

CLATHRATE THERMODYNAMICS FOR THE UNSTABLE HOST FRAMEWORK

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ABSTRACT. We have introduced the concept of clathrates whose empty host framework is unstable. In contrast to the Van der Waals theory, according to which the empty host framework is metastable, we believe it to become metastable when, in the cellular clathrates, certain type of cavities are fully occupied or, in the channel clathrates, the guest molecules are closely packed. The free energy of the channel and cellular types of clathrates has been determined using statistical thermodynamics methods. The obtained chemical potentials allowed us to describe the equilibrium of the clathrate with the stable host α -phase and the gaseous guest phase. For the cellular clathrates the equations have been obtained determining the dependence of the degree of filling of small cavities upon temperature and the gaseous phase pressure. In the case of the channel clathrates the set of equations on the composition and parameter of the orientational ordering is found. These equations enable us to describe quantitatively compressed state of the guest molecules in the channel and to find temperatures of orientational ordering.

1. INTRODUCTION

At present, clathrate compounds are considered as both ideal [1] and nonideal solid solutions [2-3] of the guest component in a crystalline framework of the host component. In the absence of the guest component, clathrate β -modification is considered to be metastable with respect to the stable α -modification under ordinary conditions, i.e. $\Delta\mu = \mu_{\alpha} - \mu_{\beta} < 0$, where μ_i is the chemical potential of the corresponding modification. A number of experimental data on water, urea and thiourea clathrates, hardly consistent with the classical theory, made us study the formation of clathrates with unstable (labile) host frameworks. A comprehensive motivation of such possibility is given in [4].

2. THERMODYNAMICS OF CLATHRATES WITH UNSTABLE HOST FRAMEWORKS

Empty host framework instability may be due to the disturbance of the mechanical equilibrium conditions and the framework dynamic instability.

If the mechanical equilibrium conditions are disturbed, some of (or all) the framework atoms (molecules) will be affected by noncompensated forces causing the destruction of the cavities. When the dynamic equilibrium conditions are upset vibrations with complex frequencies resulting in an irreversible framework destruction exist among eigenfrequencies of the empty framework or appear with the temperature increase at the expense of anharmonicity. The guest molecules getting into the framework cavity restore the mechanical equilibrium and cause the disappearance of the "vibrations" with complex frequencies.

2.1. Cryptato-Clathrates

In our model we shall assume the framework to become at least metastable when the cavities of a labile type are completely filled by the guest molecules. For simplicity, clathrates with two types of cavities (labile and stable in the absence of the guest) and one type of non-dipolar guest molecules will be considered.

Let us assume that when the guest molecules fill the labile cavities a metastable framework*) forms, whose free energy F can be determined using a number of suppositions accepted for classical clathrates.

a) A cavity cannot hold more than one guest molecule.

b) Classical statistics is valid.

c) We will assume that the forces influencing atoms (molecules) compensated at the expense of the forces created by the guest molecules are small. (The case of mechanically unstable framework.) Weak forces imply a small change of a portion of the free energy of the metastable framework concerned, when guest molecules are included into the labile cavities.

In the event of dynamic instability let us assume that the real frequencies of the empty host framework change negligibly with the inclusion of the guest molecules into the cavities and they provide a major contribution to that part of the free energy of the metastable framework which is connected with the host molecules.

d) The cell model is true, i.e., the guest molecules are in the cavity statical potential (an adiabatic approximation for the description of the guest molecules relative to the host framework).

