Use of Monte Carlo in Calculating the Thermodynamic Properties of Water Clathrates

Equilibrium dissociation pressures for monovariant three-phase (ice-solid clathrate-gas) systems were predicted for water clathrates with Ar, Kr, Xe, N_2, O_2, CO_2, and CH_4 as the guest molecules. A Monte Carlo approach of statistically sampling the states available to the guest molecule inside the host water cage was used to evaluate the configurational properties including the free volume integral. The Lennard-Jones 6-12 potential adequately described the guest-host interaction for monatomic species, for example, Ar, Kr, and Xe, while the nonspherically symmetric Kihara potential with a fixed hard-core geometry was required for polyatomic guests. The simulated motion of the guest within the cell was consistent with the geometrical features of the host lattice.

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SCOPE

Water clathrates are composed of an open network of host water molecules arranged to create several large void spaces or cages capable of entrapping guest molecules such as argon, methane, or carbon dioxide. Although there are no chemical bonds between the water hosts and the guests, the clathrate structure is stabilized by relatively weak van der Waals interactions. Clathrates are regarded as nonstoichiometric compounds since all available cages in a given unit cell need not be occupied by a guest.

Since the size and chemical nature of the guest are critical in determining the feasibility of clathrate formation, their selectivity is usually very high. In recent years, water clathrates have been utilized in desalination processes involving propane and other hydrates (Barduhn et al., 1962). Knowledge of their behavior became important in preventing the stoppage of natural gas pipelines (Schaefer and Dorsey, 1962) as well as in the inhibition of clathrate formation in a direct contact butane freezing process for desalting (Wiegandt, 1967). Clathrate or inclusion compounds are used in a variety of other specialized separation processes, including the para-meta xylene separation, the recovery of vitamin A (Schaefer and Dorsey, 1962), and the separation and storage of gases (Miller and Strong, 1945). In addition to these practical applications, clathrates have been used to isolate molecules for fundamental studies of molecular motion and chemical kinetics (Davidson, 1971).

In most cases of interest, the thermodynamic properties of the clathrate must be fully characterized. Several theoretical models have been proposed to predict these properties as an alternative to direct experimental measurement. The basic model used is an idealized cell model where stabilization occurs by the motion of individual guest molecules in the presence of a fixed potential field generated by the host molecules. The evaluation of the configurational properties of clathrates requires an understanding of the intermolecular potential between the guest and host. Previous theoretical approaches (van der Waals and Platteeuw, 1958) have simplified this problem by assuming that the host potential field is uniformly distributed on a sphere at some distance from the cell center, and that the guest itself is spherically symmetric. However, the structure of the cages and the guests are often asymmetric, so a continuum approach to the interactions is at best an approximation.

Our study accounted for these asymmetries by using a Monte Carlo approach where the potential at any point in the cell was a discrete sum of binary interactions between the guest and each host molecule. By proper sampling of the various configurational states available to the guest molecule within the cell, an ensemble average of such quantities as the potential energy can be determined and utilized in estimating the thermodynamic properties (Wood, 1968).

Recent advances in surface and solid state science have increased our appreciation of the importance of crystalline structure in determining the kinetic and thermodynamic properties of solid-gas and solid-liquid systems. In this sense, the Monte Carlo approach to the clathrate problem demonstrates the power of this technique in handling situations where the geometry of the system might be so complex that direct numerical or analytical solutions are impractical.

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CONCLUSIONS AND SIGNIFICANCE

Since the thermodynamic properties of any real system are simply a manifestation of interactions between the molecules that comprise the system, the idea of proposing a statistical model to predict these properties at least seems plausible. Van der Waals and Platteeuw (1959) proposed such a model whereby the clathrate was viewed as a solid solution of the guest component in the rigid host lattice. In this way the contribution of the host lattice itself and the encaged guest can be separated. Although the well-defined geometry of the host lattice simplifies the evaluation of the thermodynamic properties over other systems such as liquids, the situation is by no means trivial. As is frequently the case, the major problem lies in evaluating the so-called "free volume" or configurational integral. For each cell type i in the Structure I clathrate containing molecules such as Ar, N_2, CO_2, and CH_4 as guests, this integral can be represented as

$$Z_{\text{cell}_i} = \int_{V_{\text{cell}_i}} \exp[-U/kT]dV \quad i = 1, 2$$

Up to this point the model has been completely general, showing that Z_{cell_i} depends directly on the intermolecular cell potential U. However, Z_{cell_i} must somehow be related to a physical property in order to test the validity of the proposed model. In the present investigation, calculated and experimental values of the dissociation pressure were compared. For the two-component, three-phase system, ice-solid clathrate-gas, the dissociation pressure is a function only of temperature. By applying the constraints afforded by the three-phase monovariant system to the partition function which describes the clathrate, the dissociation pressure of cell$_i$ can be related to Z_{cell_i},

$$P_i = \frac{kT\left(\dfrac{y_i}{1 - y_i}\right)}{Z_{\text{cell}_i}} \quad i = 1, 2$$

Since gas phase nonidealities are often significant due to the high equilibrium pressures experienced, the dissociation pressure term P_i in the above equation would be replaced by the fugacity f_i of cell$_i$. The y_i's represent the probability that cell$_i$ will contain a guest. Their values are constrained by the equality of chemical potentials between ice and solid clathrate and the equality of pressures or fugacities between cells.

Z_{cell_i} was evaluated by Monte Carlo integration (Mueller, 1971) as

$$Z_{\text{cell}_i} \cong \exp[-<U>_i/kT]V_{\text{cell}_i}$$

where $<U>_i$ is the characteristic potential energy between a guest and all the hosts associated with that cell. $<U>_i$ was calculated by averaging over a series of allowable configurations of the guest relative to a fixed host lattice structure. Configurations were generated by moving the guest molecule a fixed distance ΔR in a random direction to different positions in the cell; in addition, if the guest were asymmetric it was rotated randomly about its center of mass to new orientations. At each position, the potential energy was calculated as a sum over all hosts using a given intermolecular potential function for each binary interaction between a single host and guest. This value was then compared to the energy at the previous location. Following the Monte Carlo scheme proposed by Metropolis et al. (1953), moves were accepted or rejected such that the arithmetic mean of U over all accepted moves approximated the ensemble average for a Boltzman $\exp[-U/kT]$ distribution. V_{cell_i} was the actual volume occupied by the guest during the sampling.

For a nonlinear asymmetric guest, Z_{cell_i} is effectively a six-fold integral over three coordinates and three α, β, γ guest orientation parameters. Thus the Monte Carlo evaluation of the integral affords a more workable solution in comparison to the many numerical or analytical determinations available which often introduce unattractive assumptions such as spherical symmetry.

Z_{cell_i} depends on the nature of the guest-host potential $<U>_i$ which for proper sampling should only depend on the cell geometry, the size and shape of the guest, and the magnitude of the interaction between the guest and host water molecule. Thus, care must be exercised in choosing an adequate empirical potential function.

The Lennard-Jones (L-J 6-12) potential was used for spherically symmetric guests such as Ar, Kr, and Xe, while the hard-core Kihara potential was utilized to account for structural asymmetry in the guest, for example, O_2, CH_4, and CO_2. When using the Kihara potential, the minimum distance from the surface of the hard core of the guest to each host was calculated to determine the potential at that point. Since these distances can be evaluated directly for a particular guest orientation in the cell, there is no need to use one of the angle averaged Kihara forms for the potential. In both symmetric and asymmetric cases the choice of the potential parameters ϵ (energy) and σ (size) as well as the hard-core geometry was critical.

