

Intermolecular potentials in gas hydrates

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From a new set of Lennard-Jones (L-J) potential parameters for water derived from relatively accurate theoretical calculations, the dissociation pressure and cage occupancy ratio of some structure I gas hydrates are calculated within the localized site - solid solution model. The cell partition functions are evaluated in both the Devonshire spherical-cell approximation and by rigorous Monte Carlo integration. The two methods gave satisfactory, and closely similar, results. The low occupancies of the small cages of the xenon and CF₄ hydrates observed experimentally are reproduced and may be explained primarily as a size effect of the encaged molecules. A procedure based on the more rigorous theory of intermolecular forces is used to construct more-realistic exp-6-8-10 potential functions for unlike pair interactions. Preliminary calculations of the Langmuir constants for some gas hydrates appear to demonstrate the superiority of the exp-6-8-10 potential over the L-J potential. The requirements for further improvement are discussed.

A partir d'un nouvel ensemble de paramètres potentiels de Lennard-Jones (L-J) relatifs à l'eau, dérivés de calculs théoriques relativement précis, on a calculé la pression de dissociation et le rapport d'insertion de certains hydrates gazeux de structure I à l'intérieur du modèle qui représente un site précis et une solution solide. On a évalué les fonctions de partition des cellules à la fois selon l'approximation de cellules sphériques de Devonshire et l'intégration rigoureuse de Monte-Carlo. Les deux méthodes ont donné des résultats satisfaisants et très semblables. On a reproduit expérimentalement le faible taux d'occupation des cages de petite taille caractérisant les hydrates de Xe et de CF₄. On pense que ce phénomène découle surtout des dimensions des molécules emprisonnées. On a employé un procédé basé sur la théorie plus rigoureuse des forces intermoléculaires, afin de construire des fonctions potentielles plus réalistes exp-6-8-10 pour représenter des interactions entre paires inégales. Il semble que les calculs préliminaires des constantes de Langmuir relatives à certains hydrates gazeux démontrent la supériorité de la fonction potentielle exp 6-8-10 par rapport à la fonction potentielle L-J. On commente les exigences qui permettraient d'améliorer ces recherches.

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Introduction

The thermodynamic theory used to describe the properties of clathrate compounds is based on a statistical solid-solution model proposed by J.H. van der Waals in the late 1950's (van der Waals and Platteeuw 1959). This model assumes the host lattice by itself to be unstable unless stabilized by inclusion of a second component, the guest species. The forces holding the guest are van der Waals in nature and enclathration can be treated as a localized adsorption phenomenon.

The contribution of the guest molecule to the stability of the system is determined by the cell partition function which is defined in terms of the configuration integral Z_i — a volume integral over the exponential function of the total interaction potential $U(r)$,

$$[1] \quad Z_i = \int_V \exp[-U(r)/kT] dV,$$

where k is the Boltzmann constant and T is the temperature of the system. Unfortunately the irregular shapes of the cavities of the host lattice makes the analytical integration intractable and very often a spherical cell model is assumed to simplify the integration (Barrer and Stuart 1957; Davidson 1973; Parrish and Prausnitz, 1972; van der Waals and Platteeuw 1959).

From the cell partition function other significant thermodynamic properties can be calculated. One of these is the Langmuir constant which characterizes the "adsorption" of the guest component

$$[2] \quad C_i = Z_i/kT.$$

If the occupancy factors θ_i of the cages are also known, one can compute the dissociation pressures of the clathrates

$$[3] \quad P = \frac{1}{C_i} \frac{\theta_i}{1-\theta_i}$$

which are the important experimental observables.

Equation 3 defines the minimum pressure at which a hydrate is stable in terms of the occupancy of the cages required to reduce the chemical potential of the water molecules in the hydrate to its value for ice according to

$$[4] \quad \Delta\mu = -kT \sum_i \nu_i \ell n(1-\theta_i),$$

where $\Delta\mu$ is the difference between the chemical potential of the empty hydrate lattice (all $\theta_i = 0$) and ice at the same temperature and pressure, and ν_i specifies the number of cavities of type i per water molecule. For structure I hydrates, $\nu_1 = 1/23$ and $\nu_2 = 3/23$ for the small and large cavities, respectively.

