Hydrates at High Pressures: Part II. Application of Statistical Mechanics to the Study of the Hydrates of Methane, Argon, and Nitrogen

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THEORETICAL DEVELOPMENT

Hydrate Structure

The structure of gas hydrates was determined by Von Stackelberg and Muller (*16, 17*) through the use of X-ray diffraction techniques. Structural arrays capable of fitting these data were formulated by Claussen (*2*) and Pauling and Marsh (*15*) who state that all gas hydrates crystalize in either of two cubic structures which have been labelled structure I and structure II. The hydrated molecules are situated in cavities formed by a framework of water molecules linked together by hydrogen bonds. The host lattice by itself is thermodynamically unstable but is stabilized by the inclusion of a second component within the lattice.

The unit cell of structure I contains forty-six water molecules enclosing two types of cavities:

1. Six pentagonal dodecahedral cavities consisting of twenty water molecules each located at the vertices and center of the unit cell.
2. Two tetrakaidecahedral cavities having two opposite hexagonal faces and twelve pentagonal faces serving to connect the regular dodecahedra.

The pentagonal dodecahedra are smaller than the two tetrakaidecahedra, having an average radius of 3.95 Å. as compared with 4.30 Å. for the tetrakaidecahedra. Thus if all cavities were filled, the maximum hydrate number for structure I would be 46/8 or 5¾.

The unit cell of structure II is composed of 136 water molecules arranged to form sixteen smaller cavities and eight larger cavities. The smaller cavities are distorted dodecahedra with an average radius of 3.91 Å., while the larger cavities are almost spherical with an average radius of 4.73 Å. Structure II is formed only by hydrated molecules which are too large to fit within the cavities of structure I. The following calculations are concerned with hydrates falling in the structure I category.

In the previous paper (*13*), it was reported that the pressure-temperature projections of methane, argon, and nitrogen hydrates exhibited no detectable abnormality at high pressure. From this it was expected that the change of the crystal structure of the same hydrates would not occur in the range of pressure studied.

Outline of the Solid Solution Theory

The derivation of the solid solution theory of clathrates is given by van der Waals and Platteeuw (*19*). The general theory is developed for a lattice former denoted by W which can exist in a metastable modification of W^β (empty clathrate lattice), a stable crystalline modification W^α, and a liquid modification W^L.

The basic equations which describe the clathrate are

$$\mu_w = \mu^\beta + kT \sum_i \nu_i \ln\left(1 - \sum_K y_{Ki}\right) \tag{1}$$

$$y_{Ki} = C_{Ki} f_K / \left(1 + \sum_J C_{Ji} f_J\right) \tag{2}$$

$$C_{Ki} = \left(\frac{1}{kT}\right) h_{Ki}(T, V)/\phi_K(T) \tag{3}$$

In Equation (1) μ_w represents the chemical potential of water in the hydrate. The term $\mu_w{}^\beta$ represents the chemical potential of water in the empty lattice structure modification. For gas hydrates of structure I $\nu_i = 1/23$ and $\nu_2 = 3/23$; for those of structure II $\nu_1 = 2/17$ and $\nu_2 = 1/17$. Equation (1) is a generalized form if Raoult's law for a solvent when the solute-solute interaction is negligible. Equation (2) is equivalent to a Langmuir isotherm for localized adsorption without interaction between the adsorbed molecules.

For a clathrate to exist in equilibrium with the crystalline modification W^α or the liquid modification W^L

$$\mu_w = \mu_w{}^\alpha \quad \text{or} \quad \mu_w = \mu_w{}^L \tag{4}$$

Here $\mu_w{}^\alpha$ and $\mu_w{}^L$ represent the chemical potentials of crystalline and liquid modifications, respectively. $\mu_w{}^\alpha$ and $\mu_w{}^\beta$ are functions of pressure and temperature alone. However $\mu_w{}^L$ is also dependent on composition. When one lets

$$\Delta\mu\ (T, P) = \mu_w{}^\beta - \mu_w{}^\alpha \quad \text{or} \quad \Delta\mu\ (T, P) = \mu_w{}^\beta - \mu_w{}^L \tag{5}$$

then

$$\sum_i \nu_i \ln\left(1 - \sum_K y_{Ki}\right) = -\Delta\mu/kT \tag{6}$$

$$\sum_i \nu_i \ln\left(1 + \sum_K C_{Ki} f_K\right) = \Delta\mu/kT \tag{7}$$

The present treatment deals primarily in detail with the fit of the solid solution theory to the experimental data (*13*) of the three-phase hydrate-water rich liquid-gas curves in the region above the ice-hydrate-water rich liquid-gas (I-H-L₁-G) quadruple point.

EVALUATION OF THE CELL PARTITION FUNCTION

The general equations for a clathrate contain only the cell partition function h_{Ji} as an unknown, the evaluation of which allows the prediction of the thermodynamic behavior of clathrates relative to the empty lattice.