For symmetric guests approximately 100,000 moves were sufficient for convergence with a move size equivalent to 1/10 of the cell radius. By selecting ϵ and σ values for the L-J 6-12 potential of the argon-water clathrate to force agreement with the experimental dissociation pressure ϵ_{H_2O} and σ_{H_2O} for the lattice could be computed using the geometric mean [Equation (7)] and hard sphere approximation [Equation (8)] (van der Waals and Platteeuw, 1959). These lattice parameters were used to calculate ϵ and σ's for krypton-water and xenon-water mixtures with the ϵ_{guest} and σ_{guest} specified by second virial coefficient data.

Using these prespecified mixture parameters, dissociation pressures were estimated. Agreement was obtained within 7% for krypton and 43% for xenon, which is within the values determined by van der Waals and Platteeuw (1959) following a continuum model.

The L-J 6-12 potential was shown to be inadequate for polyatomic guests as shown by the poor agreement of calculated and experimental dissociation pressures. Using the asymmetric Kihara potential, hard-core geometries were selected and ϵ and σ were chosen to cause agreement of dissociation pressures for O_2, N_2, CO_2, and CH_4 clathrates. Frequently 150,000 to 250,000 moves were necessary for uniform sampling even with an optimal choice of ΔR. Although this represents the standard method of calculating potential parameters, the Monte Carlo model should provide a more realistic basis over the continuum approach for characterizing the nature of the guest-host potential as the complexity of the guest and host lattice increases.

Three-dimensional plots of the volume occupied by the guest demonstrated how the asymmetries present in cell structure affect the states available to the guest. Realisti-

cally, one expects the motion of a guest to be restricted by the cell geometry; accordingly, one of the principle strengths of the Monte Carlo technique is that it does not require assumptions about the cell or guest geometry in the calculation of the macroscopic thermodynamic properties.

CHEMICAL AND THERMODYNAMIC CONSIDERATIONS

The number of crystalline forms available to a given clathrate host is limited. For example, water clathrates form two basic structures depending on the size of the guest. Argon, krypton, Cl_2, CO_2, and other similarly sized molecules form Structure I hydrates with individual guest molecules occupying two types of polyhedral cages, 2 pentagonal dodecahedrons having free diameters of 5.1 Å, and 6 tetrakaidecahedrons having free diameters of approximately 5.8 Å, for every 46 water molecules. The resulting ideal formula is $M \cdot 5\ 3/4\ H_2O$ for all voids occupied or $M \cdot 7\ 2/3\ H_2O$ with only the larger ones occupied, M = guest. Methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$) (Tester and Wiegandt, 1969) and other larger molecules form Structure II hydrates with guests occupying 8 larger voids of 6.7 Å per diameter for every 136 water molecules ($M \cdot 17\ H_2O$ for all voids occupied) (von Stackelberg et al., 1954; Claussen, 1951; Pauling and Marsh, 1952).

For any given clathrate structure, variations in the size and shape of the guest molecule do not appreciably distort the cage geometry. Some molecules, for example, hexane, are too large to fit either voids of the Structure I or II hydrate and do not form clathrates. Similarly, hydrogen and helium are too small and can escape from the cage by passing between the water hosts.

If the chemical affinity between host and guest is great enough, a new chemical species will form, not a clathrate. In addition to these properties, the host itself must have the inherent ability to form open networks upon solidification. If the host possesses a permanent dipole, for example, water, or shows considerable steric hindrance in its conformation, for example, Dianin's (1914) compound, it is more susceptible to clathrate formation (Powell, 1964).

Davidson (1971), in his study of the motion of the guest molecule in the clathrate cage, states that reorientation of the guest is influenced by the arrangement of host atoms and by the nature of the intermolecular force field generated by the dipolar water hosts. Because of their lower energy, certain spatial orientations are preferred for nonsymmetrical guests and to a lesser extent for symmetrical guests; nonetheless, most guests maintain rotational freedom in the cell.

A pure gas hydrate can be treated thermodynamically as a two-component system consisting of water and a particular guest component. By applying the Gibbs phase rule, when three equilibrium phases are present, the system will be monovariant, and fixing the temperature should fix the pressure. These equilibrium vapor pressures or fugacities are commonly measured as a function of temperature for various three phase systems. For example, when ice, solid gas hydrate, and vapor are present in equilibrium, the measured pressure is referred to as the dissociation pressure. Experimental dissociation pressures are frequently compared to values calculated from theoretical models. Van der Waals and Platteeuw (1959) proposed a classical statistical mechanical approach which modeled a clathrate as a three-dimensional localized adsorption structure. Their formulation of the partition function depended on several assumptions:

1. The motion of the guest molecule is confined to the interior of the cage.
2. A maximum of one guest is allowed per cage.
3. The contribution of the host molecules to the total free energy is independent of the type of guest present, that is, no lattice distortion.
4. Interactions between neighboring guests are neglected.

Based on their model, the difference in chemical potential between the empty clathrate (β modification) phase and the ice phase at the same temperature and pressure for a single guest can be written as a sum over cells 1 and 2 (van der Waals and Platteeuw, 1959)

$$\Delta\mu = \mu^{\beta} - \mu^{\mathrm{ice}}]_{T,P} = -kT \sum_{i=1}^{2} \nu_i \ln(1 - y_i) \qquad (1)$$

The cell occupation probability y_i is described analogously to the Langmuir adsorption isotherm as

$$y_i = \frac{C_i(T) f_i}{1 + C_i(T) f_i} \qquad (2)$$

Solving Equation (2) for the fugacity f_i

$$f_i = \frac{1}{C_i(T)} \left(\frac{y_i}{1 - y_i} \right) \qquad (3)$$

The Langmuir constant $C_i(T)$ is given by

$$C_i(T) = \frac{1}{kT} \int_{V_{\mathrm{cell}}} \exp[-U/kT] dV \qquad (4)$$

assuming the internal degrees of freedom of the entrapped guest molecule are the same as those in the gas phase. The integral in Equation (4) is often referred to as the *free volume* integral and represents the configurational contribution of the guest-host interaction. To evaluate it, some knowledge of the spatial dependence of the intermolecular guest-host potential U is necessary.

STRUCTURAL CONSIDERATIONS

Because our model treats the discrete nature of the guest-host potential, the crystallography of the clathrate cells is important. Since only Structure I hydrates are studied, detailed structural information concerning Structure II types is omitted. Numerous articles have been prepared on the structural aspects of clathrates (von Stackelberg and Muller, 1954; Claussen, 1951; Pauling and Marsh, 1952; Jeffrey, 1962). In addition, Jeffrey and McMullan (1967) have written an excellent review of the subject.

The unit cell of a Structure I hydrate is cubic with space group *Pm3n* and a lattice constant of 12 Å. For every 46 water molecules, there are 2 pentagonal dodecahedral voids and 6 tetrakaidecahedral voids. The geometrical features of the voids are illustrated in Figure 1, where an oxygen atom is located at each vertex of the polyhedron and the hydrogen atoms are found on the edges. Figure 2 shows how these polyhedra are arranged to form the unit cell. The pentagonal dodecahedral cages are composed of 20 water molecules symmetrically located about the center of the cell while the tetrakaidecahedral cages contain 24 water molecules arranged in an oblate spheroid with the primary asymmetry caused by the two hexagonal faces. Table 1 gives the location of the oxygen atoms relative to the cell centers: (0, 0, 0) for the pentagonal dodecahedron and (1/4, 1/2, 0) for the tetrakaidecahedron. The guest molecules contained in the cells move freely unless restricted by repulsive potential forces which occur when the guest gets too close to one or more of the host water molecules.