Unfortunately $\Delta\mu$, which in the simplest version of the model is independent of the nature of the guest molecules in isostructural hydrates, is not accurately known. It cannot be easily calculated from the structural differences between clathrate hydrate and ice. To make use of equation 4 in the calculation of dissociation pressures, the "reasonable" value of $\Delta\mu = 1297 \text{ J/mol}$ has been taken (Dharmawardhana *et al.* 1980).

Water-guest Interaction Potentials

If one assumes that the total interaction of the encaged species may be represented by a sum of discrete pair-wise interactions with the water molecules, the theoretical calculation of the dissociation pressure depends critically on the choice of an accurate potential function for the water-guest interaction.

The general profile of the van der Waals interaction is sketched (Figure 1). At short intermolecular separations, the potential is dominated by repulsion of the electron clouds. At large separations the potential becomes slightly attractive because of the correlated motion of the electrons in the outer orbitals of the molecules — the dispersion energy (Margenau and Kestner 1969).

The simplest functional form for representing this profile is the Lennard-Jones (L-J) 6-12 potential (Margenau and Kestner 1969)

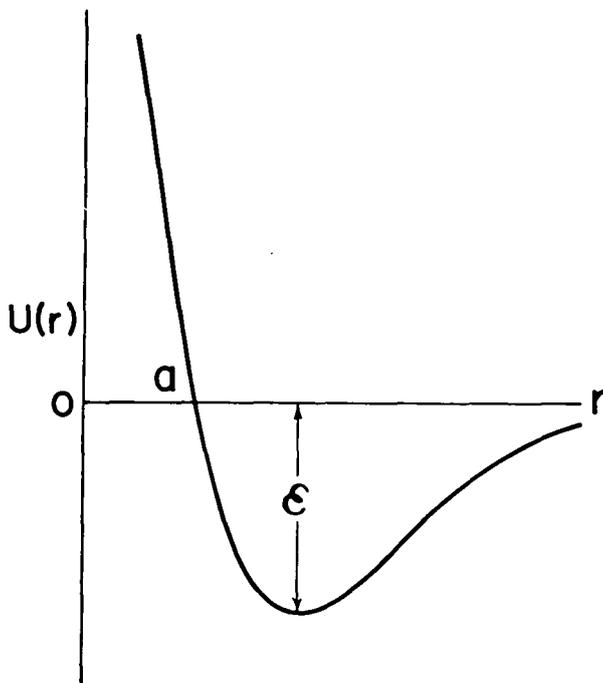


FIGURE 1. Form of the binary intermolecular potential function.

$$[5] \quad U(r) = 4\epsilon \left[\frac{\alpha^{12}}{r^{12}} - \frac{\alpha^6}{r^6} \right],$$

where the repulsive term depends on r^{-12} and the attractive term on r^{-6} . The L-J potential is uniquely defined by only two parameters: the collision parameter α and the stabilization parameter ϵ .

The two types of cavity in structure I hydrates have (average) radii of 391 and 433 pm¹. For many guest species the potential minima lie well within the cages and the dissociation pressure depends mainly on the value of ϵ and the occupancies of the two cages will be almost the same. For some guest molecules of larger dimensions it may happen that the potential within the smaller cages is repulsive while it is still attractive in the larger cages. In these cases the occupancy ratio of the small to large cages will be less than unity and the dissociation pressure will be very sensitive to both α and ϵ .

