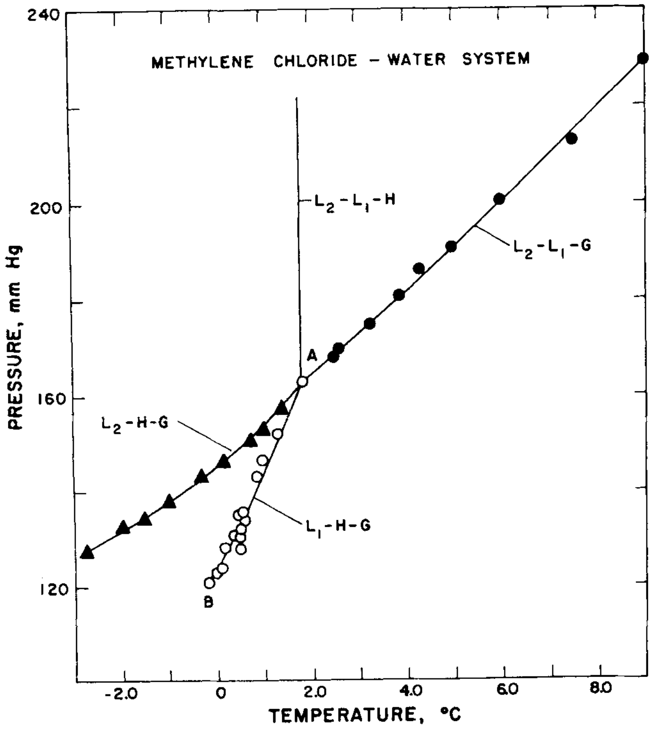

Fig. 1. Pressure-temperature equilibrium phase diagram for the methylene chloride-water system.

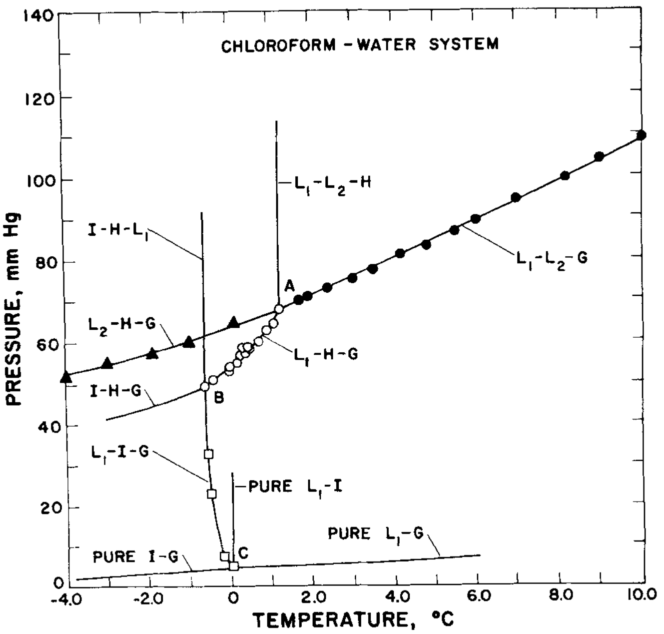

Fig. 2. Pressure-temperature equilibrium phase diagram for the chloroform-water system.

Thermal Arrest Decomposition Temperature Measurements

The thermal arrest (TA) cell was charged with approximately 240 ml. of water-rich phase, and 10 to 20 ml. of organic-rich phase. These proportions of the two immiscible liquids empirically gave the best distribution when agitated. The TA cell was placed in the temperature bath maintained at a temperature just above 0°C. (usually 0.1°C.) but below the predicted decomposition temperature (about 1.7°C.) of the hydrate. After a few minutes, with maximum stirring the temperature in the TA cell was within 0.05°C. of the bath temperature. In some cases hydrate formed by spontaneous nucleation; but when necessary a small crystal of either ice or hydrate was used for seeding. When a sufficient amount of solid hydrate had formed such that the speed of the agitator became impeded, several 500 w. immersion heaters were used to increase the bath temperature linearly as a function of time. Both the bath temperature and the temperature in the TA cell were recorded as functions of time until the hydrate had completely decomposed.