Jeffrey and McMullan (1967) point out that the guests do not appreciably distort the host lattice except for a relatively minor isotopic expansion resulting in a lattice constant variation of 12 ± 0.12 Å for over 20 Structure I hydrates.

Since our investigation was concerned with predicting the properties of the Ar, Kr, Xe, N_2, O_2, CH_4, and CO_2 hydrates, it was necessary to know whether the guest size was sufficiently small to allow occupancy of both cell types. For all of the above except CO_2, both cells are known to be occupied resulting in an ideal stoichiometric formula of $M \cdot 5\,3/4\ H_2O$ (Jeffrey and McMullan, 1967). However, with CO_2 there has been some controversy: with a linear size of 4.6 Å, it may possibly be too large to occupy the smaller 5.1 Å cells. Herreilers (1936) in his thesis research made indirect measurements of the composition of the CO_2 hydrate and found the formula to be $CO_2 \cdot 6\ H_2O$, indicating that three is at least partial occupancy of the smaller cells. If only the larger cells were occupied the formula would be ideally $CO_2 \cdot 7\,2/3\ H_2O$.

INTERMOLECULAR POTENTIAL FUNCTION

Van der Waals and Platteeuw (1959) modified the Lennard-Jones Devonshire liquid cell model (Hirschfelder et al., 1954) to evaluate Equation (4). They assumed that the host potential was uniformly distributed on a spherical surface and that the spherically symmetric Lennard-Jones (L-J) 6-12 potential applied to the guest-host interaction. Thus the free volume integral of Equation (4) could be integrated numerically as,

$$Z_{\text{cell}} = 4\pi \int_0^{R_{\text{cell}}} r^2 \exp[-U(r)/kT]\, dr \tag{5}$$

with $U(r)$ given by the L-J 6-12 potential,

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \tag{6}$$

The choice of R_{cell} is unimportant because the term, $\exp(-U(r)/kT)$ goes to zero as r approaches the radius of the host potential sphere.

Using the L-J 6-12 potential necessitated choosing two parameters, σ and ϵ. In addition, the intermolecular potential is between two different species, that is, water host and guest. Since suitable parameters for the contribution of the water lattice molecules to ϵ and σ are not known, parameters for the guest-host mixture can be chosen in an empirical fashion such that experimental and theoretical results agree. Van der Waals and Platteeuw (1959) followed another scheme. Assuming σ_{H_2O} for the host lattice to be 2.50 Å, (Pauling, 1945), they chose ϵ for the argon-water clathrate to obtain agreement between calculated and experimental dissociation pressures at 0 K. Using the geometric mean approximation for ϵ and the hard sphere approximation for σ, and assuming that the encaged argon guest behaved as a free gas, ϵ_{H_2O} was obtained by

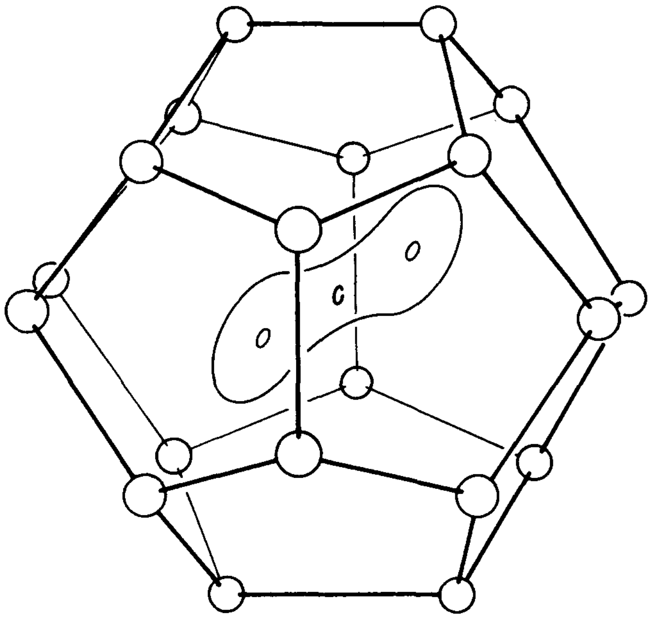
$$\epsilon = \sqrt{\epsilon_{H_2O}\, \epsilon_{\text{guest}}} \tag{7}$$

with

$$\sigma = \frac{\sigma_{H_2O} + \sigma_{\text{guest}}}{2} \tag{8}$$

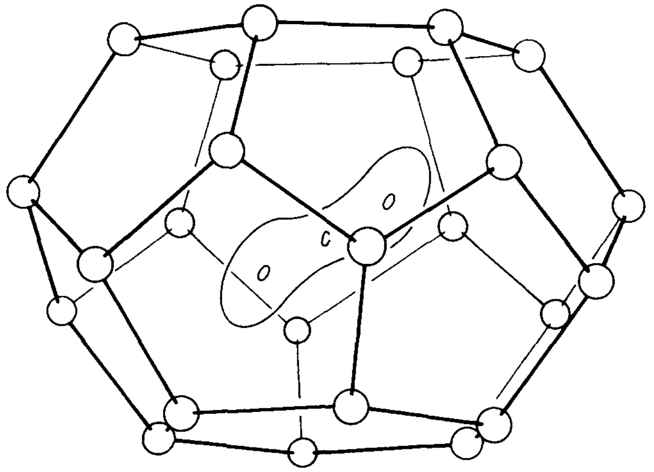
If there are no lattice distortions, ϵ_{H_2O} and σ_{H_2O} should be independent of the type of included guest. By making this assumption, ϵ and σ for the mixture [Equations (7) and (8)] can be estimated using known values of ϵ_{guest}

CELL I



12 Sided
Pentagonal Dodecahedron

CELL 2



14 Sided
Tetrakaidecahedron

Fig. 1. Clathrate cell structure, cell 1—pentagonal dodecahedron 20 H_2O molecules; cell 2—tetrakaidecahedron, 24 H_2O molecules.

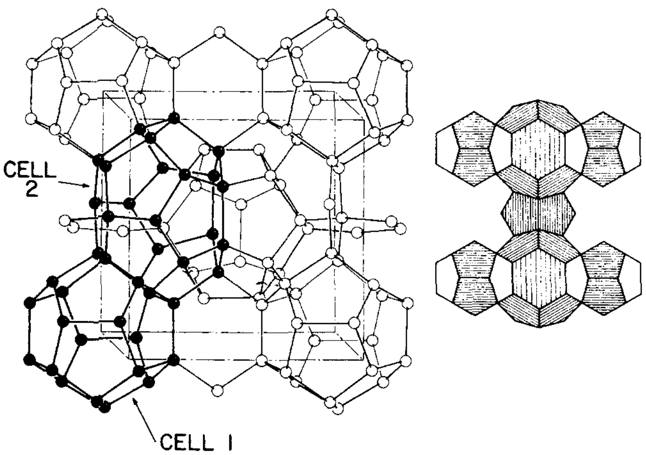


Fig. 2. Clathrate Structure I showing arrangement of both cell types, $a = 12$ Å cubic, space group Pm3n, cell 1 at (0, 0, 0) cell 2 at (¼, ½, 0) outlined in bold lines, Jeffrey and McMullan (1967).

and σ_{guest} obtained from viscosity or second virial coefficient data.

