Measurement and Prediction of Dissociation Pressures of Isobutane and Propane Hydrates Below the Ice Point

A gravimetric technique has been developed for measuring three phase vapor-ice-hydrate (VIH) equilibria. This technique has been used for measuring VIH dissociation pressures for propane and isobutane hydrates to temperatures as low as 241.4 K. Kihara parameters, based upon the experimental dissociation pressure data, have been obtained. Because the range of experimental three phase equilibrium data has been considerably extended, the parameters based on this data should be more useful in predicting hydrate dissociation pressures.

G. D. HOLDER
and
S. P. GODBOLE
Chemical and Petroleum Engineering
Department
University of Pittsburgh
Pittsburgh, PA 15261

SCOPE

Because the presence of heavier hydrate forming gases such as isobutane can have a dramatic effect upon the dissociation pressures of gas hydrates (Wu et al., 1976), molecular parameters used for modeling their role in hydrate equilibria need to be accurately determined. Among the important molecular parameters involved in predicting hydrate equilibrium conditions are the potential parameters which describe the gas-water interaction in the hydrate phase; most current models use the spherical core Kihara potential function for describing such interaction (Parrish and Prausnitz, 1972; Ng and Robinson, 1976; Holder and Hand, 1982).

In general, parameters for a particular gas are determined by forcing agreement between experimental and predicted hydrate dissociation pressures. The experimental data, in the majority of cases, are taken above the ice point, but for larger molecules the region of hydrate stability above the ice point is limited. For example, hydrates in equilibrium with isobutane vapors are not stable at temperatures greater than 1.1 K above the ice point. Hence parameters for larger molecules cannot always be based upon binary gas-water data taken solely above 273 K.

In the present study, dissociation pressures of gas hydrates formed from isobutane and from propane are measured over relatively large temperature ranges (20 K) below 273 K. A new experimental technique employing gravimetric measurements permits accurate determination of incipient hydrate formation conditions without the need for visual detection of the hydrate phase. This technique requires the formation of only very small amounts of the hydrate phase and avoids the problems, such as phase occlusion, which are associated with extensive hydrate phase formation.

Using this data, model parameters can be determined with a greater degree of confidence. From the experimental data, Kihara parameters for gas-water interactions in the hydrate phase have been determined for the various values of the thermodynamic reference properties which are presented in the literature (Sortland and Robinson, 1962; Dharmawardhana et al., 1980). A comparison of the parameters determined from the experimental data to the parameters predicted by the corresponding states approach of Holder et al. (1980) is also made.

CONCLUSIONS AND SIGNIFICANCE

Dissociation pressures of isobutane hydrate and of propane hydrate have been obtained at temperatures below the ice point and are used for determining gas-water Kihara parameters for these gases. Because such parameters are determined from data taken over a much larger experimental temperature range than was previously available, they can be used with a greater degree of confidence.

The experimental technique used involves the measurement of the weight of the hydrate phase and can detect the presence of hydrates when as little as one half percent of the ice is converted to hydrates. Problems with the phase occlusion are avoided since the presence of such small amounts of hydrate cannot occlude the relatively large amount of ice present.

Molecular parameters for describing gas-water hydrate phase interactions for isobutane and propane have been determined using the data obtained in the present and in previous studies (Deaton and Frost, 1946; Rouher and Barduhn, 1969). For propane, the data base covers temperatures ranging from 246.9 K to 278.5 K. For isobutane the corresponding temperature range is 241.4 K to 274.3 K. These relatively large ranges are likely to allow a more general set of molecular parameters to be determined for each gas.

Because the value of the reference chemical potential, $\Delta\mu^o$, for structure II hydrate, (the structure thought to form from the gases studied here) is not well known experimentally, molecular parameters were determined using different values of this thermodynamic property. Depending upon the value of $\Delta\mu^o$ used, an appropriate set of molecular parameters can be selected. No unique set of Kihara parameters was obtainable from pure component data. This is particularly evident when one notes the values for the Kihara parameters reported herein are considerably different than those reported by other investigators (Parrish and Prausnitz, 1972; Ng and Robinson, 1977). In particular, the values of the Kihara distance parameter reported here are larger than those reported in earlier investigations.