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The cell partition functions have been evaluated by van der Waals and Platteeuw (*19*) under the following assumptions:

1. The solute molecules can rotate freely in their cavities.
2. The potential energy of a solute molecule at a distance r from the center of its cage is given by the spherically symmetrical potential $\omega(r)$ proposed by Lennard-Jones and Devonshire (*11*):

$$h_i = \phi(T) \exp[-\omega(0)/kT] 2\pi a_i^3 g_i \qquad (8)$$

The potential energy of the solute molecule at the center of the cage is given by

$$\omega(0) = Z_i \bar{\epsilon} [\alpha_i^{-4} - 2\,\alpha_i^{-2}] \qquad (9)$$

and g_i is a dimensionless integral given by

$$g_i = \int_{\text{cell}} {}^{\{Z_i \bar{\epsilon}/kT\,[-L(x)/\alpha_i^4 + 2M(x)/\alpha^2]\}} x^{1/2}\,dx \qquad (10)$$

The functions $L(x)$ and $M(x)$ are

$$L(x) = (x^4 + 12\,x^3 + 25.2\,x^2 + 12\,x + 1)/(1-x)^{10} - 1 \qquad (11)$$

$$M(x) = (1+x)/(1-x)^4 - 1 \qquad (12)$$

The constant α_i is defined as

$$\alpha_i = (a_i/\bar{\sigma})^3/\sqrt{2} \qquad (13)$$

The variable of integration is defined as

$$x = (r/a_i)^2 \qquad (14)$$

Since the contribution to the partition function from portions of the cell outside the sphere of $a_i/2$ is negligible, the integration is carried out between the limits 0 and ¼. The value of Z_i is a constant derived from structural considerations.

When one substitutes Equation (8) into Equation (3), the Langmuir constant C_{Ki} becomes

$$C_{Ki} = (2\pi a_i^3/kT)\, g_{Ki} \exp[-\omega(0)/kT] \qquad (15)$$

In order to evaluate Equation (15) for a chosen set of molecular parameters and a temperature, a numerical integration of g_i was required. The integration was carried out with Simpson's one-third rule.

The constants used in the evaluation of C_{Ki} for hydrates of structure I are as follows (*19*):

$Z_1 = 20 \quad a_1 = 3.95$ Å. $\quad k = 1.38 \times 10^{-16}$ erg./deg.
$Z_2 = 24 \quad a_2 = 4.30$ Å.

Thus if $\bar{\epsilon}$ and $\bar{\sigma}$ are known, the Langmuir constant may be evaluated for a given system.

DETERMINATION OF $\bar{\epsilon}$ AND $\bar{\sigma}$ FOR METHANE

For the solid solution theory to be exact a unique set of molecular parameters should exist for all data on each gas hydrate.

The set of molecular parameters used throughout the theoretical calculations for methane was derived in the following manner.

Below the quadruple point the physical system is composed of ice, hydrate, and gas in univariant equilibrium. This system admits to a theoretical treatment more readily than the system above the quadruple point which consists of hydrate, gas, and aqueous solution. Below the I-H-L₁-G quadruple point a simplification results because the chemical potential difference between the stable and metastable forms of the lattice former is a function of the system pressure and temperature alone.

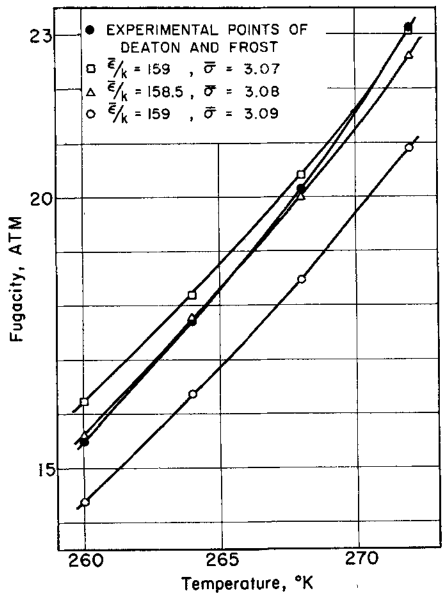

Fig. 1. Theoretical fit below ice point for methane.

From these considerations it was decided that the force constants for methane should be fitted below the I-H-L₁-G quadruple point where the solid solution theory could be applied exactly. Then these parameters were used to correlate the experimental data above the I-H-L₁-G quadruple point.

Experimental data of Deaton and Frost (*5*) on the three-phase locus, ice-hydrate-gas, were used to determine the best set of molecular parameters for methane along the hydrate locus. With the various sets of the molecular parameters, fugacities in equilibrium with the hydrate were calculated from Equations (7) and (15) and then compared with the experimental values. In order to solve Equation (7) a numerical calculation was carried out with Newton's method. Thus the set of molecular parameters which exhibited the least deviation from the data of Deaton and Frost (*5*) was chosen for use in all subsequent calculations for methane. As shown in Figure 1 the values chosen were $\bar{\epsilon}/k = 158.5$ (°K.) and $\bar{\sigma} = 3.08$ (Å.). Figure 1 shows that Equation (7) is so sensitive to $\bar{\epsilon}$ and $\bar{\sigma}$ that $\bar{\epsilon}$, $\bar{\sigma}$ from published data can not be substituted in Equation (7) directly.