In Structure I hydrates, the pentagonal dodecahedral cells (type 1) are approximately spherical, but the larger tetrakaidecahedral cells (type 2) are distorted spheres (see Figure 1). When the guest molecule itself is spherically symmetric, for example, argon, krypton, and xenon, the Lennard-Jones Devonshire model assumptions are probably reasonable. Calculations of the dissociation pressure for the inert gas clathrates using the L-J 6-12 potential have agreed well with experiments (Platteeuw and van der Waals, 1958). Using this same potential one finds that as the guest increases in asymmetry, for example, CO_2, N_2, and O_2, agreement between calculated and experimental results is poor (> 1000%). McKoy and Sinanoglu (1963), Nagata and Kobayashi (1966), and Parrish and Prausnitz (1972) improved the continuum model somewhat by using a Kihara hard-core potential to describe the guest-host interaction. However, the improvements were again dependent on the choice of parameters, and the Kihara potential has an additional adjustable quantity, the hard-core radius.

In view of the asymmetry present in the cell geometry and that of the guest molecule itself, the total intermolecular cell potential should be calculated by a discrete rather than continuous model. This potential is represented as a sum of binary interactions between guest and host;

$$U = \sum_{i=1}^{H = \left\{ \begin{matrix} 20\text{: cell } 1 \\ 24\text{: cell } 2 \end{matrix} \right\}} U_{ij}(r_{ij}, \epsilon, \sigma, \ldots) \tag{9}$$

This discrete formulation more realistically accounts for the stabilizing effect of the guest on the host lattice. Using Equation (9) to define U, the free volume integral [Equation (4)] can be evaluated. A Monte Carlo technique was developed to accomplish this. When the guests were spherically symmetric, a L-J 6-12 potential was used for each term in the sum of Equation (9). For asymmetrical guests, the original Kihara (1953) potential was used. A hard-core geometry was selected for the guest, for example, a rod for CO_2, N_2, and O_2 and a tetrahedron for CH_4. For each position in the cell, the minimum distance ρ from the surface of the hard-core of the guest to each water host (assumed spherical centered at the oxygen atom) was determined and used to evaluate each U_{ij} in the sum of Equation (9).

$$\begin{aligned} U_{ij} &= 4\epsilon \left(\left(\frac{\sigma}{\rho}\right)^{12} - \left(\frac{\sigma}{\rho}\right)^{6} \right) & \rho &> R_{\text{coll}} \\ U_{ij} &= \infty & \rho &\leq R_{\text{coll}} \end{aligned} \tag{10}$$

MONTE CARLO TECHNIQUE

Basically the Monte Carlo technique consists of moving the guest molecule randomly in uniformly sized steps to

TABLE 1. HOST ATOM COORDINATES IN STRUCTURE I CLATHRATES

Cell 1—pentagonal dodecahedron centered at (0, 0, 0)

Host number	X	Y	Z	Distance from cell center Å
1	−0.183	0.183	0.183	3.803
2	0.183	−0.183	−0.183	3.803
3	0.183	0.183	0.183	3.803
4	0.183	−0.183	0.183	3.803
5	0.183	0.183	−0.183	3.803
6	−0.183	−0.183	−0.183	3.803
7	−0.183	−0.183	0.183	3.803
8	−0.183	0.183	−0.183	3.803
9	0.310	−0.116	0.000	3.972
10	−0.310	0.116	0.000	3.972
11	−0.310	−0.116	0.000	3.972
12	0.000	−0.310	0.116	3.972
13	0.116	0.000	−0.310	3.972
14	0.000	−0.310	−0.116	3.972
15	−0.116	0.000	−0.310	3.972
16	0.000	0.310	−0.116	3.972
17	0.116	0.000	0.310	3.972
18	0.000	0.310	0.116	3.972
19	0.310	0.116	0.000	3.972
20	−0.116	0.000	0.310	3.972

Cell 2—tetrakaidecahedron centered at (¼, ½, 0)

Host number	X	Y	Z	Distance from cell center Å
1	0.000	0.500	0.250	4.243
2	0.500	0.750	0.000	4.243
3	0.500	0.250	0.000	4.243
4	0.000	0.500	−0.250	4.243
5	0.317	0.317	0.317	4.465
6	0.317	0.317	−0.317	4.465
7	0.317	0.683	−0.317	4.465
8	0.183	0.183	−0.183	4.465
9	0.183	0.183	0.183	4.465
10	0.317	0.683	0.317	4.465
11	0.183	0.817	0.183	4.465
12	0.183	0.817	−0.183	4.465
13	0.000	0.310	−0.116	4.017
14	0.500	0.384	−0.190	4.017
15	0.000	0.310	0.116	4.017
16	0.500	0.616	0.190	4.017
17	0.000	0.690	−0.116	4.017
18	0.500	0.384	0.190	4.017
19	0.000	0.690	0.116	4.017
20	0.500	0.616	−0.190	4.017
21	0.310	0.884	0.000	4.664
22	0.190	0.500	0.384	4.664
23	0.310	0.116	0.000	4.664
24	0.190	0.500	−0.384	4.664

X, Y, Z—fractional Miller indices coordinates based on a cubic unit cell, 12A, on each side.

different locations in the clathrate cell and if the guest is asymmetric, spinning it randomly about its center of mass. Then at each location its total potential energy is calculated from Equation (9) and the proposed move is accepted or rejected on the basis of the Metropolis et al. (1953) technique in order that the energy probability distribution, $\exp[-U/kT]$, is sampled properly. To accomplish this, Metropolis et al. suggest that given the potential energy of the system, U_j in state j, one must move to a new state $j+1$ in a random fashion and calculate U_{j+1}.

$$\text{If} \left\{ \begin{array}{l} U_{j+1} < U_j; \\ \quad \text{or} \\ \text{random number} \\ \text{between 0 and 1} < \exp\left[-(U_{j+1}-U_j)/kT\right] \end{array} \right\}$$

accept move $j+1$. Otherwise reject move $j+1$, move back to state j, and count it as the next accepted move.

Metropolis et al. (1953) and Wood and Jacobson (1959) have shown from the mathematical theory of random processes that this technique will indeed select U's with a frequency proportional to $\exp[-U/kT]$ as the number of moves becomes large. Therefore, the ensemble average of $<U>$ can be represented as

$$<U> = \frac{\int_{V_{cell}} U \exp[-U/kT]dV}{\int_{V_{cell}} \exp[-U/kT]dV} = \left. \frac{\sum_{j=1}^{N} U_j}{N} \right|_{\text{Monte Carlo}} \quad (11)$$

where the U_j's are selected according to the suggested technique.

In effect, the Monte Carlo random walk proposed for the guest molecule results in a Markov chain since the probability of accepting a new state is dependent on the energy of the previous state.

The Monte Carlo experiments were performed on the Maniac II Computer at the Los Alamos Scientific Laboratory at the University of California. The procedure for generating a uniformly distributed sequence of pseudo random numbers was based on the multiplicative congruential method of Lehmer (1951).

The Monte Carlo scheme was coded in MADCAP V, a language which was developed at the Los Alamos Scientific Laboratory (Wells, 1971). The code itself required about 8,000 words of absolute storage on the Maniac II, an 81,000 word machine. The polyatomic code, being somewhat more complex, required a nominal running time of 5 to 10 min./1000 moves depending on the structure of the guest compared to 1 min./1000 moves for monatomic guests.