On the basis of the suppositions a)-d), the expression for the metastable framework free energy \bar{F} , both for mechanical and dynamic instability of the empty host framework can be written as follows:

$$\bar{F} = F_Q - kTN_1 \ln h_1 + \frac{1}{2} N_1 U_1, \quad (1)$$

where on the basis of the c-th supposition the part of the free energy F_Q dependent upon the host molecule is separated, N_1 is the number of

*) In this case the framework is a clathrate compound, such as hydrates $\text{THF} \cdot 17\text{H}_2\text{O}$, $\text{CHCl}_3 \cdot 17\text{H}_2\text{O}$, in which only one type of cavity is filled.

the labile cavities. The second term describes the behaviour of the guest molecules in the cavity, whose expression will look as follows if one uses the designation of [1-3]:

$$h_1 = 2\pi a_1^3 g_1 \exp[-W_1(0)/kT] \cdot \Phi_1(T), \quad (2)$$

$$\Phi_1(T) = \sum_{\{n\}} \int \frac{d^3 p}{(2\pi\hbar)^3} \exp[-(\epsilon_n + p^2/2m)/kT], \quad (3)$$

$$g_1 = (2\pi a_1^3)^{-1} \int d^3 r \cdot \exp\{-[W_1(\vec{r}) - W_1(0)]/kT\}, \quad (4)$$

where ϵ_n is the n -th inner level of the guest molecule energy in the cavity; $W_1(\vec{r})$ is the potential energy of the guest-host interaction; a_1 is the size of the cavity.

The third term in (1) describes the interaction among the guest molecules, where U_1 is the energy of the interaction between a guest molecule and other molecules.

If one knows the expression for the free energy of a metastable structure consisting of a framework whose labile cavities are filled with guest molecules, the further theory is created just as the traditional clathrate solution theory [1-3]. The expression for the clathrate free energy will look as follows:

$$F = \bar{F} + kTN_2[-y \ln h_2 + \frac{1}{2} y^2 U_2/kT + (1-y) \ln(1-y) + y \ln y], \quad (5)$$

where N_2 is the number of stable cavities, $y = \bar{N}/N_2$ is the filling degree of these cavities; \bar{N} is the total number of the guest molecules, situated in the stable cavities; U_2 is the energy of the interaction of a guest molecule, which completely fill the stable cages.

The expression for h_2 is derived from (2)-(4), where the expression for the potential energy of the interaction between the guest molecules, which is in the stable cavity, with the host molecules and other guest molecules in the labile cavities, should be inserted instead of $W_1(\vec{r})$, a_2 should be inserted instead of a_1 , where a_2 is the size of the stable cavity; and ϵ'_n should be inserted instead of ϵ_n (ϵ'_n is the inner energy level of the stable cavity). The chemical potentials of the guest molecules are determined by the appropriate differentiation over the number of the host molecules N_Q and the number of the guest molecules $N_g = N_2 + \bar{N}_g$:

$$\mu_Q = \left(\frac{\partial F}{\partial N_Q} \right)_{N_g, T, V} = \left(\frac{\partial F_Q}{\partial N_Q} \right)_{T, V} - kT (v_1 \ln h_1 - v_2 \ln h_2) + \quad (6)$$

$$+ \frac{1}{2} v_1 [U_1 - 2yU_2] + v_2 kT [\ln(1-y) + \frac{v_1}{v_2} \ln \frac{1-y}{y}] - \frac{v_2}{2} y^2 U_2,$$

$$\mu_g = \left(\frac{\partial F}{\partial N_g} \right)_{N_Q, T, V} = -kT \cdot \ln \frac{y}{(1-y)h_2} + yU_2, \quad (7)$$

where v_1, v_2 are determined in the usual way: $N_i = v_i N_Q$, $i = 1, 2$.
Expressions (1)-(7) solve this task.

2.2. Tubulato-Clathrates

For the canal type of clathrates we will assume that to stabilize the lattice the guest molecules arrange in densely packed chains and that in addition to the suppositions b)-d) (see section 2.1), the following suppositions are realized:

e) The canal is considered to be smooth, i.e. the energy of a guest molecule does not depend on its coordinate along the canal axis. Furthermore, we can divide the energy levels connected with transversal and longitudinal motion of a guest in the canal.

f) The guest molecules are considered to be incompressible, i.e. their length does not change when the inner degree of freedom is excited. This shows that we discuss harmonical molecule vibrations with small amplitudes.