EXPERIMENTAL RESULTS AND DISCUSSION

Phase Equilibria for the Binary Systems
Methylene Chloride-Water and Chloroform-Water

Vapor pressures of the binary systems methylene chloride-water and chloroform-water were measured at fixed temperatures for several of the monovariant three-phase equilibria. The data are presented in Figures 1 and 2 and Tables 1 to 3.

Total vapor pressure data were collected for L_2-L_1-G, L_2-H-G, and L_1-H-G (Figure 1) three-phase equilibria for the methylene chloride-water binary. Total vapor pressures for those three-phase equilibria listed above were also measured for the chloroform-water binary (Figure 2). In addition, data were collected on L_1-I-G three-phase line (BC) which terminates at the triple point (C) for pure water. For both binaries, the L_1-L_2-H and L_1-I-H phase lines are drawn as vertical straight lines, which is essentially correct for the pressure range studied. Tables 2 and 3 present data which can be converted to the form of

$\log_{10} p$ as a function of $1/T(°\mathrm{K.})$ for use in the Clausius-Clapeyron relation previously developed in the Introduction. Two four-phase quadruple points were determined for each binary system, one corresponding to L_1-H-I-G phases and the other to L_1-L_2-H-G phases in equilibrium. Point A in Figures 1 and 2 represents the L_1-L_2-H-G four-phase equilibrium, while point B represents the L_1-H-I-G equilibrium. Table 1 compares the data with those recorded by Von Stackelberg (*25*).

TABLE 1. QUADRUPLE POINT DATA FOR METHYLENE CHLORIDE-WATER AND CHLOROFORM-WATER SYSTEMS

System	Phases present	Quadruple Points			
		this work		Von Stackelberg (*25*)	
		Temp. °C.	Pressure mm. Hg.	Temp. °C.	Pressure mm. Hg.
methylene chloride-water	L_1-L_2-H-G	1.85	163.3	1.70	160
	L_1-H-I-G	−0.10	121.2	0.0	116
chloroform-water	L_1-L_2-H-G	1.10	67.8	1.6	70
	L_1-H-I-G	−0.60	49.2	0.0	50

TABLE 2. TOTAL VAPOR PRESSURE (p)—TEMPERATURE (t) DATA FOR THE SYSTEM METHYLENE CHLORIDE-WATER

p mm. Hg.	t °C.	Phases present
229.6	9.0	L_1-L_2-G
213.2	7.5	
200.6	6.0	
191.2	5.0	
186.3	4.3	
180.6	3.90	
168.1	2.50	
174.8	3.30	
170.1	2.60	
165.1	2.00	
160.3	1.70	
160.1	1.65	
163.3	1.85	L_1-H-G
152.7	1.35	
146.7	1.00	
143.2	0.90	
134.2	0.60	
131.5	0.60	
128.2	0.50	
135.2	0.50	
135.9	0.60	
132.2	0.50	
131.2	0.40	
128.2	0.20	
124.7	0.10	
123.2	0.00	
121.2	−0.10	
157.2	1.40	L_2-H-G
153.7	1.00	
150.7	0.75	
146.7	+0.15	
143.2	−0.30	
138.2	−1.00	
134.4	−1.55	
133.4	−1.80	
127.9	−2.75	