In the earlier studies, L-J parameters were taken over from gas-phase virial coefficient and viscosity measurements (Davidson 1973; van der Waals and Platteeuw 1959), with arbitrary combining rules used to relate the parameters for pairs of unlike molecules to those of like pairs (*see below*). Most recent studies, aimed at a more accurate prediction of dissociation pressures of mixed hydrates (several guest species), have determined the parameters by *ad hoc* procedures to fit experimental dissociation pressures for a particular set of hydrates (e.g. Parrish and Prausnitz 1972). The L-J parameters thus obtained are not uniquely defined and tend to lose their physical significance. For instance, the effective collision diameter of water can vary from the initial estimate of 260 pm (van der Waals and Platteeuw 1959) to a recent value of 375 pm (Holder *et al.* 1980).

One must look for a more consistent way of choosing the interaction parameters, while at the same time maintain a simple physical picture of the interaction. The suitability of the spherical cell approximation for the cages must be examined; this approximation may be an important limitation, particularly to adequate treatment of the larger structure I cages which are the least spherical of the cages which occur in the two hydrate structures.

Choice of Lennard-Jones Parameters

In seeking more realistic potential parameters for the water molecule we have fitted an L-J function was fitted to an accurate theoretical neon-water potential curve to give α and ϵ for this system. More details are given in Appendix I. Since the L-J parameters for the

¹pm = picometre = 10⁻¹² m

neon-neon interaction are known, the usual combination rules (Hirshfelder *et al.* 1954) namely,

$$[6] \quad \begin{aligned} a &= (a_{ii} + a_{ww})/2 \\ \epsilon &= (\epsilon_{ii} \cdot \epsilon_{ww})^{1/2} \end{aligned}$$

may be used to extract the potential parameters a_{ww} and ϵ_{ww} for water. These combination rules are not entirely justifiable on theoretical grounds. The arithmetic mean rule for the diameter parameter is valid only for a hard-sphere model of the interacting molecules and does not allow for deformation of the electron clouds. Generally it overestimates the diameter a (Kong 1973) and gives too high a dissociation pressure. The geometric mean rule for estimating the stabilizing energy of the unlike pair can be shown to be the upper bound of the true value (Tang 1968) and thus, in general, leads to too low a dissociation pressure. This tendency for the errors to cancel each other may account for the apparent success of these combining rules in previous applications. The values of a_{ww} and ϵ_{ww} used are effective values only, defined in this case for the neon-water system; they are not derived specifically from water-water interaction potentials.

The Spherical Cell Approximation and Monte Carlo Integration

To test the validity of the spherical cell (Lennard-Jones-Devonshire) approximation frequently used in the evaluation of configuration integral (equation 1), this model is compared with the results of a Monte-Carlo integration scheme of the kind first applied by Tester, Bivins, and Herrick (1972) to clathrate hydrates.

The potential energy at any point within the cage is the sum of discrete binary interactions between the guest molecule and individual water molecules forming the cage

$$[7] \quad U(r) = \sum U_{iw}(r_{iw}).$$

In this way, the discrete structure of the cage (and its asymmetry) is taken into account. By proper sampling of a sufficient number of the configurations available to the encaged molecule, an ensemble average of the potential energy is determined (Metropolis *et al.* 1953):

$$[8] \quad \begin{aligned} Z &= \langle \exp(-U/kT) \rangle V_{\text{cage}} \\ \langle \exp(-U/kT) \rangle &\cong \exp(-\langle U \rangle/kT) \\ \langle U \rangle &= \sum_j U_j/N. \end{aligned}$$

Normally $N = 10,000$ to $20,000$ random moves were found to be required to achieve a convergence of better than five per cent in the cell partition function (Tester *et al.* 1972).

With use of the L-J parameters for water given in the Appendix and L-J like-pair parameters for a number of guest molecules (Hirshfelder *et al.* 1954), the dissociation pressures of the corresponding hydrates were calculated at 0°C for the spherical cell approximation and Monte-Carlo integration. These are given in Table 1, along with the ratios θ_1/θ_2 of the small to large cage occupancy factors at the calculated dissociation pressures.