The above suppositions allowed us to consider the contributions to the free energy, related with the framework and the guest molecules, and in the last item we can single out the part responsible for the longitudinal motion of the guest molecules in a clathrate. Thus, the clathrate free energy is the sum of three parts:

$$F = F_Q + F_{g-h} + F_2. \quad (8)$$

The expression for F_{g-h} is found as in reference [1]:

$$F_{g-h} = -N_g kT \cdot \ln h, \quad (9)$$

where

$$h = g(T) \phi(T) \cdot \exp\{-W(0)/kT\}, \quad (10)$$

$$g = \int d^2 r \cdot \exp\{-(W(\vec{r}) - W(0))/kT\}. \quad (11)$$

In this expression N_g is the number of the guest molecules, $W(\vec{r})$ is the guest molecule energy depending on its mass centre remoteness from the canal axis, \vec{r} is a two-dimensional vector in the plane perpendicular to the canal axis. The expression for the free energy portion connected with the longitudinal motion of the guest molecules in a canal looks as follows:

$$F_2 = -kT \cdot \ln \sum_{\{l\}} \exp(-E_l/kT). \quad (12)$$

Here l numbers the totality of the quantities, describing the configuration of the guest molecules in the canal, i.e. the orientation of molecules and the distance between them. E_l can be divided into two parts, one of them depending on the orientation of the interacting molecules. Thus for the interaction energy of the chain of the guest molecules located in the same canal one has:

$$E_l = \sum_i \varphi(a_i) - \sum_i J(a_i) \sigma_i \sigma_{i+1} - 6\bar{J} \sum_i \langle \sigma_i \rangle \sigma_i, \quad (13)$$

where a_i is the distance between the ends of the i -th and $(i+1)$ -th guest molecules; $\varphi(a_i)$ is the potential energy of the interaction between them; $\sigma_i = \pm 1$ depending on the i -th molecule orientation; $J(a_i)$ is the quantity determining the strength of the interaction between the adjacent molecules in the canal; \bar{J} is the same as $J(a_i)$ but for the interaction between the molecules situated in the neighbouring canals; $\langle \sigma_i \rangle = \sigma$ is the mean value of the order parameter. The substitution of the sum over the molecules from the adjacent chains by σ corresponds to the mean field approximation. The last two items in the expression for E_1 determine the orientation contribution to the guest chain interaction energy. Unlike in [5] we neglect the dependence of the guest-guest interaction upon the guest orientation (in [5] it was shown that this item changes the transition temperature negligibly) and consider \bar{J} to depend on a . For F_2 we have

$$F_2 = F_2^a + F_2^\sigma, \quad F_2^{a,\sigma} = -kT \cdot \ln Z_2^{a,\sigma}, \quad (14)$$

$$Z_2^a = \sum_{\{a_i\}} \exp\left[-\frac{1}{kT} \sum_i \varphi(a_i)\right], \quad (15)$$

$$Z_2 = \sum_{\{\sigma_i\}} \exp\left\{-\left[\sum_i J(a_i) \sigma_i \sigma_{i+1} + 6\bar{J}\sigma \sum_i \sigma_i\right]/kT\right\}, \quad (16)$$

where $\{a_i\}$ and $\{\sigma_i\}$ are arbitrary chosen sets of quantities a_1, \dots, a_N and $\sigma_1, \dots, \sigma_N$, respectively; the summation in (15), (16) is carried out over all possible sets. Having substituted $J(a_i)$ by $J(a)$ where $a = \langle a_i \rangle$ is the average distance between the ends of the adjacent guest molecules, one can single out both F_2^a and F_2^σ . Thus, F_2^a is in a quasiharmonic approximation [6] which is true in the event of a weak anharmonicity, i.e. when $|a - a_0|/a_0 \ll 1$, where a_0 is the distance between the last carbon atom of one molecule and the first one of the adjacent molecule, corresponding to the minimum of the potential energy of the interaction between them. The orientational contribution to the free energy F_2^σ in the mean field approximation accepted by us is determined accurately as the free energy of one-dimensional Ising model in the external field. The final expression for the free energy of the clathrate type in question will have the following appearance:

$$F = F_Q + N_g \left\{ -\frac{1}{2} kT \ln [2\pi kT h^2 f^{-1}(a)] - J(a) + \varphi(a) - kT \cdot \left(-\frac{\bar{h}kT}{8\bar{f}^2} + \frac{\bar{g}^2 kT}{12\bar{f}^3} \right) - kT \cdot \ln[\text{ch}x + A(\sigma)] \right\}, \quad (17)$$

$$x = \frac{6\bar{J}\sigma}{kT}, \quad y = \frac{2J(a)}{kT}, \quad f(a) = \frac{d^2 \varphi}{da^2}, \quad \bar{f} = f(a_0), \quad \bar{g} = \varphi'''(a_0), \quad *)$$

$$\bar{h} = \varphi''''(a_0), \quad A(\sigma) = \text{ch}^2 x - 2\text{sh} y \cdot \exp(-y),$$

where σ is determined according to the equation

*) The prime over $\varphi(a)$ here and below means the differentiation over the argument.

$$\sigma = \text{sh } x [A(\sigma) + \frac{kT}{6J} \text{ch } x] / A(\sigma) \cdot [\text{ch } x + A(\sigma)]. \quad (18)$$

To determine the chemical potentials of the host and the guest components in a clathrate it is necessary to differentiate the free energy accordingly over the number of the host and guest molecules. Doing so one should take the following expression into account:

$$N_Q = N_g [a + L(n-1)] / d, \quad (19)$$

where L is the distance between the adjacent carbon atoms in the same molecule (along the canal axis), n is the number of carbon atoms in a molecule, d is the distance between the framework layers, perpendicular to the 6-th order axis.

Equation (19) is obtained by calculating the number of the guest molecules per one host molecule. Thus, assuming $\partial F_Q^\sigma / \partial a = 0$ in the first approximation we obtain

$$\mu_Q^\beta = \mu_Q + d\varphi'(a) + \frac{1}{2} dkT \frac{\varphi''(a)}{\varphi'(a)} \quad (20)$$

where $\mu_Q = \partial F_Q / \partial N_Q$ is the contribution to the chemical potential, connected with the host structure;

$$\begin{aligned} \mu_g^\beta = & \varphi(a) - [a + L(n-1)]\varphi'(a) - \frac{1}{2} kT \cdot \ln(2\pi kT h^2 f^{-1}(a)) - \\ & - \frac{1}{2} [a + L(n-1)] kT \frac{\varphi''(a)}{\varphi'(a)} - kT \left[-\frac{\hbar kT}{8f^2} + \frac{-2kT}{12f^3} \right], \end{aligned} \quad (21)$$

(17), (20), (21) comprise the distance between molecules, whose expression is deduced from the equilibrium conditions of the phases concerned. As an example we shall discuss the host α and β phases equilibrium and the gaseous and clathrate phases of the guest molecules. Equating the chemical potentials of different host and guest phases, we obtain the equation, describing this equilibrium:

$$\Delta\mu = d\varphi'(a) + \frac{1}{2} dkT \frac{\varphi''(a)}{\varphi'(a)}, \quad (22)$$

$$\begin{aligned} P = & \frac{kT}{g} \frac{\Phi}{\phi} \left(\frac{f(a)}{2\pi kT} \right)^{1/2} \exp \left\{ \frac{W(0) + \varphi(a) - [a + L(n-1)]\varphi'(a)}{kT} - \right. \\ & \left. - \frac{1}{2} (a + L(n-1)) \frac{\varphi''(a)}{\varphi'(a)} - \left(-\frac{\hbar kT}{8f^2} + \frac{-2kT}{12f^3} \right) \right\}, \end{aligned} \quad (23)$$

where P is the guest component pressure in the gaseous phase, $\Phi_g(T)_\alpha$ is the guest molecular partition function in the gaseous phase, $\Delta\mu = \mu_Q^\beta - \mu_Q^\alpha$, μ_Q^α is the host chemical potential in the α -phase.