The random walk was accomplished in the following manner. The guest was positioned in the center of the clathrate cell with a particular orientation. By specifying a random direction, the center of mass of the guest was moved to a new location a fixed distance ΔR away from the cell center but with the same relative orientation of the guest atoms. By choosing another random direction the guest was reoriented, keeping its center of mass in a fixed location. The next move would be in another random direction, a distance ΔR from the previous move. However, since spinning was uniformly random, the original orientation was used as a starting point for each spin. This sequence of sliding and spinning the guest was repeated to generate new configurations.

The choice of ΔR is somewhat restricted. In general, ΔR was chosen as a certain fraction of the average cell radius, Rsi

$$Rsi = 3.9 \text{ Å} \quad \text{cell 1}$$

$$Rsi = 4.3 \text{ Å} \quad \text{cell 2}$$

Since the guest is confined to a particular cage, too large a ΔR will cause too many moves to be rejected because its motion would have placed it outside the cell. For larger moves, that is, $\Delta R = Rsi/q$; $q = 2$ to 5, a fair portion of the moves would place the guest very close to one or more of the hosts, resulting in a large positive U (repulsive energy); consequently the Metropolis rejection scheme would forbid many moves on the basis of energy ($> 85\%$) and the sampling of new configurations will be severely limited. If ΔR is too small, that is, $q = 100$ or greater, the energy does not change significantly between moves and the rejection ratio is lower ($\sim 10\%$). This creates two problems:

1. More computer time (configurations) is required for proper sampling.
2. Since the guest is moving in a sphere of radius Rsi, the probability of moving into a spherical shell at radius R should be proportional to R^2. This condition is met for $q = 2$ to 20 with a minimum of 10,000 moves, but for $q = 100$ it requires 500,000 moves, and with $q = 1000$ it requires over 5,000,000 moves.

Our studies have shown that $\Delta R = Rsi/q$, $q = 10$ to 15, not only samples uniformly in the sphere for a minimum number of moves but also results in a rejection ratio of 30 to 40% which, on the basis of limited information, is suggested by Wood (1968) to be near the optimum.

MONTE CARLO EVALUATION OF Z_{cell}

The integral part of Equation (4) can be rewritten in spherical coordinates as

$$Z_{cell} = \int_0^{R_{cell}} \int_0^{\pi} \int_0^{2\pi} \exp[-U/kT] R^2 \sin\theta \, d\phi d\theta dR \quad (12)$$

One expects U to be a well-behaved function of R, θ, and ϕ and of the orientation of the guest molecule within the cage. Since the guest in general has a maximum of three degrees of rotational freedom, Z_{cell} is really

$$Z_{cell} = \int_0^R \int_0^{\pi} \int_0^{2\pi} \int_{\alpha} \int_{\beta} \int_{\gamma} \exp\left[-U(R,\theta,\phi,\alpha,\beta,\gamma)/kT\right] R^2 \sin\theta \, d\phi d\theta dR d\alpha d\beta d\gamma \quad (13)$$

where α, β, and γ are the normalized orientation angles for the guest. Thus the maximum number of integrals is six for a guest with three rotational degrees of freedom while a spherically symmetric guest such as argon reduces Equation (13) to a three-fold integral.

Although the three-fold integral could be determined numerically on a high speed computer, the six-fold integral is more efficiently handled with a Monte Carlo technique (Wood, 1971; Mueller, 1971). From the mean value theorem of integral calculus, there will be some value of $<\exp[-U/kT]>$ defined on the interval of interest such that

$$Z_{cell} = \int_{V_{cell}} \exp[-U/kT]dV = <\exp(-U/kT)> V_{cell} \quad (14)$$

V_{cell} should be equivalent to that portion of the cell volume occupied by the guest molecule during the Monte Carlo sampling process. By dividing the cell into 100 spherical shells which extend to the cell radius *Rsi*, V_{cell} is approximated as

$$V_{\text{cell}} = V_{\text{uncond.}} + \sum_{j=k}^{100} \frac{4\pi}{3} (R^3{}_j - R^3{}_{j-1}) \frac{Acc_j}{Num_j} \quad (15)$$

$V_{\text{uncond.}}$ is the unconditionally accepted volume based on the actual size of the guest molecule. For example for CO_2, with a C–O spacing of *a*,

$$V_{\text{uncond.}} = \frac{4\pi}{3} (a)^3 \quad (16)$$

and

$$k = \frac{100a}{Rsi} + 1 \quad (17)$$

The second term of Equation (15) divides the clathrate cell into $(100 - k)$ spherical shells with each shell given a weight equal to the ratio of the number of accepted moves into spherical shell *j* to the number of attempted moves into shell *j*, Acc_j/Num_j. Assuming that moves are made uniformly in the sphere, the ratio Acc_j/Num_j should be proportional to the occupation probability of being in that particular shell. Clearly the innermost shells will have a weight close to unity, but the outermost shells will have a weight close to zero since most of the moves will be rejected on the basis of the Metropolis scheme because *U* gets very positive and repulsive as the guest gets close to any one of the host molecules. Although V_{cell} is an approximation of the real volume, it is very sensitive to asymmetries in the cell geometry and guest orientation, which is a distinct advantage over the previous spherically symmetrical continuum approaches.

There are indirect methods to check the reliability of our method. For instance, our results with spherically symmetric monatomic guests such as argon, krypton, and xenon should agree approximately with the theoretical results based on the continuum model.

The term $<\exp(-U/kT)>$ has been approximated by

$$<\exp(-U/kT)> \cong \exp(-<U>/kT) \quad (18)$$

where $<U>$ is the ensemble average of the potential energy obtained by Monte Carlo sampling. One can rewrite Equation (14) as

$$Z_{\text{cell}} = \exp[-<U>/kT] \int_{V_{\text{cell}}} \exp[-(U - <U>)/kT] dV \quad (19)$$

where the integral is a first-order fluctuation type integral. If the fluctuations about $<U>$ are uniform in the Monte Carlo averaging then Equation (18) will be a good approximation.

Salsburg et al. (1959) and Chestnut and Salsburg (1963) had some success in calculating the canonical partition function directly by a Monte Carlo method by substituting the term $\exp[+U/kT]$ into the distribution average, for our case using Equation (11).

$$<\exp(+U/kT)> = \frac{\int_{V_{\text{cell}}} dV}{\int_{V_{\text{cell}}} \exp[-U/kT] dV} = \frac{V_{\text{cell}}}{Z_{\text{cell}}} \quad (20)$$

so Z_{cell} can be estimated without evaluating the integral. However, as Wood (1968) points out, this technique has a serious disadvantage in that those values of *U* which are large and positive (repulsive) contribute more to the average, and this is impractical because the Monte Carlo method is designed to sample efficiently from those states where value of $\exp[-U/kT]$ is large, that is, *U* is small. A comparison was made between the above method of estimating Z_{cell} and our method of Equation (14) for the argon clathrate with 100,000 moves and $\Delta R = Rsi/10$. Agreement was obtained within 6%. Although this agreement is encouraging it does not justify the impracticality of the alternate techniques.

The disadvantages of Chestnut and Salsburg's (1963) technique are exposed when one compares the rate of convergence of our technique for evaluating Z_{cell} [Equation (14)] with theirs [Equation (20)]. For all practical purposes our Monte Carlo technique has converged to a value of Z_{cell} (±1%) after 10,000 moves for the argon clathrate while the Chestnut and Salsburg (1963) method requires almost 100,000 moves to achieve this level of convergence. Furthermore, by choosing ΔR's $\neq Rsi/10$ the difference in the convergence rates becomes even more pronounced.