It appears that the values of $\Delta\mu^o = 937$ J/mol for structure II hydrate is the best of the currently available values. It is based on a combination of direct and indirect experimental data and appears more likely to be accurate than other values which are subject to considerable experimental uncertainty. The value of the parameters obtained using this value of $\Delta\mu^o$ are, in a comparative sense, physically reasonable, although they are not clearly superior to the parameters obtained using other values

---

0001-1541-82-6221-0930-$2.00.

of $\Delta\mu^{o}$.

The corresponding states approach of Holder et al. (1980) was not successful in predicting the experimental dissociation pressures. It appears that this method must be modified especially when modeling the hydrates of large, aspherical molecules such as propane and isobutane.

BACKGROUND

Gas hydrates are crystalline compounds composed of water and light nonpolar gases such as paraffins with four carbon atoms or less. In the hydrate phase, water forms a solid lattice network, similar to ice, in which the water molecules are connected through hydrogen bonding. This structure has large interstitial vacancies or cavities, each of which may or may not contain a gas molecule. Because only a fraction of the cages are occupied by a gas molecule, the hydrates are nonstoichiometric in nature and the exact water-to-gas mole ratio in the hydrate phase is dependent upon pressure, temperature and the equilibrium gas phase composition.

The network of hydrogen bonds "bypasses" the gas molecules in the hydrate lattice; the gas molecules are not bonded to the water molecules and gas-water interaction is thought to consist primarily of dispersion forces. The actual interaction between the encaged gas molecule and the water lattice can be modeled using classical statistics (van der Waals and Platteeuw, 1959) and relatively minor adjustments to this model allow fairly accurate prediction of three phase (gas; water-rich-liquid or solid; and hydrate) equilibria when experimental data is available for determining gas-water potential function parameters (Parrish and Prausnitz, 1972; Ng and Robinson, 1977; Holder and Hand, 1982; Holder et al., 1980).

PHASE BEHAVIOR OF GAS HYDRATES

Although some studies have focused on two, four and five-phase equilibria in hydrate containing systems, the majority of studies have examined three-phase equilibria conditions in which a vapor phase (V), a water-rich liquid phase (L_1) and a solid hydrate phase (H) are all present. Such three-phase studies have the advantage that the equilibrium conditions are univariant (a line on pressure-temperature coordinates) for a gas of fixed composition, and a single experiment for a gas-water binary can be conducted by fixing the temperature and measuring the equilibrium pressure.

For the heavier hydrate-forming gases such as propane and isobutane, the three-phase, VL_1H equilibrium locus extends only a few degrees above the ice point—to 274.3K for isobutane and to 278.7 K for propane. These temperatures represent the four-phase invariant quadruple points, where a hydrocarbon-rich liquid phase is also present, for the respective gases. At temperatures above the quadruple point the hydrocarbon-rich liquid is a more stable condensed phase than is the hydrate, and the latter does not form except at very high pressures or near the vapor-liquid critical point (Verma, 1974).

Because of the limited stability range above the ice point, VL_1H measurements do not provide a large data base from which to determine molecular parameters needed for hydrate equilibrium calculations. However, the stability range of such hydrates below the ice point is larger (greater than 50 K) and measurements in the three-phase vapor, solid-hydrate, solid-ice (VHI) region can provide a more than adequate data base. Parameters determined from such data would also be applicable to calculations above the ice point. Hence measurements in the region below 273 K are desirable.

The experimental technique needed for measurements at temperatures above the ice point is well-defined elsewhere (Holder and Grigoriou, 1980), but part of the procedure is pertinent here. Because excessive amounts of crystalline hydrate can occlude either gas or water and impede the approach to equilibrium, most experiments are carried out with only small amounts of the hydrate phase present. The presence of the small amounts of hydrates is determined by visual observation through a glass-windowed cell. Because hydrates usually float on the water phase, and because they cause visually detectable light defraction, their presence in small quantities is easily determined.