TABLE 3. TOTAL VAPOR PRESSURE (p)—TEMPERATURE (t) DATA FOR THE SYSTEM CHLOROFORM-WATER

p mm. Hg.	t °C.	Phases present
109.3	10.1	L_1-L_2-G
104.2	9.0	
99.4	8.2	
94.2	7.0	
89.0	6.0	
86.4	5.5	
83.8	4.80	
81.8	4.15	
77.8	3.50	
75.8	3.00	
73.2	2.40	
71.3	1.90	
70.3	1.70	
68.0	1.20	
65.2	1.05	L_1-H-G
63.2	0.90	
60.2	0.75	
58.2	0.50	
58.7	0.45	
57.2	0.40	
58.3	0.40	
56.7	0.30	
54.7	0.20	
53.0	0.00	
51.6	−0.40	
49.2	−0.60	
65.2	0.10	L_2-H-G
60.0	−1.00	
57.2	−1.90	
55.4	−3.00	
52.4	−4.00	
32.2	−0.50	L_1-I-G
23.2	−0.50	
7.7	−0.26	

Two methods were used for quadruple point measurements. One method employed a thermal arrest technique, because with four phases present in a two component mixture the system is invariant and will not leave the arrest point until one of the phases has disappeared. Heating curves were used with both temperature and pressure recorded as a function of time. The second method was graphical; particular quadruple points were determined by the intersection of the three-phase pressure-temperature equilibrium lines.

Phase Equilibria for the Ternary System Chloroform-Methylene Chloride-Water

Von Stackelberg, et al. (*25*) found the X-ray diffraction patterns of pure chloroform hydrate and pure methylene chloride hydrate to be almost identical. Both hydrates are of the structure II type with following ideal stoichiometry:

$$M \cdot 17\,\mathrm{H_2O}$$

The lattice constant for chloroform hydrate measured 17.30 Å., and that for methylene chloride hydrate 17.31 Å. Because of the similarity of crystal structure and the general enclosure characteristics of clathrate compounds, one might propose that a ternary mixture of chloroform, methylene chloride and water would result in a continuous solid solution of structure II hydrate phase. Von Stackelberg and Meinhold (*25*) investigated mixtures of ethyl chloride and ethylene chloride in water. They determined the liquidus curve of hydrate decomposition temperature vs. composition of the organic binary under isobaric conditions and found no eutectic behavior. Instead they observed a smooth curve beginning at the decomposition temperature of pure ethyl chloride hydrate and ending at the decomposition temperature for ethylene chloride hydrate. Reamer, Selleck, and Sage (*21*) found similar isobaric behavior for the system propane-propene-water. This evidence suggests that a continuous solid solution hydrate exists in the chloroform-methylene chloride-water ternary.

According to the phase rule, a ternary system becomes monovariant when four phases are in equilibrium. Therefore, if a continuous solid solution hydrate really exists for this ternary system, a quadruple locus in the ternary total vapor pressure-temperature-composition three-dimensional space should exist for the monovariant four-phase equilibrium: solid solution hydrate-L_1-L_2-G. The equilibrium cell apparatus was used to measure the total vapor pressure and resulted in a smooth curve between the critical decomposition points *F* and *G* for the two pure hydrate binary systems (Figure 3 and Table 4). These data were extremely difficult and tedious to obtain; 10 to 12 hr. were necessary for equilibration of the four phase system.

In addition, an isobaric temperature-composition study of the chloroform-methylene chloride-water ternary was conducted using the thermal arrest cell. Although Von Stackelberg (*25*) measured only the final decomposition temperature of the hydrate solid solution, it was our belief that both the initial (solidus) and final (liquidus) solid solution hydrate decomposition temperatures could be determined by employing a carefully controlled thermal arrest study. Reamer, Selleck, and Sage (*21*) measured both initial and final temperatures, but found more uncertainty in the final decomposition temperature.

The isobaric study showed that a continuous range of decomposition temperatures existed at a particular composition. The composition refers to the initial composition of the chloroform-methylene chloride binary on a water-free basis. No eutectic behavior was observed, and a smooth curve resulted for the upper or liquidus decomposition temperature from pure methylene chloride (1.85°C.) to pure chloroform (1.30°C.). Difficulty was experienced in determining the lower or solidus decomposition temperature.