RESULTS

Dissociation Pressure

Assuming the Lennard-Jones 6-12 potential [Equation (6)] is adequate for spherically symmetric guests such as argon, krypton, and xenon, the dissociation pressure or fugacity can be calculated for a given set of potential parameters ϵ and σ.

There are several constraints in this calculation, however. Because argon, krypton, and xenon occupy both cell 1 and cell 2 in the Structure I hydrate, the fugacity is given by

$$f = \frac{kT \dfrac{y_1}{1 - y_1}}{Z_{\text{cell 1}}} = \frac{kT \dfrac{y_2}{1 - y_2}}{Z_{\text{cell 2}}} \quad (21)$$

$Z_{\text{cell 1}}$ and $Z_{\text{cell 2}}$ are the configurational integrals for each cell type and are evaluated separately by the Monte Carlo method. The occupation probabilities y_1 and y_2, as yet unspecified, are fixed by the equilibrium constraint expressed in Equation (1). For a Structure I hydrate, Equation (1) can be rewritten as

$$\frac{-\Delta\mu}{kT} = \frac{2}{46} \ln(1 - y_1) + \frac{6}{46} \ln(1 - y_2) \quad (22)$$

Assuming the molar volume difference between an empty clathrate lattice (β) and ice Δv is independent of pressure, then $\Delta\mu(273, K, P)$ can be expressed as

$$\Delta\mu[273\ K, P] = \Delta\mu[273\ K, P = 0] + \Delta v(P) \quad (23)$$

Child (1964) and Parrish and Prausnitz (1972) estimated $\Delta\mu[273\ K, P = 0]$ from experimental data to be approximately 302 gcal/mole. Van der Waals and Platteeuw (1958), McKoy and Sinanoglu (1963), and Nagata and Kobayashi (1966) used a value of 167 gcal/mole for $\Delta\mu(273\ K, P = 0)$ based on bromine hydrate data. However, Allen and Jeffrey (1963) reinvestigated the bromine hydrate lattice by single crystal x-ray diffraction and concluded that bromine does not crystallize in either a Structure I or II cubic lattice but rather in a tetragonal lattice.

Equations (21) and (22) constrain the system. Optimum values of y_1 and y_2 were selected by an exhaustive grid search which simultaneously minimized the difference between the calculated value of $\Delta\mu$ from Equation (22) and the experimental value from Equation (23), and the difference between the fugacity calculated for cell 1 versus cell 2, Equation (21). In practice, the quantity W

$$W = (\Delta\mu_{\text{exp}} - \Delta\mu_{\text{calc}})^2 + \left[\frac{f_{\text{cell 1}} - f_{\text{cell 2}}}{f_{\text{exp}}}\right]^2 \quad (24)$$

was minimized. Initial values of y_1 and y_2 were chosen randomly and the optimization was repeated several times to insure that the real minimum for W was approached. Differences between the values for $f$cell 1 and $f$cell 2 never exceeded 1%.

In order to test the reliability of the Monte Carlo method in calculating clathrate properties, the potential parameters for argon hydrate were selected to force agreement between the calculated and experimental fugacity at 273 K. Then, following the technique suggested by van der Waals and Platteeuw (1959), a value for ϵ_{H_2O} was calculated from Equation (7) with σ_{H_2O} assumed to be 2.50 Å. These values were then used to calculate ϵ and σ's for the krypton and xenon hydrates with Equations (7) and (8). In the preliminary experiments, values for ϵ_{guest} and σ_{guest} were taken from several sources, including viscosity, spectroscopic, and 2nd virial coefficient data (Hirshfelder et al., 1954). The second-virial ϵ_{guest} and σ_{guest} always gave the best agreement between experimental and calculated dissociation fugacities, for example, for krypton using ϵ, σ from viscosity data resulted in a 25% deviation versus 6% for 2nd virial coefficient data. The results of these calculations are tabulated in Table 2. Frequently, 10,000 moves were sufficient for convergence.

The agreement obtained for krypton ($\approx$ 7%) and xenon ($\approx$ 43%) is reasonable when compared to the calculations of van der Waals and Platteeuw (1958) using the continuum approach. At this point it is difficult to say whether deviations are caused by variations in the cell potential parameters indicating lattice distortion, or whether the guest itself does not behave exactly as a free gas, for example, restricted translation in the cage.

Having completed the analysis of the monatomic guests, several nonspherically symmetric polyatomic guests including CO_2, N_2, O_2, and CH_4 were studied. The same constraints of pressure and chemical potential [Equations (21) and (22)] apply since both cells are occupied. However, because of geometrical asymmetry the guest-host

TABLE 2. DISSOCIATION PRESSURES FOR MONATOMIC GUESTS AT 273K

	Mixture Potential Parameters				Cell occupation probabilities						
Guest	$\epsilon/k^{+}_{\text{guest}}$, K	$\sigma^{+}_{\text{guest}}$, Å$^{\lambda}$	ϵ/k, K	σ, Å	y_1	y_2	f/P	P 10^6 N/m²	f_{exp} 10^6 N/m²	$f_{\text{calc.}}$ 10^6 N/m²	% difference
Argon	119.8	3.405	175.6	2.955	0.957	0.960	0.9125*	9.70	9.70□	9.70	0
Krypton	171.0	3.60	209.8	3.050	0.965	0.958	0.975φ	1.47	1.42□	1.33	7
Xenon	217.0	3.963	236.3	3.2315	0.968	0.956	0.99φ	0.145	0.145○	0.083	43
	ϵ_{H_2O}/k	σ_{H_2O}	K	Å							
		Host Water	257.33$^{\Delta}$	2.50							

100,000 accepted moves, approximately 33% rejection

$^{+}$ 2nd viral data Hirschfelder, et al. (1954).
* Estimated from Berlin correlation (Cook, 1961).
φ Estimated from generalized charts (Reid and Sherwood, 1966).
Δ Calculated from Equation (6) using ϵ/k for argon.
○ Parrish and Prausnitz (1972).
□ Barrer and Edge (1967) and von Stackelburg and Muller (1954).
λ 1A = 10^{-10} m.

TABLE 3. DISSOCIATION PRESSURES FOR POLYATOMIC GUESTS AT 273K

Guest molecule	Hard-core geometry$^{\Phi}$	Potential function	Mixture potential parameters ϵ/k	σ	R_{coll}	Cell occupation probabilities y_1	y_2	Number of moves	ΔR	% rejected	$f_{\text{calc.}}$	f_{exp}	References
			K	A□	A				A		10^6 N/m²	10^6 N/m²	
CO_2	Rod C-O distance 1.1615 A	spherically symmetric Kihara	221.35	2.343	1.15	0.969	0.956	160,000	Rsi/15	35	1.29	1.26	Unruh and Katz (1949)
		nonspherically symmetric Kihara	224.0	2.3315	0.30	0.970	0.956	200,000	Rsi/15	50	1.24	1.26	
		L-J 6-12*	221.4	3.493	0.0	0.984	0.945	100,000	Rsi/10	45	0.196	1.26	
N_2	Rod N-N distance 1.094 A	L-J 6-12*	156.39	3.099	0.0	0.972	0.955	200,000	Rsi/10	10	4.60	15.77	van Cleeff and Diepen (1965)
		nonspherically symmetric Kihara	115.5	2.9845	0.27	0.929	0.967	200,000	Rsi/15	40	16.19	15.77	
O_2	Rod O-O distance 1.100 A	L-J 6-12*	165.7	2.9835	0.0	0.965	0.958	250,000	Rsi/10	15	6.09	11.19	Saito, et al. (1964) van Cleeff and Diepen (1965)
		nonspherically symmetric Kihara	123.4	2.984	0.25	0.948	0.963	100,000	Rsi/15	40	10.39	11.19	
CH_4	Tetrahedron C-H distance 1.093 A	nonspherically symmetric Kihara	253.0	2.036	0.15	0.975	0.952	250,000	Rsi/10	45	2.43	2.48	Saito et al. (1964)