Analogous measurements below the ice point substitute an ice phase for the water-rich liquid; vapor, solid hydrate, and solid ice phases are all present at equilibrium conditions. The presence of ice makes the visual detection of the ice-like hydrate impossible. Consequently, the required experimental technique is more complex. The general method used in such cases is to form large amounts of the hydrates at low temperatures. Since gas enters the dense hydrate phase, the formation of hydrates results in a significant pressure reduction. The temperature is then slowly increased resulting in corresponding pressure increases as the hydrate phase gradually decomposes. The point at which the pressure-temperature curve breaks corresponds to the end of hydrate dissociation. The measurements at this break are taken as equilibrium conditions.

The difficulty with such measurements is that the break in the P-T curve is not always a break, but rather a rapid change in slope, and the actual equilibrium conditions are considerably more ambiguous than when a liquid water-rich phase is present. (If sufficient time is allowed for equilibrium, thermodynamics requires that a sharp break occur, but frequently for the ice hydrate experiments this time tends to be excessive.) Part of this problem is due to the fact that the dissociated hydrates are converted to vapor and ice; and the ice can potentially occlude the hydrate phase thereby restricting the approach to equilibrium. In the present study an entirely different dependent variable (weight) is used to determine hydrate equilibrium conditions in order to eliminate the need for the formation of excessive amounts of the hydrate phase.

THEORY

The statistical model developed for gas hydrates follows classical Langmuir adsorbtion thermodynamics. The chemical potential of water in the hydrate phase μ_H is related to the chemical potential of water in the hypothetical empty lattice, μ_β, through the fraction of the cages which are occupied, θ_i, (van der Waals and Platteeuw, 1959)

$$\mu_\beta - \mu_H \equiv \Delta\mu_H = -kT \sum_{i=1}^{2} [\nu_i \ln (1 - \theta_i)] \tag{1}$$

where ν_i is the number of water molecules per cage of type i in the hydrate phase. The summation is over the two hydrate cages. The fractional occupancy is given by Langmuir's isotherm

$$\theta_i = \frac{\sum_j C_{ij} f_j}{1 + \sum_j C_{ij} f_j} \tag{2}$$

where C_{ij} is the Langmuir constant for gas species j in cavity i.

The Langmuir constants are determined by the potential interaction between a gas molecule and the water molecules which encage it. Spherically symmetric models (McKoy and Sinanoglu, 1963) produce

$$C_{ij} = \frac{4\pi}{kT} \int_0^{R_i} \exp\left(-\frac{W_{ij}}{kT}\right) r^2 dr \tag{3}$$