In general, the dissociation pressures and occupancy ratios calculated from the spherical cell approximation are very similar to the values given by the more elaborate Monte-Carlo calculation. Thus, where serious disagreements exist between observed dissociation pressures and those calculated by the spherical cell approximation (Davidson 1973; McKoy and Sinanoglu 1962; Tester *et al.* 1962; van der Waals and Platteeuw 1959) these disagreements are not primarily due to the approximation of discrete pair interactions by a spherical continuum.

The occupancy ratios for gas hydrates with small guest species (argon, krypton, and methane) are close to unity, while for xenon and CF_4 the ratios are substantially smaller. For xenon the calculated ratios are in general agreement with the recent experimental values of $\theta_1/\theta_2 = 0.77 \pm 0.02$ for xenon deuterohydrate (Ripmeester and Davidson 1981), in contrast with values very near unity given by previous calculations (Davidson 1973; McKoy and Sinanoglu 1962; Parrish and Prausnitz 1972; Tester *et al.* 1972; van

TABLE 1. Calculated dissociation pressure of some structure I gas hydrates at 273.16 K using the L-J 12-6 potential*

Hydrate	Method	θ_1/θ_2	$P_{\text{cal}}(\text{kPa})$	$P_{\text{obs}}(\text{kPa})$
Ar	SC	.987	8517	9126
	MC	.993	9227	
Kr	SC	1.00	1278	1450
	MC	.984	1430	
Xe	SC	.887	47.6	149
	MC	.702	50.7	
CH_4	SC	.944	1237	2555
	MC	.954	1237	
CF_4	SC	10^{-7}	1683	4208
	MC	10^{-7}	730	

* $a_{ww} = 304$ pm, $\epsilon_{ww} = 1561$ J.

SC = spherical cell approximation.

MC = Monte-Carlo integration.

$\Delta\mu = 1297$ J/mol.

der Waals and Platteuw 1959). Likewise, previous calculations have not anticipated negligible occupancy of the small cages by CF_4 , although this is clearly indicated by Miller's experimental composition estimates for this hydrate (S.L. Miller, *pers. commun.*).

Again, the calculated dissociation pressures for the larger guest molecules are smaller than the experimental ones, although significantly less so than before (McKoy and Sinanoglu 1962; van der Waals and Platteuw 1959) for CF_4 hydrate. A more theoretically rigorous potential function than that of Lennard-Jones must be sought.

Construction of an Exp-6-8-10 Potential Function

If the interaction between two molecules is entirely van der Waals in nature, the interaction potential can always be separated into independent repulsive and attractive contributions. The short-range repulsive energy may best be represented as a polynomial in exponential functions of the separation. Often the one-term Born-Mayer function is adequate to describe the overlap energy of the system (Fowler and Guggenheim 1956; Hirshfelder *et al.* 1954; Margenau and Kestner 1969)

$$[9] \quad U^R(r) = A \exp(-br).$$

(The r^{-12} term in the L-J potential does not give the correct asymptotic overlap energy.) The attractive interaction can be expressed as a polynomial series in r^{-1} . On theoretical grounds the first term of the expansion is proportional to r^{-6} and arises mainly from induced dipole-induced dipole dispersive interaction. It is normally necessary only to include as well terms in r^{-8} and r^{-10} from mutually induced higher moments (dipole-quadrupole, quadrupole-quadrupole):

$$[10] \quad U^A(r) = -\frac{C_6}{r^6} - \frac{C_8}{r^8} - \frac{C_{10}}{r^{10}}.$$

For interactions between like species the Born-Mayer potential parameters may be obtained by fitting the potential to an accurate theoretical repulsive curve. The dispersive coefficients C_6 , C_8 , and C_{10} can be determined from experimental molecular beam data (Bernstein and Muckerman 1967) or, less accurately, from theory (Hirshfelder and Meath 1967).