Note: Reid and Sherwood (1966) used for estimating f/P for CO_2, N_2, O_2 and Din (1961) for CH_4.
* ϵ_{H_2O} and σ_{H_2O} as determined from a force fit of argon-water data, were used to estimate ϵ and σ by hard sphere and geometric mean approximations.
Φ Intermolecular distances from spectroscopic data Herzberg (1966).
□ 1A = 10^{-10} m.

potential will also be asymmetric and the L-J 6-12 potential should be inadequate. The L-J 6-12 potential was used for N_2 and O_2 in the same manner as before with monatomic guests. The fugacities agreed to within 70% for N_2 and 45% for O_2. However, for CO_2 and CH_4 agreement was poor (> 100%).

The nonspherically symmetric Kihara potential was found to be most suitable for describing nonsymmetric guest-host interactions. This did involve choosing a hard-core geometry for the guest. For CO_2, N_2, and O_2 a rod shaped core was selected while for CH_4 a tetrahedral core was used (Table 3). The host water molecules were assumed to be spherical and to be centered about the oxygen atom. The results of the Monte Carlo sampling are presented in Table 3. Because the polyatomic guests are normally larger than monatomic guests and because they are asymmetric, the guest-host potential is more sensitive to position and orientation within the cell. Consequently, considerably more moves are required for convergence. For example, at least 100,000 moves were necessary when the optimum move size of *Rsi*/10 was employed.

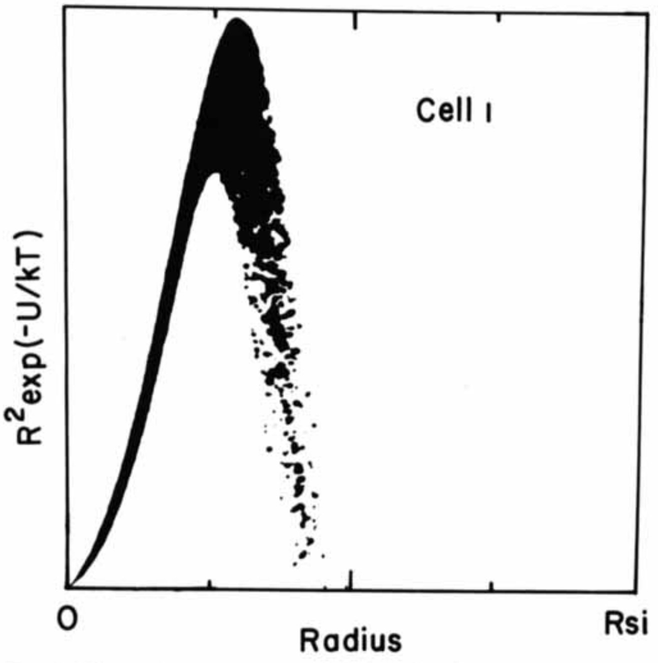


Fig. 3. Spherically symmetric probability of finding an argon guest at a given radius in cell 1.

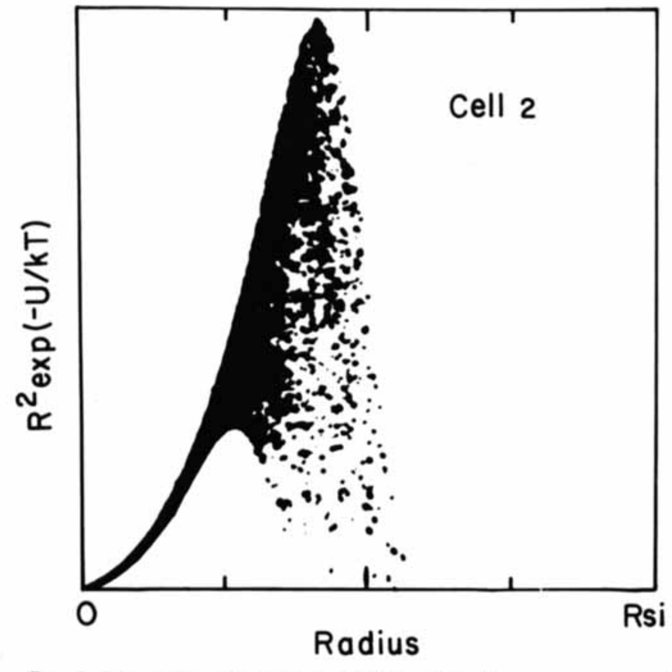


Fig. 4. Spherically symmetric probability of finding an argon guest at a given radius in cell 2.

The Kihara potential parameters were selected by trial and error to minimize the difference between calculated and experimental fugacities.

Guest Free Volume

One advantage of the Monte Carlo model is that the discrete nature of the guest-host interaction is easily treated by sampling the various configurational states available to each guest. If the guest-host potential were spherically symmetric, the probability of finding a guest at a given position in the cell would be proportional to $R^2 \exp(-U(R)/kT)$ for any given value of R. In Figures 3 and 4, this quantity is plotted as a function of R for 10,000 moves with argon as the guest. In cell 1 the probability distribution is almost uniquely defined by a single line, which was expected since cell 1 is spherical. However, in cell 2 where asymmetries are present considerable scatter of the points is observed. These deviations from spherical symmetry become even more pronounced as the symmetry of the guest decreases, for example, CO_2, N_2, O_2.

Three-dimensional plots of the volume occupied by an argon molecule in cells 1 and 2 are given in Figures 5 and 6. Only one-half of each cell is shown. The almost spherical shape in cell 1 is consistent with the spherical symmetry of the guest and the pentagonal dodecahedral cell itself. In cell 2, the nonspherical shape is consistent with the distortions characteristic of the tetrakaidecahedral cell, for example, a maximum penetration is observed in the center of the larger hexagonal face. The structural aspects of the free volume are more apparent as the asymmetry of the guest increases. The free volume is influenced primarily by the shape of the guest, the spatial arrangement of host molecules, and the nature of the guest-host potential.

For a given Monte Carlo sample the normalized probability of finding a guest in a spherical shell of thickness ΔR at a distance R from the cell center can be represented as the number of accepted moves into that shell divided

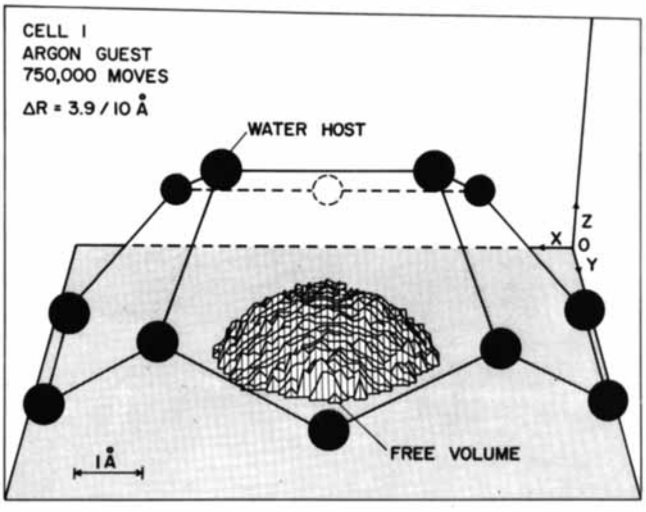


Fig. 5. Free volume occupied by an argon guest in cell 1, with host atom positions illustrated.