where the potential function for a j molecule in i type cavity is

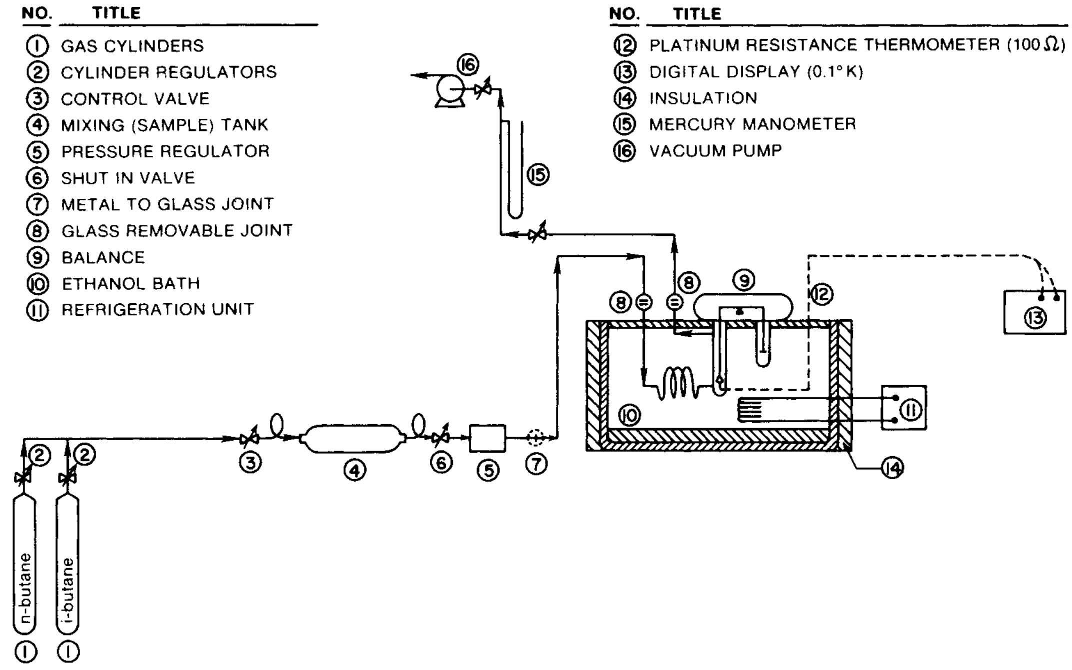

Figure 1. Experimental apparatus.

given by W_{ij}. The integration is over the (spherical) cage radius R_i.

The spherical core, gas-water Kihara parameters determine the potential function.

$$W_{ij}(r) = 2z\epsilon_j \left[\frac{(\sigma_j)^{12}}{R_i^{11} r}\left(\delta^{10} + \frac{a_j\delta^{11}}{R_i}\right) - \frac{\sigma_j^{6}}{R_i^{5} r}\left(\delta^{4} + \frac{a_j\delta^{5}}{R_i}\right)\right] \quad (4)$$

where

$$\delta^N = \left[\left(1 - \frac{r}{R_i} - \frac{a_j}{R_i}\right)^{-N} - \left(1 + \frac{r}{R_i} - \frac{a_j}{R_i}\right)^{-N}\right] \Big/ N \quad (5)$$

where σ_j is the gas-water Kihara diameter; ϵ_j is the gas-water Kihara energy parameter, and a_j is the core radius of the *gas* molecule. The core radius of the water molecule is taken as zero.

Kihara parameters are fitted using Eqs. 1 through 5 along with experimental data on fugacities of gases in equilibrium with hydrates. For large gas molecules the Langmuir constants are especially sensitive to the Kihara parameters and an accurate evaluation of these parameters can only be obtained from a sufficiently large experimental base.

EXPERIMENTAL

A gravimetric apparatus was used for determining *VHI* data for pure isobutane. A diagram of the equipment is shown in Figure 1. Essentially it constists of a C.I. Electronics Mark 2C electronic balance enclosed in a vacuum head. In this apparatus, a sample can be attached to a suspension wire and connected to the balance beam. The wire is enclosed in a 0.2 m hangdown tube with a 40 mm diameter. Ports allow admission of pure gases at any desired pressure less than 100 kPa.

A fine mesh copper screen, about 30 mm × 60 mm in size, was saturated with 75 to 125 mg of distilled water and attached to the bottom of the suspension wire which was then enclosed in the hangdown tube. A panel display meter displayed sample weights on a 100 mg scale which could be read to ± 0.3 mg. Counter weights were used to keep the meter reading on scale. Smaller scale ranges were available but not used. The tubes and their enclosed suspension wires were immersed in an insulated refrigerated bath, 10 liters in volume, which could be controlled to ± 0.05 K using a Neslab Cryocool CC-100 and Exatrol 30 temperature controller. The actual water sample was about 15 cm below the surface of the refrigeration fluid (ethanol).

A circulating pump extracted ethanol from one corner of the bath and pumped it through coils in a metal enclosure containing the vacuum head and finally back into the diagonally opposite corner of the bath. By cooling the vacuum head which contained most of the gas, temperature gradients inside the system were minimized. The residence time of the ethanol in the bath was roughly 20 seconds and the bath temperature was uniform to better than 0.1 K.

Temperatures were measured with two calibrated (± 0.2 K) 100 ohm platinum resistance thermometers. One was suspended in the bath with its sensing element about 10 mm from the sample, and the other was inserted into the thermocouple well in the sample tube, with its sensing element about 2 mm from the sample. Temperature measurements for calibrating the system were made with a bare thermometer inserted into the evacuated sample zone (with no sample present). This allowed temperature dependent correction (0.1 to 0.3 K) of the thermowell readings and compensated for any temperature gradients within the system. The total error in any reported temperature did not exceed 0.3 K. Pressures were measured using a mercury manometer and barometer in conjunction and are accurate to 0.2 kPa.