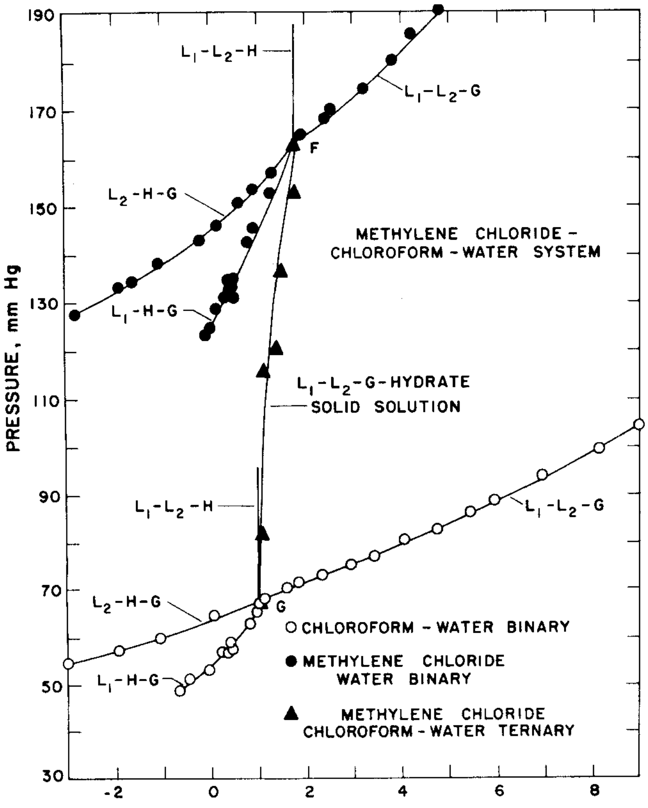

Fig. 3. Pressure-temperature equilibrium phase diagram for the ternary system methylene chloride-chloroform-water with the quadruple locus included.

TABLE 4. TOTAL VAPOR PRESSURE (*p*)—TEMPERATURE (*t*) DATA FOR THE TERNARY SYSTEM METHYLENE CHLORIDE-CHLOROFORM-WATER. QUADRUPLE LOCUS DATA

p mm. Hg.	*t* °C.	Phases present
163.3	1.85	L_1-L_2-H-G
153.0	1.84	
137.2	1.63	
120.5	1.42	
116.0	1.20	
80.1	1.15	
67.8	1.10	

From both isobaric temperature-composition and quadruple locus total vapor pressure studies, the continuous solid solution hydrate hypothesis is substantiated. An X-ray and microscopy investigation of the proposed solid solution hydrate could critically analyze the crystal structure.

The Effect of Hexane on the Phase Equilibria of the Binary System, Methylene Chloride-Water

Barduhn (*2*) and others have investigated the depressant effect of salt on the thermodynamic equilibrium properties of hydrate systems. Salt essentially acts as a diluent in the water-rich liquid, L_1, phase. For many years operating problems resulted from the blocking of natural gas pipelines by gas hydrates. As a practical solution, hydrate formation has been avoided by adding a water soluble compound such as ethylene glycol, methanol, or ethanol.

Up to the present, relatively little study has been made of how hydrates are affected by compounds that are essentially soluble only in the organic-rich liquid, L_2, phase but which do not themselves form hydrates, for example, hexane and benzene. Von Stackelberg and Meinhold (*25*) present an isobaric diagram of the ethyl chloride hydrate decomposition temperature as a function of benzene concentration. Data show a decrease in the decomposition temperature as the benzene concentration increases.

Hexane was chosen for our experiments as the organic soluble diluent for several reasons. First, hexane and methylene chloride are mutually soluble for the temperature range studied. Secondly, hexane and methylene chloride have approximately the same molecular weight, hexane = 86.17 g./g.mole and methylene chloride = 84.94 g./g.mole; and the difference in their boiling points, 69°C. for hexane and 40°C. for methylene chloride, is relatively small when compared to the difference for water and salt; and third, the hexane molecule with six carbon atoms is too large to fit into any of the void spaces of either a structure I or II hydrate. Hexane and other long chain paraffins, and benzene and other aromatics being too large to form hydrates are classified as nonhydrate-formers. Therefore, in an aqueous mixture of a hydrate-former such as methylene chloride and a nonhydrate-former such as hexane the solid phase that appears above 0.0°C. will be the pure fluid hydrate of the hydrate-former. There will be no complications of solid solution hydrates or double hydrates as are experienced when two hydrate formers are present in water.