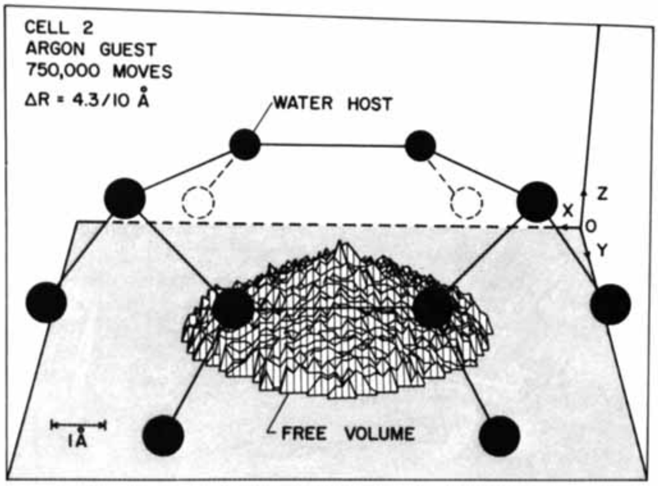


Fig. 6. Free volume occupied by an argon guest in cell 2, with host atom positions illustrated.

by the total number of attempted moves. In Figure 7, this probability is plotted as a function of R for two different move sizes $\Delta R = Rsi/10$ and $Rsi/1000$ for 4,000,000 moves with the argon hydrate. The graph is cut off at an R corresponding to the maximum linear dimension of the guest since it must occupy a volume at least this large. At moderate R's ($j = 13\text{-}22$) both lines coincide, but as R gets larger the guest has a slightly higher probability of occupying any shell at R_j ($j > 23$). This has the effect of increasing V_{cell} [Equation (15)] by placing more weight on those shells which are farther from the center.

As ΔR decreases, more moves are accepted and the guest creeps further out in the cell because ΔU is smaller for any given move. Furthermore, the statistics become poorer for small ΔR's as R increases simply because there are not a sufficient number of moves in the outer shells to give a reasonable estimate of Acc_j/Num_j. For 4,000,000 moves V_{cell} ($\Delta R = Rsi/10$) is about 20% smaller than V_{cell} ($\Delta R = Rsi/1000$).

CONCLUSIONS AND RECOMMENDATIONS

The Monte Carlo approach to the study of clathrates can be regarded as a prototype study to show the potential usefulness of Markov type processes in modeling complex phenomena. The structural aspects of the guest molecule as it moves in the clathrate cell were realistically accounted for in determining its configurational properties. The multidimensional integration required in the estimation of the thermodynamic properties of the clathrate was handled easily by a Monte Carlo approach. A continued effort will be made at understanding the configurational properties of more complex clathrate compounds having polyatomic guest components such as CH_2ClF or $CHCl_3$. Specifically, the limitations afforded by fitting the data to a set of empirical potential parameters should be reduced as other guest component structures are studied. Ideally, a continued analysis of this type should reveal general characteristics of the host lattice potential and the effects of cell geometry on the potential parameters of the enclathrated gas versus the free gas state.

Certainly other related problems in chemical engineering could be modeled using a similar Monte Carlo or molecular dynamics approach, for example, the motion of a reacting molecule in a molecular sieve zeolite or similar inclusion compound, polymer molecule interactions in solutions, as well as impurity defect incorporation in metals, order-disorder effects, and lattice gas studies of various compounds of interest in solid state chemistry (Beeler, 1970). The essential feature common to all these applications is that the structural or crystallographic aspects of a kinetic or thermodynamic process are being utilized in an appropriate model.

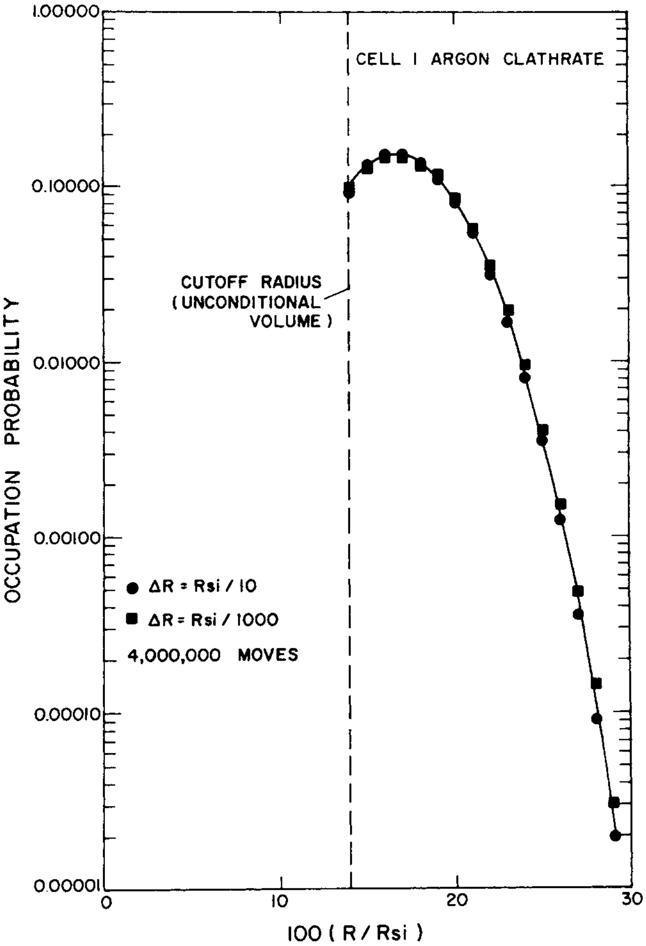


Fig. 7. Probability of finding an argon guest in spherical shell *j* in the Monte Carlo sampling.

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NOTATION

a = atomic spacing, Å
Acc_j = number of accepted moves into spherical shell j
$C_i(T)$ = Langmuir coefficient
f_{cell_i} = fugacity of cell i, N/m^2
k = Boltzmann constant, 1.38054×10^{-23} J/K
Num_j = number of attempted moves into spherical shell j
P = pressure, N/m^2
r or R = radius variable, m
r_{ij} = separation distance between guest and host, m
R_{coll} = collision radius, hard-sphere model, m

Rsi = cell radius, m
T = absolute temperature, K
U = intermolecular potential energy, J
v = molar volume, m^3/mole
V = volume parameter, m^3
V_{cell} = volume occupied by the guest molecule, m^3
$V_{uncond.}$ = unconditionally accepted volume corresponding to the size of the guest, m^3
y_i = occupation probability of cell i
Z_{cell_i} = configurational partition function of cell i, m^3

Greek Letters

α, β, γ = orientation angles of the guest
ϵ = potential energy parameter, J
ΔR = distance per move, m
R, θ, ϕ = spherical coordinates
ρ = minimum distance between surface of the hard core of the guest and the host, m
σ = collision parameter, m
ν_i = ratio of the number of cells of type i to the number of water molecules
μ = chemical potential, J

Sub and Superscripts

β = empty clathrate host lattice
j = move number
i = cell type 1 = pentagonal dodecahedron
2 = tetrakaidecahedron
$< >$ = ensemble average

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