After a water sample was suspended from the balance, the temperature was set to a value below the ice point and the sample was frozen. The system was then evacuated to 0.1 kPa and filled with water saturated isobutane or propane to the desired pressure. After repeating the evacuation/filling procedure, the temperature was lowered to 200 K overnight and the sample gained between 3 and 10 mg in weight due to hydrate formation. The temperature was then increased to a value estimated to be about 5 K colder than the dissociation pressure of gas and increased in small temperature increments (0.3 K) until a weight loss of at least 1 to 2 mg was observed. [This weight loss was more than sufficient to insure that the loss was not due to evaporation of water. Weight variation due to buoyancy changes and temperature gradients between the electrobalance body and the sample were measured in dry runs (where standard weights were substituted for ice) and found to be negligible.] The temperature at which this weight loss occurred was taken as the dissociation temperature. One to two hours were allowed for equilibrium to be reached at each temperature. Repeating the procedure allowed the temperature to be determined to a precision of 0.1 K and an estimated accuracy of 0.3 K. The volume of the vacuum system is so large that the formation and dissociation of the hydrates affects the total pressure by less than 0.1 kPa per mg of hydrate. The data can be reproduced within the precision of the measurement. Each point reported is the result of several successively more precise experiments. Temperature uniformity could not be maintained at pressures less than approximately 15 kPa and hence data were not taken at pressures less than this value. Quantitative measurements of hydrate stoichiometry could be made if the entire water phase was converted to hydrate, but this condition was not experimentally obtainable.

RESULTS

The experimental results obtained for isobutane and propane hydrates are given in Table 1. These data provide a smooth locus

TABLE 1. DISSOCIATION PRESSURES OF ISOBUTANE AND PROPANE ALONG THE THREE PHASE (VIH) EQUILIBRIUM LOCUS

Temperature, K	Pressure, kPa Exptl	Smoothed
Isobutane		
269.5	91.3	92.1
269.4	89.7	91.6
268.1	85.5	84.9
263.3	66.4	64.0
259.7	53.5	51.7
256.5	42.8	43.5
253.7	35.1	36.3
248.4	26.4	26.7
243.4	20.2	19.9
241.4	17.6	17.6
Propane		
262.1	99.4	101.1
260.9	94.5	95.1
260.8	90.5	94.6
258.2	81.1	82.7
255.4	69.6	71.4
251.6	58.3	58.1
251.4	58.3	57.5
247.9	48.2	47.3

TABLE 2. MOLECULAR PARAMETERS FOR HYDRATE PHASE-ISOBUTANE-WATER INTERACTIONS AS A FUNCTION OF THE REFERENCE STATE CHEMICAL POTENTIAL

Set	$\Delta\mu$ J/gmol	σ^{**} m × 10^{10}	ϵ/K K	Standard Error,* %
I	883	3.3731	191.34	8.9
	1047	3.3731	203.37	3.9
	1106	3.3731	207.79	2.4
	1138	3.3731	211.11	1.9
	1152	3.3731	214.78	2.5
	1256	3.3731	218.84	4.1
	1465	3.3731	234.39	3.2
	1675	3.3731	250.00	16.4
II	883	3.2726	195.22	11.3
	883	3.3728	191.35	9.0
	883	3.4230	192.69	7.8
	883	3.6214	241.45	2.4
	883	2.6711	280.30	2.0
	883	3.7163	344.02	3.4
	883	3.7376	393.23	4.5
III	1194	3.3217	215.72	1.9
	937	3.6363	245.25	1.9
	883	3.6711	280.30	2.0

---

* Standard errors are given for the percent deviation between calculated and experimental dissociation pressures for isobutane hydrate.

** A core radius of 0.8593 × 10^{-10}m was used for isobutane.

on $\ln(P)$ vs. $(1/T)$ coordinates as shown in Figure 2. The absolute average percent error between smoothed and experimental pressures is 1.8% for iso-butane and 1.85% for propane (based on the experimental pressures).