Theoretically rigorous combining rules exist for both the repulsive and attractive contributions (Smith 1972; Tang 1969), thus making possible the estimation of unlike-pair parameters from the constituent like-pair parameters. The repulsive combining rules

$$[11] \quad \frac{1}{b_{iw}} = \left(\frac{1}{b_{ii}} + \frac{1}{b_{ww}} \right) / 2$$

$$A_{iw} = \frac{2/b_{iw}}{1/b_{ii} + 1/b_{ww}} = A_{ii} \times A_{ww}$$

are derived (Smith 1972) from the assumption that repulsion is entirely due to charge overlap, distortion of the electron clouds being taken into effect. The attractive combining rule (Tang 1969)

$$[12] \quad C_n^{iw} = \frac{2C_n^{ii}C_n^{ww}}{\frac{\alpha_n^i C_n^{ii}}{\alpha_n^w} + \frac{\alpha_n^w C_n^{ww}}{\alpha_n^i}}$$

relates the dispersion coefficients for unlike pairs to the corresponding coefficients and the n^{th} order polarizabilities α_n of the constituent species. Values of both are tabulated in the literature (Hirshfelder *et al.* 1954; Thomas and Meath 1969; Thomas *et al.* 1980) for the common hydrocarbons and rare gases.

To account for the correct asymptotic behaviour of the attractive term at small r , it is advisable to introduce a damping factor $S(r)$ which reduces the contribution of the dispersive energy and gives a better potential near the minimum in $U(r)$ at r_m . This is a universal function (Ng *et al.* 1978, 1979)

$$[13] \quad S(r) = \begin{cases} \exp[-\beta(ar_m/r-1)^2] & r < ar_m \\ 1 & r \geq ar_m \end{cases}$$

in which α and β need only be determined once from a model calculation.

The complete interaction potential now has the form

$$[14] \quad U(r) = A \exp(-br) - \left(\frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} \right) S(r).$$

With the data available for the parameters relating to the argon-argon (Ng *et al.* 1979) and water-water (Watts 1977) interactions, a potential function has been constructed from the combining rules outlined above in the form of equation 14 for the binary argon-water interaction. One finds 354 ± 4 pm for the separation at the potential minimum and a well depth of 1372 ± 166 J, in excellent agreement with the values of 329 ± 25 pm and 1363 ± 91 J measured by a molecular beam experiment (Bickes *et al.* 1975).

Application of the Exp-6-8-10 Potential to Clathrate Hydrates

From tabulated values (Ng *et al.* 1978, 1979; Tang *et al.* 1976; Thomas and Meath, 1979) of the potential parameters the Monte Carlo integration method has been used to calculate the dissociation pressures of a number of structure I hydrates (Table 2). The upper

TABLE 2. Dissociation pressures of some structure I gas hydrates at 273.16 K from theoretical potentials*

Hydrate	θ_1/θ_2		P_{cal} (kPa)		P_{obs} (kPa)
	upper	lower	upper	lower	
Ar	1.01	1.00	11560	3550	9126
Kr	1.02	.99	8213	608	1450
Xe	.81	.73	9328	3245	149
CH ₄	1.00	.95	11150	1724	2555

*The exp-6-8-10 potential function with $\alpha = 1.38$, $\beta = 1.28$.

and lower limits of the occupancy ratios and dissociation pressure were estimated from the experimental error attached to the dispersion coefficients. The occupancy ratios are in good agreement with our previous values (see Table 1). The observed dissociation pressures lie within the bounds of those calculated, except for xenon hydrate. Although the uncertainty limits are considerable, the new potential function gives reasonable estimates of the hydrate dissociation pressure from first principles (without any adjustment of parameters to fit hydrate data). Where the results differ substantially from experiment there is good reason to suspect that the general model (a single guest molecule interacting dispersively only with the water molecules of its immediate cage) is inadequate, not that the model has been inaccurately applied. Thus, the relatively high polarizability of the xenon atom may lead to additional stability through interactions with xenon atoms in neighbouring cages and with non-vanishing electric fields generated by permanent moments of the water molecules forming the lattice (Davidson 1971).