The chemical potential difference between ice and hydrate along the equilibrium curve was calculated from the following equation:

$$d(\Delta\mu/RT) = -(\Delta H/RT^2)\,dT + (\Delta V/RT)\,dP \qquad (16)$$

This equation holds for any value of dP and dT. On the equilibrium curve

$$dP = (dP/dT)\,dT \qquad (17)$$

Integration of Equation (16) between T and 273°K. along the equilibrium curve gives

$$\Delta\mu/RT = -\int (\Delta H/RT^2)\,dT + \int (\Delta V/RT)\,\frac{dP}{dT}\,dT \qquad (18)$$

$$dP/dT = 0.03299\, e^{(0.03299T - 5.780)} \qquad (19)$$

$$\Delta\mu\,(273\ ^\circ\text{K.}, P_{\text{atm.}}) = 167 + 0.073P \qquad (20)$$

Stackelberg and Muller (*17*) have determined a value of 3.0 for ΔV. Equation (19) was obtained from the data of Deaton and Frost (*5*). Equation (20) has been derived by van der Waals and Platteeuw (*19*). ΔH is not known, but van der Waals and Platteeuw suggested $\Delta H \simeq 0$.

TABLE 1. CHEMICAL POTENTIAL AND HYDRATE NUMBERS OF METHANE HYDRATE AT VARIOUS PRESSURES

P, (lb./sq.in. abs.)	T, (°K)	f, (atm.)	C_1 (1/atm.)	C_2, (1/atm.)	$\Delta\mu$, (cal.)	$\Delta\mu'$ Equation (23), (cal.)	n
382	273.1	24.5	0.2028	0.2175	172.8	172.3	6.85
2,000	289.0	106.2	0.1285	0.1450	276.5	275.1	6.13
4,000	294.4	191.0	0.1099	0.1257	324.1	322.0	6.00
6,000	297.5	286.2	0.1006	0.1166	359.9	357.5	5.93
8,000	300.3	409.9	0.0950	0.1110	394.4	391.7	5.88
10,000	302.3	558.0	0.0908	0.1064	424.1	421.1	5.84
12,000	303.8	732.2	0.0861	0.1010	448.9	445.8	5.83
15,000	306.1	1,106.1	0.0810	0.0960	489.9	486.4	5.81

THE THEORETICAL FIT TO THE GAS HYDRATE EQUILIBRIUM CURVES ABOVE THE I-H-L₁-G QUADRUPLE POINT

In order to fit the experimental data to the solid solution theory for gas hydrates above the I-H-L₁-G quadruple point the following procedure was adopted.

Initially a series of Langmuir constants were calculated for the methane-water rich liquid-hydrate system and presented in Table 1.

Next the assumption was made that the chemical potential of the water in contact with the equilibrium hydrate could be estimated from an ideal solution relationship. With this assumption the chemical potential of the lattice former can be written as

$$\mu_w{}^L = (\mu_w{}^L)^* + RT \ln x_w \tag{21}$$

where $(\mu_w{}^L)^*$ is a function of pressure and temperature only.

Then the chemical potential difference can be expressed by

$$\begin{aligned}\Delta\mu &= \mu_w{}^\beta - \mu_w{}^L \\ &= \mu_w{}^\beta - (\mu_w{}^L)^* - RT \ln x_w \\ &= \Delta\mu' - RT \ln x_w\end{aligned} \tag{22}$$

That is, the chemical potential difference $\Delta\mu'$ is a function of pressure and temperature alone.

Combining Equations (7) and (22) one obtains

$$\begin{aligned}\Delta\mu' = RT\,\{&\nu_1 \ln (1 + C_{K1} f_K) \\ &+ \nu_2 \ln (1 + C_{K2} f_K) + \ln x_w\}\end{aligned} \tag{23}$$

The pressure and temperature effects on this chemical potential then become

$$d(\Delta\mu'/RT) = -(\Delta H'/RT^2)dT + (\Delta V'/RT)dP \tag{24}$$

where $\Delta H'$ denotes the difference between molar heat functions and $\Delta V'$ the difference between the molar volumes of the β and L modifications. The value of $\Delta V'$ is 4.6 (*17*). It is doubtful that $\Delta V'$ will retain this constancy at higher pressure, but it was assumed that the change of $\Delta V'$ is negligible because of a lack of data on the effect of pressure.

Integrating Equation (24) along the equilibrium curve one gets

$$\Delta\mu'/RT = -\int (\Delta H'/RT^2)dT + \int (\Delta V'/RT)(dP/dT)dT \tag{25}$$

Anticipating that $\Delta H'$ takes the same form as the heat function difference between water and ice one can write

$$\Delta H' = -\lambda\, e^{-\gamma T} \tag{26}$$

Substituting (26) into (25) and equating it with (23) one obtains

$$\begin{aligned}&[\nu_1 \ln (1 + C_{K1} f) + \nu_2 \ln (1 + C_{K2} f_K) + \ln x_w]_{T_1}^{T_2} \\ &= \int_{T_1}^{T_2} (\lambda\, e^{\gamma T}/RT^2)\, dT + \int_{T_1}^{T_2} (\Delta V'/RT) \left(\frac{dP}{dT}\right) dT\end{aligned} \tag{27}$$