Because the values obtained for the Kihara parameters depend upon the value of the chemical potential difference at 273 K, $\Delta\mu^o$, the Kihara parameters, σ and ϵ/k, for these gases were determined as a function of the value of this property. The core radius, a, is not dependent on experimental data, its value is constant for any gas—85.93 pm for isobutane and 74.52 pm for propane from the correlations of Tee et al. (1966).

Tables 2 and 3 give the Kihara parameters for propane and for isobutane. The Kihara parameters here are defined by the following pair potential, $\Gamma_{H_2O\text{-gas}}$, which is the same as used by Parrish and Prausnitz (1972).

$$\Gamma_{H_2O\text{-gas}}(r^*) = 4\epsilon\left[\left(\frac{\sigma}{r^*-a}\right)^{12} - \left(\frac{\sigma}{r^*-a}\right)^{6}\right] \quad r > a \qquad (6)$$
$$= \infty \qquad r \leqslant a$$

Parrish and Prausnitz's *reported* pair potential is slightly different, but the above potential is the one they actually used. In this function, r^*, is the separation between the gas and water molecule. It is different than the r used in Eq. 5.

The parameters obtained in Tables 2 and 3 are those which minimize the standard percent error, S, given by

$$S = 100\left[\left(\frac{P_{\text{calc}} - P_{\text{exp}}}{P_{\text{exp}}}\right)^2 \Big/ N\right]^{1/2} \qquad (7)$$

Here, P_{exp} is the smoothed experimental dissociation pressure reported herein and by others (Deaton and Frost, 1946; Rouher and Barduhn, 1969). For smoothing the data, a linear regression of $(\ln P)$ vs. $(1/T)$ was used. Only data below the ice point were used, although the parameters obtained can also be used to predict dissociation pressures above the ice point within experimental error.

Tables 2 and 3 are divided into four sets of data. In each table, the first set (I) of data shows how the Kihara energy parameter depends upon the value of $\Delta\mu^o$ where σ is determined according to the mixing rules given by Holder et al. (1980) and not by fitting experimental data. In this set of results, it is clear that a value of $\Delta\mu^o$ near 1,100–1,200 J/mol will give a better fit of experimental data for both propane and isobutane.

The second set (II) of parameters shows how the fitted energy parameter depends upon the value of σ when Sortland's and Robinson's (1964) value for $\Delta\mu^o$ is used. The searching technique used determined both σ and ϵ/k in this set of data, but the value

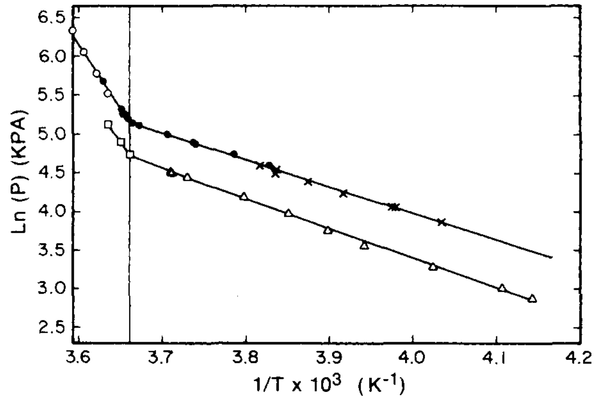

Figure 2. Dissociation pressures of isobutane and propane hydrate. Isobutane: ■ Rouher and Barduhn (1969) : ▲ experimental data from current study Propane: ● Verma (1974) : + experimental data from current study

TABLE 3. MOLECULAR PARAMETERS FOR HYDRATE PHASE-PROPANE-WATER INTERACTIONS AS A FUNCTION OF THE REFERENCE STATE CHEMICAL POTENTIAL

Set	$\Delta\mu^o$ J/gmol	σ^{**} m × 10^{10}	ϵ/K K	Standard Error,* %
I	883	3.3347	192.55	6.4
	1047	3.3347	205.99	2.6
	1127	3.3347	212.74	0.7
	1199	3.3347	218.42	0.9
	1256	3.3347	233.12	2.3
	1465	3.3347	240.27	7.0
	1674	3.3347	257.41	17.5
II	883	3.2342	205.05	7.86
	883	3.2842	198.22	7.16
	883	3.3347	192.60	6.40
	883	3.3867	188.34	5.65
	883	3.5838	189.78	2.26
	883	3.6795	207.67	0.30
	883	3.7731	246.72	1.53
III	1192	3.2862	224.28	0.1
	937	3.6349	201.24	0.1
	883	3.6795	207.67	0.3

---

* Standard errors are given for the percent deviation between calculated and experimental dissociation pressures for propane hydrate.