A more stringent test of the potential model can be achieved through calculation of the Langmuir constant, since this does not depend on the choice of $\Delta\mu$. Unfortunately these constants are very difficult to measure directly and have only been reported for the rare gases in the small cages of structure II chloroform hydrate (Barrer and Edge 1967). In Table 3, calculated Langmuir constants for the small cages of the structure I hydrates of argon, krypton, and xenon are compared with the Barrer and Edge values measured for the small structure II cages. Since the pentagonal dodecahedral cages in the two structures are nearly identical, the Langmuir constants are expected to be very similar for the two small cages.

For argon and krypton hydrates the agreement with experiment is substantially better for the exp-6-8-10 potential than for either the Lennard-Jones potential already described or for the Parrish-Prausnitz L-J spherical cell potential (in which the parameters were adjusted to fit experimental dissociation pressures).

TABLE 3. Langmuir constant for the small cage of some gas hydrates (MP/a)

Method	Ar (263 K)	Kr (263 K)	Xe (269 K)
MC (exp-6-8-10) ^a	2.16	18.4	1.32
MC (L-J 12-6) ^a	3.93	27.4	182
Parrish and Prausnitz ^a	4.57	30.8	104
Experiment ^b	1.50	10.9	23.8

^aStructure I hydrate

^bStructure II hydrate; data from Barrer and Edge (1967).

Conclusions

The Lennard-Jones-Devonshire spherical cell method provides a reasonably good approximation to the more detailed summation of discrete guest-water binary interactions in clathrate hydrates when the same form of the intermolecular potential function is used. In preference to *ad hoc* adjustment of L-J potential parameters to fit known dissociation pressures, an attempt has been made to treat the problem in terms of the modern theory of intermolecular interactions. A more realistic form of interaction potential which requires comparatively little computational effort for application to clathrate hydrates has been proposed.

Further theoretical elaboration is obviously necessary, as is improvement in the experimental values of the exp-6-8-10 potential parameters. It is clear that careful consideration must be given to the adequacy of the isotropic two-body treatment of the proper multi-body guest-host lattice interaction and of the neglect of non-vanishing electrostatic fields within the cage and of interactions between neighbouring guest species.

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Appendix I

The Lennard-Jones potential parameters for the neon-water system were obtained by least squares fitting of the theoretical interaction energies calculated from an accurate *ab initio* Hartree-Fock method (Losonczy *et al.* 1973) to the 12-6 power law. It is well known that the Hartree-Fock approximation ignores the electron correlation contributions to the potential energy of the system (Margenau and Kestner 1969). Correlation energy terms are present over the whole range of interaction. At very short separations where the two interacting species are strongly repelling, the Hartree-Fock representation is likely to be sufficiently accurate. At large separations the dominant contribution to the correlation energy arises from the induced dipole-induced dipole interaction. This term is proportional to the inverse sixth power of the distance between the centres of the molecules. Therefore, to the Hartree-Fock interaction energies have been added an additional dispersion contribution, ΔE_{disp} ,

$$[15] \quad \Delta E_{\text{disp}} = - \frac{C_6}{r^6}.$$

C_6 is the dispersive coefficient of the neon-water system which is calculated from equation 12 and the like-pair interaction parameters (Hirshfelder *et al.* 1954; Kolos *et al.* 1980).

Once the L-J potential parameters were determined ($a_{\text{NeW}} = 289$ pm, $\epsilon_{\text{NeW}} = 742$ J), the water parameters were extracted from the L-J parameters for the Ne-Ne system ($a_{\text{NeNe}} = 275$ pm, $\epsilon_{\text{NeNe}} = 355$ J) by use of the combination rules of equation 6. The L-J potential parameters obtained for water were $a_{\text{ww}} = 304$ pm and $\epsilon_{\text{ww}} = 1561$ J.