The solubility data of Culberson and McKetta (*4*) for methane in water was used to obtain the composition of water in the liquid phase, and the fugacities of methane were calculated from thermodynamic table of Din (*18*). The methane P-T projection of the data of Deaton and Frost is linear between 32° and 70°F. when plotted in semilog scale and in this region can be expressed as

$$\frac{dP}{dT} = 2.635 \times 10^{-12}\, e^{0.101097T} \tag{28}$$

If this expression is substituted in Equation (27), then λ and γ can be determined. The value of λ and γ determined numerically were 16.7 and 0.016, respectively. It is noted that the values were very close to those for the heat function difference between ice and water of 17.1 and 0.0162, which were calculated from the data of Bridgman (*1*). From this result it was concluded that the difference in enthalpy between the β lattice and ice must be small.

At constant temperature the pressure effect on the chemical potential difference $\Delta\mu'$ becomes

$$(\partial\Delta\mu'/\partial P)_T = \Delta V' \tag{29}$$

Integrating Equation (29) at constant temperature one gets

$$\Delta\mu' = \Delta\mu'_o + \Delta V'\,(P - P_o) \tag{30}$$

If $\Delta\mu'$ and P of methane are used for the reference values $\Delta\mu'_o$ and P_o, then the chemical potential difference for argon and nitrogen can be calculated:

$$\Delta\mu' = \Delta\mu'_{CH_4} + 7.573 \times 10^{-3}\,(P - P_{CH_4}) \tag{31}$$

Here the unit of chemical potential and pressure are calories per mole and pounds per square square inch absolute, respectively.

Equations (23) and (30) should be equivalent.

Each set of molecular parameters for argon and nitrogen was adjusted at 280°K. so that the chemical potential difference calculated by Equation (23) might agree exactly with that calculated from Equation (31). The resulting $\bar{\epsilon}/k$ and $\bar{\sigma}$ were 142.0 (°K.), 2.992 (Å.) for argon-water and 123.0 (°K.), 3.027 (Å.) for nitrogen-water. From these values C_{Ki} of argon and nitrogen were calculated and are presented in Tables 2 and 3.

TABLE 2. CHEMICAL POTENTIAL AND HYDRATE NUMBER OF ARGON HYDRATE AT VARIOUS PRESSURES

P, (lb./sq.in. abs.)	T, (°K)	f, (atm.)	C_1 (1/atm.)	C_2, (1/atm.)	$\Delta\mu$, (cal.)	$\Delta\mu'$ Equation (23), (cal.)	n
1,402	273.1	88.0	0.06423	0.07344	186.9	185.1	6.67
2,000	277.5	122.5	0.05750	0.06640	208.9	206.9	6.49
4,000	283.7	237.5	0.04945	0.05810	260.2	257.9	6.18
6,000	287.0	361	0.04568	0.05420	295.7	293.3	6.06
8,000	289.4	508	0.04330	0.05165	325.5	322.9	5.98
10,000	291.2	689	0.04150	0.04980	354.0	351.0	5.93
20,500	297.0	2,275	0.03655	0.04445	469.7	466.8	5.81
30,000	300.0	5,600	0.03426	0.04193	561.0	557.9	5.78
50,000	303.9	30,000	0.03160	0.03900	736.2	733.0	5.76

Table 3. Chemical Potential and Hydrate Number of Nitrogen Hydrate at Various Pressures

P, (lb./sq. in. abs.)	T, (°K)	f, (atm.)	C_1 (1/atm.)	C_2, (1/atm.)	$\Delta\mu$, (cal.)	$\Delta\mu'$ Equation (23), (cal.)	n
2,370	273.1	155.7	0.03262	0.04172	185.1	184.1	6.69
4,000	278.5	273.4	0.02880	0.03822	228.5	227.0	6.34
6,000	282.3	443.8	0.02651	0.03460	266.3	264.4	6.15
8,000	285.3	658.1	0.02482	0.03270	300.3	298.0	6.04
10,000	287.6	926.5	0.02365	0.03130	331.2	328.5	5.97
15,000	292.0	1,937	0.02160	0.02881	400.3	396.7	5.86
20,000	295.2	3,600	0.02028	0.02720	461.1	457.0	5.81
30,000	300.0	11,200	0.01842	0.02498	576.5	571.2	5.77
40,000	303.3	30,106	0.01725	0.02372	680.3	674.2	5.76
50,000	306.1	88,000	0.01635	0.02250	793.5	786.8	5.75

As a test of the theory Equation (31) was used to calculate the remaining values of the chemical potential differences over the pressure range 1,400 to 50,000 lb./sq. in. abs. for argon and 5,000 to 50,000 lb./sq. in. abs. for nitrogen. The values derived in this way were compared with the right-hand side of Equation (23). These are shown in Tables 1, 2, and 3 and in Figure 2. The results of these calculations showed that the solid solution theory may be applied to predict the hydrate-water rich liquid-gas equilibrium loci when gas is a spherical molecule. Here the solubilities of argon and nitrogen in water were extrapolated or interpolated from the data of Linke (*12*) and Krichevsky and Kasarnovsky (*10*), respectively.