** A core radius of 0.7452 × 10^{-10}m was used for propane.

of σ always remained near the starting value even though a multivariable gradient search technique was used. Each pair of parameters reported in the second set obviously represent local minima in the standard error. It is not significant that both isobutane and propane data are fitted with similar values of σ. It is interesting to note, however, that these values are both much larger than the values reported by Parrish and Prausnitz (1972) or Ng and Robinson (1977). For the values of ϵ/k obtained, isobutane's energy parameter is considerably larger than propane's, whereas Parrish and Prausnitz (1972) reported values of ϵ/k which were similar for propane (ϵ/k = 200.94 K) and isobutane (ϵ/k = 220.52 K).

The third set (III) of parameters, in Tables 2 and 3 are the "best" fit parameters for three values of $\Delta\mu^o$. For a value of $\Delta\mu^o$ of 1192 J/mol, the value of σ found is somewhat consistent with the σ_{H_2O} used by Holder et al. (1980) where σ_{H_2O} is 3.75×10^{-10}m and σ, which is the gas-water parameter, is 3.3347×10^{-10}m for propane and 3.3731×10^{-10}m for isobutane. It is interesting that the value of $\Delta\mu^o$ is the same for both gases in this instance, since this value should be universal for structure II hydrate. The other values of $\Delta\mu^o$ used in this third set of parameters are the values determined by Sortland and Robinson (1962) and Dharmawardhana et al. (1980) which are 883 J/mol and 937 J/mol respectively. The fact that the values of σ are the same for these two gases when $\Delta\mu^o$ is the same is merely coincidence and not the result of any preconditions in the parameter fitting procedure. In fact, conventional mixing rules would indicate that σ for isobutane-water interactions should be larger than σ for propane-water interactions.

Another notable aspect of the third set of parameters is that ϵ tends to decrease as $\Delta\mu^o$ increases for isobutane whereas ϵ appears to go through a minimum as $\Delta\mu^o$ increases for propane.

If the values for the Kihara parameters for water given by Holder et al. (1980) are used along with the following mixing rules

$$\sigma = \tfrac{1}{2}(\sigma_{H_2O} + \sigma_{gas}) \qquad (8)$$

$$\epsilon = (\epsilon_{H_2O} \cdot \epsilon_{gas})^{1/2}$$

the values obtained for σ and (ϵ/k) for propane-water interactions are 3.3347×10^{-10}m and 250.3 K respectively. For isobutane-water these parameters would have the values of $\sigma = 3.3731 \times 10^{-10}$m and $(\epsilon/k) = 269.4$ K. These parameters do not fit the experimental dissociation pressure data well and do not agree well with any set of optimized parameters. If the corresponding states approach, used with moderate success by Holder and coworkers for the structure I hydrates of methane, argon, krypton and their mixtures, was also valid for the structure II hydrates of propane and isobutane, these parameters should have reasonably predicted the experimental dissociation pressures of these hydrates. Since the parameters are not successful in predicting dissociation pressures, the corresponding states approach must be discounted, or modified for larger aspherical molecules such as used in this study. In any case, the corresponding states model, with rules and parameters as developed by Holder et al. (1980), is not a successful predictor of hydrate dissociation pressures for propane and isobutane hydrates.

ACKNOWLEDGMENT

This material is based upon work supported by the National Science Foundation under Grant No. ENG79-21022.