An isobaric study of the decomposition temperature of pure methylene chloride hydrate using the thermal arrest cell was made for several mixtures of methylene chloride and hexane in an excess amount of water. The procedure and apparatus were exactly the same as used for determining properties of the solid solution hydrate of meth-

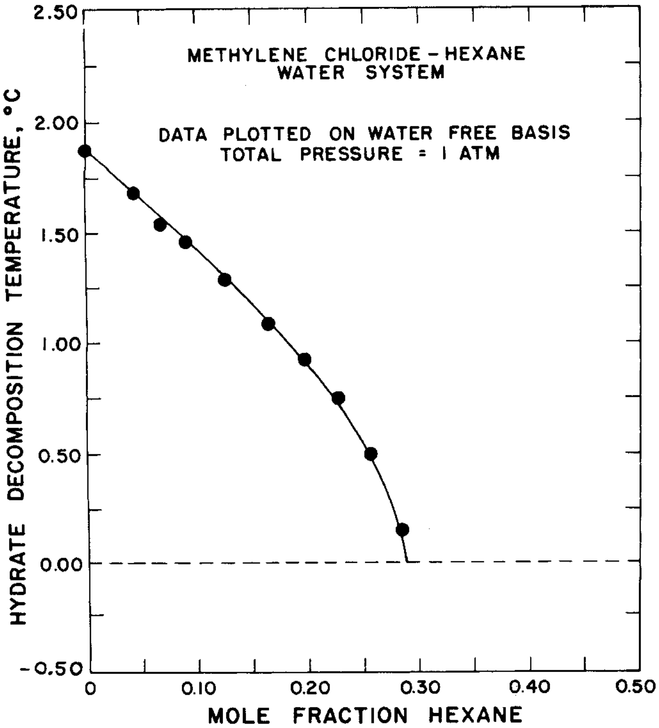

Fig. 4. The influence of hexane as a third component additive on the system methylene chloride-water. Critical decomposition temperature vs. mole fraction of hexane.

ylene chloride and chloroform. Figure 4 presents the results of these experiments. The hydrate decomposition temperature decreases linearly in the range where the mole fraction of hexane (on a water-free basis) is less than 0.18, and then slopes downward reaching 0.0°C. when the mole fraction of hexane is approximately 0.30. The linear portion for dilute concentrations of hexane is described by:

$$\Delta T = -K(X_c) \qquad (5)$$

K had a value of 4.8 ± 0.2°C. as measured from the slope of Figure 4.

Pieroen and Korvezee (*20*) discuss the thermodynamic aspects of the depressant action of a third component on the three-phase equilibrium temperature in binary systems. Their work can be directly applied to the three-phase equilibrium of L_1-L_2-H for the methylene chloride-water system.

Assuming the presence of ideal liquid and solid phases, and complete immiscibility between the L_1 and L_2 phases, a theoretical equation can be reduced to the same form as Equation (5). Its derivation is based on the manipulation of the chemical potential function through consideration of the Gibbs-Helmholtz relationship and the hydrate phase reaction stoichiometry and thermochemistry for the reaction between liquid organic and water to give hydrate. The equation obtained using these simplifying assumptions was:

$$\Delta T = -5.5(X_c) \qquad (6)$$

The coefficient of 5.5°C. in Equation (6) is 15% larger than the value for K of 4.8°C. obtained in the empirical Equation (5). This difference in coefficients could be caused by the approximations used in deriving Equation (6).