At higher pressures nitrogen showed some deviation between Equations (23) and (31). This somewhat poorer agreement between the two methods can be explained as follows. On applying the L-J-D potential to this theory, the assumption is made that the gas molecules encaged in the hydrate are spherical. This assumption applies equally well to argon and methane, both essentially spherical molecules. However nitrogen, being nonspherical in shape, does not strictly conform to this theoretical treatment.

Very near the I-H-L₁-G quadruple point both argon and nitrogen showed slight deviation between Equations (23) and (31), but the reason is not apparent to the authors.

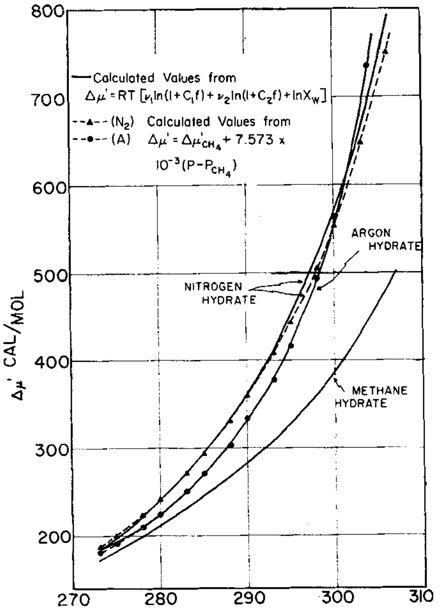

Fig. 2. Chemical potentials for methane, argon, and nitrogen above the quadruple point.

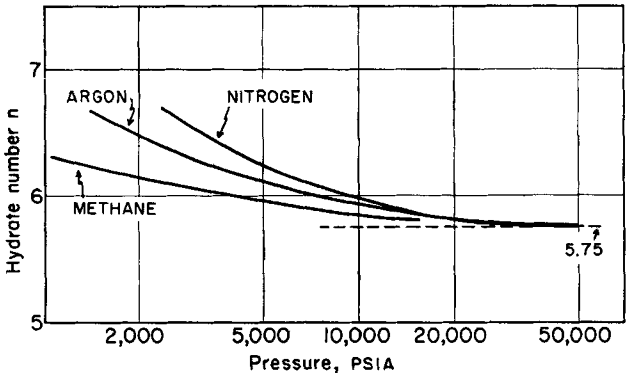

Fig. 3. Variation of hydrate numbers with pressure.

The elimination of $\Delta\mu'$ from Equations (23) and (31) for a given temperature leads to the evaluation of a single pressure for hydrate formation provided fugacity data on the gas are available. A comparison between this calculated and experimental hydrate formation pressure for nitrogen is shown in Figure 5. It is evident that a given deviation in the $\Delta\mu'$ leads to a correspondingly greater deviation in the calculated and experimental pressure. However since the $\Delta\mu'$ for the argon hydrate obtained by Equations (23) and (31) are identical, the calculated and experimental pressure will be the same.

The hydrate numbers n were calculated by the following equation and are shown in Tables 1, 2, and 3 and in Figure 3.

$$n = 23/\{C_{K1}f_K/(1 + C_{K1}f_K) + 3\,C_{K2}f_K/(1 + C_{K2}f_K)\} \quad (32)$$

At higher pressure it was shown that the hydrate numbers approach the minimum hydrate number of 5¾ as shown in Figure 3 and Tables 1, 2, and 3.

The potential fields within argon hydrate cages were determined by the Lennard-Jones-Devonshire method (*11*) and are shown in Figure 4. In the large cavities the minimum point of potential energy is not situated in the center.

ESTIMATION OF ϵ_K AND σ_K FOR METHANE, ARGON AND NITROGEN

In the previous sections the sets of molecular parameters $\bar{\epsilon}$ and $\bar{\sigma}$ for methane, argon, and nitrogen were determined.

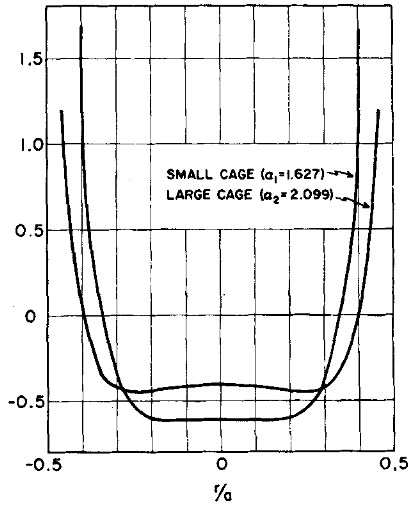

Fig. 4. Potential fields within argon hydrate cages.