NOTATION

a = core radius, m
C_{ji} = Langmuir constant for an i molecule in a j cavity, MPa^{-1}
f_i = gas phase fugacity of the i^{th} gas species
H = hydrate phase
I = ice phase
k = Boltzmann's constant, J/K/molecule
n_i = number of moles of species i
L = liquid phase
N = integer constant in Eq. 5, or number of data points
P_{exp} = dissociation pressure of hydrate, MPa
r = radial distance from center of hydrate cavity, m
r^* = intermolecular separation for pair potential, m
R = gas constant, J/mol/K; or cavity radius, m
R_i = spherical cage radius, m
S = standard error, %
T = temperature, K
V = vapor phase
$W(r)$ = spherically symmetric cell potential, J/molecule
z = coordination number of the lattice cavity

Greek Letters

ϵ = Gas-water Kihara energy parameter, J/molecule
θ = fractional occupancy of the cavity
Γ = intermolecular pair potential, J/molecule/K
$\Delta\mu^o$ = the difference between the reference chemical potential of the hydrate and the reference chemical potential of the hypothetical empty (gas free) hydrate lattice, J/mol
ν_1,ν_2 = constants equal to the number of small and large cavities per water molecule in the hydrate phase
σ = gas-water Kihara distance parameter, m
δ = function give by Eq. 5

LITERATURE CITED

Deaton, W. M., and E. M. Frost, "Gas Hydrates and Their Relation to the Operation of Natural Gas Pipelines," U.S. Bur. Mines Monogr., No. 8 (1946).

Dharmawardhana, P. B., W. R. Parrish, and E. D. Sloan, "Experimental Thermodynamic Parameters for the Prediction of Natural Gas Hydrate Dissociation Conditions," *Ind. Eng. Chem. Fund.*, **19**, 410 (1980).

Holder, G. D., G. Corbin, and K. D. Papadopoulos, "Thermodynamic and Molecular Properties of Gas Hydrates from Mixtures Containing Methane, Argon and Krypton," *Ind. Eng. Chem. Fund.*, **19**, 282 (1980).

Holder, G. D., and G. C. Grigoriou, "Hydrate Dissociation Pressures of Methane + Ethane + Water Mixtures: Existence of a Locus of Minimum Pressure," *J. Chem. Thermo.*, **12**, 1093 (1980).

Holder, G. D., and J. H. Hand, "Multiple Phase Equilibria in Hydrate Forming Mixtures of Methane, Ethane and Propane," *AIChE J.* **28** (3), 440 (1982).

McKoy, V., and O. Sinanoglu, "Theory of Dissociation Pressures of Some Gas Hydrates," *J. Chem. Phys.*, 38 (12), 2946 (1963).

Ng, H. J., and D. B. Robinson, "The Measurement and Prediction of Hydrate Formation in Liquid Hydrocarbon-Water Systems," *Ind. Eng. Chem. Fund.*, **15**, 293 (1976).

Ng, H. J., and D. B. Robinson, "The Prediction of Hydrate Formation in Condensed Systems," *AIChE J.*, **22**, 656 (1977).

Parrish, W. R., and J. M. Prausnitz, "Dissociation Pressures of Gas Hydrates Formed by Gas Mixtures," *Ind. Eng. Chem. Proc. Des. Dev.*, **11**, 26 (1972).

Rouher, O. S., and A. J. Barduhn, "Hydrates of Iso and Normal Butane and Their Mixtures," *Desalination*, **6**, 57 (1969).

Sortland, L. D., and D. B. Robinson, "The Hydrates of Methane and Sulfur Hexafluoride," *Can. J. Chem. Eng.*, **42**, 38 (1964).

Tee, L. S., S. Gotoh and W. R. Stewart, "Molecular Parameters for Normal Fluids," *Ind. Eng. Chem. Fund.*, **5**, 363 (1966).

van der Waals, J. H., and J. C. Platteeuw, "Clathrate Solutions," *Adv. Chem. Phys.*, **2**, 1 (1959).

Verma, V. K., "Gas Hydrates from Liquid Hydrocarbon-Water Systems," Ph. D. Dissertation, Univ. of Michigan, Ann Arbor (available from University Microfilms) (1974).

Wu, B. J., D. B. Robinson, and H. J. Ng, "Three and Four Phase Hydrate Forming Conditions in Methane-Isobutane-Water System," *J. Chem. Thermo.*, **8**, 461 (1976).

Manuscript received March 16, 1981; revisions received November 2, and accepted November 5, 1981.