ACKNOWLEDGMENT

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NOTATION

C = number of distinct components
F = systemic degrees of freedom
G = gas or vapor phase
H = solid hydrate phase
ΔH_a = actual enthalpy change of the equilibrium phase reaction
I = solid water or ice phase
K = empirical constant, °C.
L_1 = water rich liquid phase
L_2 = organic rich liquid phase
M = enclosed, hydrated molecule
P = number of distinct phases
p = total vapor pressure, mm. Hg.
t = temperature, °C.
T = absolute temperature, °K.
T_o = critical decomposition temperature
ΔT = decomposition temperature lowering = $T - T_o$ = $T - 1.85$ (°K. or °C.) for methylene chloride hydrate
ΔV_a = actual volume change of the equilibrium phase reaction
X_c = mole fraction of hexane on a water-free basis

LITERATURE CITED

1. Banks, W. P., B. O. Heston, F. F. Blankenship, *J. Phys. Chem.*, **58**, 962 (1954).
2. Barduhn, A. J., H. E. Towlson, Y. C. Ho, *AIChE J.*, **8**, 176 (1962).
3. Carson, D. B., and D. L. Katz, *Trans. Am. Inst. Mech. Eng.*, **146**, 150 (1942).
4. ———, and D. L. Katz, and W. Wilcox, *Ind. Eng. Chem.*, 33, 662 (1941).
5. Chinworth, H. E., and D. L. Katz, *J. Am. Soc. Refrig. Eng.*, **54**, 359 (Oct., 1947).
6. Claussen, W. F., *J. Chem. Phys.*, **19**, 1425 (1951).
7. Davy, H., *Phil. Trans.*, 101 (1811).
8. Faraday, M., *Quart. J. Sci., Literature Arts*, **15**, 71 (1833).
9. Forcrand, R. de, *Compe, Rend.*, **134**, 835, 991 (1902).
10. Gilmont, H., "Thermodynamic Principles for Chemical Engineers," p. 126, McGraw Hill, New York (1955).
11. Glew, D. N., *Can. J. Chem.*, **38**, 208 (1960).
12. ———, Nature, **184**, 545 (1959).
13. ———, and E. A. Moelwyn-Hughes, *Disc. Faraday Soc.*, no. 15, 150 (1953).
14. Korvezee, A. E., and A. P. Pieroen, *Rec. Trav. Chim.*, **81**, 385 (1962).
15. Mandelcorn, L., *Chem. Rev.*, 827 (1959).
16. Nagata, I., and R. Kobayashi, *Ind. Eng. Chem. Fundamentals*, **5**, 344 (1966).
17. Noaker, L. J., and D. L. Katz, Petrol. Trans. Am. Inst. Mech. Eng., 135 (Sept., 1964).
18. Olds, R. H., B. N. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **34**, no. 10, 1223 (1942).
19. Otto, F. D., and D. B. Robinson, *AIChE J.*, **16**, 602 (1960).
20. Pieroen, A. P., and A. E. Korvezee, *Rec. Trav. Chim.*, **81**, 898 (1962).
21. Reamer, H. H., F. T. Selleck, and B. N. Sage, *Petrol. Trans. Am. Inst. Mech. Eng.*, **192**, 197 (1952).
22. Roberts, O. L., E. R. Brownscombe, and L. S. Howe, *Oil Gas J.*, **39**, no. 30 (1940).
23. Roozeboom, H. W. B., *Z. Phys. Chemie*, **2**, 449 (1888).
24. Scheffer, F. R. C., and C. Meyer, *Proc. Acad. Sci. (Amsterdam)*, **21**, 338, 1204, 1338 (1919).
25. Von Stackelberg, M., H. Frühbuss, W. Jahns, W. Meinhold, and H. R. Müller, *Z. Elektrochem.*, **58**, 104, 99, 162, 40, 25 (1954).
26. Van der Waals, J. H., and J. C. Platteeuw, *Adv. Chem. Phys.*, **2**, no. 2, (1959).
27. ———, J. C. Platteeuw, and R. M. Barrer, *Nature*, **183**, 462 (1959).

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