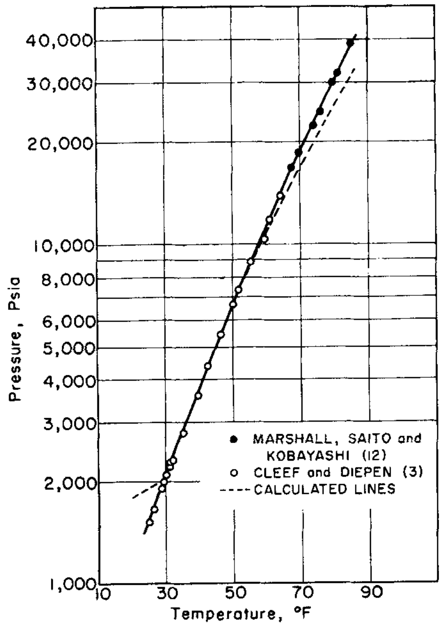

Fig. 5. Comparison between calculated and experimental hydrate formation pressure for nitrogen.

The following empirical combining laws which relate the force constants between unlike molecules were used to calculate the force constants for the pure solute K:

$$\bar{\sigma} = \frac{1}{2}(\sigma_w + \sigma_K) \qquad (33)$$

$$\bar{\epsilon} = (\epsilon_w \epsilon_K)^{1/2} \qquad (34)$$

Here if the value of $\bar{\sigma} = 2.50$ Å. which corresponds to Pauling's van der Waals radius of 1.40 Å. for a covalently bound oxygen atom (*14*) is adopted as the distance parameter of the wall of the hydrate cage, σ_K for the pure solute K can be estimated. From the value of ϵ_w the energy parameter ϵ_K for pure solute K also can be estimated. But ϵ_w is unknown and cannot be calculated theoretically. So the value of $\epsilon_w/k = 169$°K. was estimated from Equation (34) by using a value of $\epsilon_K/k = 119.8$°K. for argon obtained from second virial coefficient data. With this value the energy parameters ϵ_K for methane and nitrogen can be estimated.

The force constants obtained are compared in Table 4 with the values (*8*) of molecular parameters derived from viscosity and virial data for those gases.

TABLE 4. COMPARISON OF MOLECULAR PARAMETERS FROM VIRIAL, VISCOSITY (*8*), AND HYDRATE DATA (THIS WORK)

Substance	Method	ϵ/k	σ
Methane	Viscosity	137	3.822
	Viscosity	144	3.796
	Virial	148.2	3.817
	Hydrate	148.6	3.66
Argon	Viscosity	124	3.418
	Viscosity	116	3.465
	Virial	119.8	3.405
	Virial	122	3.40
	Hydrate	119.8*	3.48
Nitrogen	Viscosity	91.5	3.681
	Viscosity	79.8	3.749
	Virial	95.05	3.698
	Virial	95.9	3.71
	Hydrate	89.5	3.55

* Taken from reference 8.

DETERMINATION OF HEATS OF FORMATION OF METHANE, ARGON, AND NITROGEN HYDRATES

The heats of formation of hydrates are calculated by the Clapeyron equation:

$$n\,H_2O\ (\text{Liq.}) + \text{Gas} = \text{Gas} \cdot n\,H_2O$$

$$dP/dT = \Delta H''/T\,\Delta V'' \qquad (35)$$

which is a thermodynamic identity valid for all univariant equilibria, no matter how the compositions of the phase change along the equilibrium line. The double primed quantities $\Delta H''$ and $\Delta V''$ should be the differences of partial molal quantities $\Delta\overline{H}''$ and $\Delta\overline{V}''$ but are closely approximated by the change of enthalpy and volume resulting from the pure components in the reaction equation stated above because of the small solubilities of gases in water (*9*).

The data points plotted as log P vs. absolute temperature were fitted approximately along several straight lines (*13*) which may be represented by

$$\log P = A + BT \qquad (36)$$

Equation (36) leads itself readily to the differentiation required to solve for the heat of formation of the hydrate.

The mathematical analysis followed in calculating the heats of formation above the quadruple point from the data shown in a previous report (*13*) is

$$\Delta H'' = T\Delta V''\,dP/dT \qquad (37)$$

$$dP/dT = 2.303\,BP \qquad (38)$$

$$\Delta H'' = 2.303\,BTP\Delta V'' \qquad (39)$$

The slopes of equilibrium lines B were obtained from the previous report (*13*), and the volume of the gas under investigation at T and P of interest here was obtained from thermodynamical tables of Din (*6, 7, 18*).

At higher pressure the difference between the volume of hydrates resulting from the hydrate forming reaction and that of the water combined with a mole of the gas is not negligible compared with the volume of 1 mole of the gases. This difference was obtained by $n\Delta V'$ on the assumption that at higher pressures the volumes of hydrates and water are constant.

The heat of formation of the hydrates may be calculated from Equation (39) by using the values of B and $\Delta V''$. The values calculated are given in Table 5.

The heat of formation of the hydrates also may be calculated numerically by the following equations on the assumption that reaction gases are perfect:

$$\Delta H'' = n N \Sigma\, \nu_i y_i \{Z \epsilon [-2\,(1 + g_m/g)\,\alpha^{-2} + (1 + g_l/g)\alpha^{-4}]\} + P\Delta V'' - 16.7\, e^{0.016T} \qquad (40)$$

N is Avogadro's number and the functions g_l and g_m are defined by

TABLE 5. COMPARISON OF HEATS OF FORMATION OF HYDRATES FROM CLAPEYRON AND FROM SOLID SOLUTION THEORY

P, (lb./sq. in. abs.)	Methane B.t.u./lb. mole Equation (39)	Methane B.t.u./lb. mole Equation (40)	Argon B.t.u./lb. mole Equation (39)	Argon B.t.u./lb. mole Equation (40)	Nitrogen B.t.u./lb. mole Equation (39)	Nitrogen B.t.u./lb. mole Equation (40)
2,000	24,700	22,000	21,100	19,800		
4,000	26,000	22,400	22,100	21,900	20,400	21,600
6,000	26,800	24,700	22,600	21,000	20,900	21,300
8,000	27,300	24,300	23,000	21,200	21,400	22,200
10,000	27,800	24,300	23,400	21,100	21,700	24,000

$$g_l = \int_0^{1/4} x^{1/2}\, l(x) \exp \{Z\, \epsilon/kT\, [-l(x)/\alpha^4 + 2m(x)/\alpha^2]\} dx \quad (41)$$

$$g_m = \int_0^{1/4} x^{1/2}\, m(x) \exp \{Z\, \epsilon/kT\, [-l(x)/\alpha^4 + 2m(x)/\alpha^2]\} dx \quad (42)$$

The values calculated by Equation (40) are compared with those obtained from Equation (39) in Table 5. The agreement between two calculations are comparable but not exact owing to the assumptions involved in Equation (40).

PREDICTION OF P-T PROJECTION OF NITROGEN HYDRATE BELOW THE I-H-L$_1$-G QUADRUPLE POINT

At the I-H-L$_1$-G quadruple point the differences in the heats of formation of the hydrate from liquid water and from ice will be equal to the heat of solidification of the number of moles of water combined in a mole of hydrate, as shown by the following equations:

$$\begin{array}{rl} - \left[\begin{array}{l} n\,\mathrm{H_2O\ (Liq.) + Gas = Gas} \cdot n\,\mathrm{H_2O\ (Hydrate)} \\ n\,\mathrm{H_2O\ \ (Ice) + Gas = Gas} \cdot n\,\mathrm{H_2O\ (Hydrate)} \end{array} \right] & \begin{array}{c} \Delta H_1 \\ \Delta H_2 \end{array} \\ \hline n\,\mathrm{H_2O\ (Liq.)} = n\,\mathrm{H_2O\ (Ice)} & n \cdot \Delta H^* \\ \Delta H_1 - \Delta H_2 = n \cdot \Delta H^* & \end{array} \quad (43)$$

The heats of formation of hydrate can be calculated by Equation (39), and the hydrate number also is known. Therefore the slope of equilibrium line below the I-H-L$_1$-G quadruple point B_2 can be calculated by

$$B_2 = 1/\Delta V_2''\ (B_1\, \Delta V_1'' - n\Delta H^*/2.303\, PT) \quad (44)$$

where ΔH^* is the heat of fusion of ice. B_1 is the slope of equilibrium line above the I-H-L$_1$-G quadruple point. $\Delta V_1''$ and $\Delta V_2''$ are the changes in volume of the sum of the reacting substances above and below the I-H-L$_1$-G quadruple point, respectively. B_2 of nitrogen hydrate was calculated and is compared with the experimental points of Cleef and Diepen (3) in Figure 5. Though the calculated line showed the discontinuity at the I-H-L$_1$-G quadruple point, the experimental points below the I-H-L$_1$-G quadruple point fall on an extension of the equilibrium line above the I-H-L$_1$-G quadruple point.

It is felt that the experimental points reported in reference 3 represent metastable equilibrium gas-hydrate-water rather than the true equilibrium state of gas-hydrate-ice.

CONCLUSIONS

The statistical mechanics solid solution theory of van der Waals and Platteeuw combined with classical thermodynamical principles have been applied to study the conditions for equilibrium for hydrate formation in the methane-water, argon-water, and nitrogen-water systems above the I-H-L$_1$-G quadruple point to pressures in excess of 3,000 atm. The heat function difference between water and β modification has been determined by using the data of Deaton and Frost (5), and it was found that this function is very close to that between ice and water.

Then it was found that the chemical potential difference between the empty hydrate lattice and the pure liquid water $\Delta\mu' = \mu_w{}^\beta - (\mu_w{}^L)^*$ for argon and nitrogen hydrates calculated by two methods—the chemical potential difference for methane and the isothermal effect of pressure on the chemical potential difference, Equation (31), and the solid solution theory—were in close agreement. The argon hydrate showed agreement between the chemical potential difference calculated by the two methods throughout the entire pressure range studied. The nitrogen hydrates showed some deviation at the highest pressure studied. The discrepancy is believed to be caused by the slightly nonspherical nature of the nitrogen molecule.

At higher pressure it was shown that the hydrate numbers approached the minimum hydrate number for structure I hydrates of 5¾.

With the simple combining rules given by Equations (33) and (34) and $\sigma_w = 2.50$ Å. *(12)* and $\epsilon_w/k = 169$°K. the Lennard-Jones-Devonshire force constants for methane, argon, and nitrogen have been determined and found to be in essential agreement with the force constants predicted from second virial and viscosity data, again pointing to the essential validity of the theory.

The heat of formation for the hydrates calculated from the Clapeyron equation was found to be in essential agreement with the values predicted by the solid solution model.

The calculated heat of formation for the nitrogen hydrate and its hydrate number on the ice point for the nitrogen-water system has been used as a basis for predicting the gas-ice-hydrate locus below the I-H-L$_1$-G quadruple point and as a basis for the criticism of reported experimental data points for the same (3).

The solid solution theory together with classical thermodynamics principles has provided a means of studying the required conditions for hydrate formation above the I-H-L$_1$-G quadruple point for essentially spherical molecules. It will later be shown that the calculation procedures can be extended to systems comprised of mixtures of essentially spherical molecules and water in the hydrate region above the I-H-L$_1$-G quadruple point.

ACKNOWLEDGMENT

This work was conducted under the support of NASA Research Grant NSG 6-59. Mr. Alan J. Vennix aided in carrying out some of the numerical calculations.

NOTATION

a_i = cell radius
A,B = constant in Equation (34)
C_{Ki} = Langmuir constant
f_K = fugacity of solute K in the hydrate
g = function defined by Equation (10)
g_l = function defined by Equation (39)
g_m = function defined by Equation (40)
G = gas
$h_{Ki}(T,V)$ = molecular partition function of a solute molecule, K, enclosed in a cavity, i
H = hydrate
ΔH = molar enthalpy difference
I = ice
k = Boltzmann constant
L_1 = water-rich liquid
n = hydrate number
P = pressure
r = radial position
R = gas constant
T = temperature
ΔV = molar volume difference
W = lattice former (water)
x_w = mole fraction of water in the water-rich liquid phase

x = $(r/a_i)^2$
y_{Ki} = fraction of cavities of type i occupied by a gas molecule K
Z_i = structural constant

Greek Letters

α_i = $(a_i/\sigma)^3/\sqrt{2}$
λ,γ = constants in Equation (26)
ϵ,σ = energy and distance parameters in the Lennard-Jones-Devonshire potential
ν_i = number of cavities of the type i per mole of water
μ = chemical potential
$\phi_K(T)$ = molecular partition function of a solute molecule K with the volume factor removed
$\omega(r)$ = Lennard-Jones-Devonshire potential

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Manuscript received October 14, 1963; revision received March 9, 1964; paper accepted March 20, 1964. Paper presented at A.I.Ch.E. San Juan meeting.

Vapor-Liquid Equilibria for Aqueous Sulfuric Acid

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Because the precise composition of the vapor phase over aqueous sulfuric acid is not accessible experimentally a method is described for calculating the partial pressures of water, sulfuric acid, and sulfur trioxide starting from liquid-phase partial molal thermodynamic quantities. Graphs and tables are provided which give the partial pressures from —50° to 400°C., between 10 and 100 wt. % acid.

The vapor phase over sulfuric acid solutions is composed of water and sulfuric acid, together with sulfur trioxide from the dissociation of the acid:

$$H_2SO_4(g) = H_2O(g) + SO_3(g) \qquad (1)$$

In principle the distribution of these three components at various temperatures and acid concentrations can be determined by either experimental partial-pressure measurements or calculation of partial pressures from liquid-phase thermodynamic data.

The first method, although more direct, is not fully applicable to the sulfuric acid system because of the low volatility of sulfuric acid. Experimental difficulties notwithstanding, the total vapor pressure of sulfuric acid, which in most cases is due entirely to the partial pressure of water, was the subject of numerous investigations between 1845 and 1923. Greenewalt (*8*), who in 1925 assembled the available data, reviewed nineteen separate vapor-pressure determinations. His final result, based essentially on the measurements of Burt (*4*) and of Daudt (*5*), is the accepted standard that appears in today's reference works.

The second method, the calculational approach to partial pressures, requires two types of thermodynamic data: pure-component data for two liquids and three gases ($H°_{298}$, $S°_{298}$, and $C°_p$) and partial molal data for binary solutions ($\overline{H}_{298}$, $\overline{S}_{298}$ or $\overline{F}_{298}$, and $\overline{C}_p$). This approach was first used by Abel (*1*) in 1946, based in part on work by Bodenstein and Katayama (*3*) who had measured K_p for Equation (1) at 300° to 500°C. with 85 to 100 wt. % acid. The calorimetric data available at that time were incomplete, necessitating cross correlations from various sources in order to determine partial molal quantities. More important, values of $C°_p$, $H°_{298}$, and $S°_{298}$ for $H_2SO_4(g)$ were not available. This lack necessitated the use of K_p for Equation (1) in the calculation of $p_{H_2SO_4}$, which in turn required an extrapolation of Bodenstein and Katayama's high-temperature equilibrium measurements down to 25°C. The experimental K_p data are shown in Figure 1.

Since 1946 additional data have become available which make the calculation of partial pressures by the second method considerably more reliable. Extremely complete tables of partial molal quantities at 25°C., tested for internal consistency, have been published by Giauque et al. (*6*), who give free energies, enthalpies, entropies, and heat capacities at 109 different sulfuric acid concentrations from 8.93 to 100 wt. %. In addition Giguère (*7*)