Notice, that the distance between the guest molecules a and, con-

*) As will be shown further σ differs from 0 at low temperatures, when the thermal expansion of the chain is negligible.

sequently, the clathrate composition, too, are determined by the guest-guest interaction and depend only on temperature, while the guest-host interaction determines the equilibrium vapour pressure of the guest.

To determine the thermodynamic clathrate functions it is necessary to find $a(T)$ and $\sigma(T)$. The order parameter σ is determined according to eq.(18). The solution for $\sigma \neq 0$ is well known to become possible for this equation at $T < T_c$, where T_c is the phase transition temperature, determined by the interaction constants J and \bar{J} . In the event of urea clathrates with n-paraffins, as it follows from the calculations and the experiments [5], the transition temperature $T_c \sim 100K$, i.e., it is rather low. This allows us to single out two temperature regions and find $a(T)$ and $\sigma(T)$ in these regions.

a) High temperatures ($T > T_c$).

For several values of $\Delta\mu^c$ the $a(T)$ dependence has been calculated according to equation (22) (in the approximation of incompressible molecules). Lennard-Jones potential ($\varphi(a) = 4\epsilon[(\frac{\sigma}{a})^{12} - (\frac{\sigma}{a})^6]$) has been chosen for the function $\varphi(a)$. The parameter ϵ had the value of 148.2K - the same as for the CH_4-CH_4 interaction, and the parameter σ has been chosen so that $\sigma \cdot 2^{1/6}$ should give 4.06 Å - the equilibrium distance between the carbon atoms in the crystalline lattice of n-paraffins. The distance between the urea molecules along the sixth order axis $d = 1.834 \text{ Å}$.

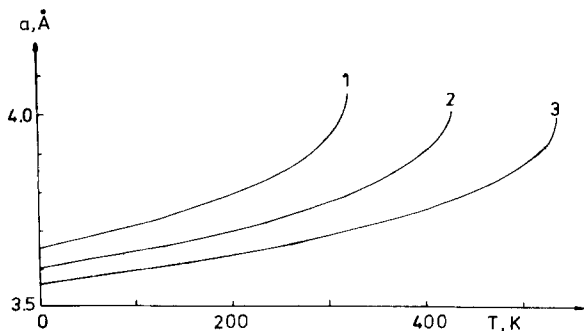


Figure 1. $a(T)$ dependence for $\Delta\mu = -2.96$ kcal/mole (1); $\Delta\mu = -3.94$ kcal/mole (2); $\Delta\mu = -4.93$ kcal/mole (3).

The diagrams $a(T)$ for three values of $\Delta\mu$ are shown in figure 1. Each $\Delta\mu$ has its own value of $T = T_0$, above which the clathrate cannot exist any longer, and the reason for this is not the structure instability but the fact that the equilibrium condition $\mu_O^\alpha = \mu_O^\beta$ is not realized at any a . The value of $\Delta\mu$ at which the maximum clathrate existence temperature T_0 is equal to the destruction temperature of the urea clathrate with polyethylene ($T_0 = 148^\circ C$, $\Delta\mu = -3.94$ kcal/mole [7]) has been accepted accurate. The equilibrium distance between the neighbouring molecules at room temperature appears to be equal to 3.76 Å, which is very similar to the experimental value of 3.74 Å [8,9].

b) Low temperatures ($T < T_c$).

The equation for T_c follows from equation (18) and has the form:

$$\left(\frac{kT}{6J}\right) = \exp\left(\frac{2J(a)}{kT_c}\right). \quad (24)$$

To solve equation (24) we neglect the dependence $a(T)$, which is possible in the temperature region concerned. The values of T_c obtained are in good agreement with the calculations and experiment [5].

3. CONCLUSIONS

The expression (17) obtained for the free energy of the clathrate of canal type makes possible to restore all the thermodynamics functions. Thus, the chemical potentials obtained allowed us to write equations (22), (23) for the equilibrium concerned, determining a and the equilibrium pressure P , respectively. From equation (22) it follows that $a(T)$ does not correspond to a_0 , determined by the equation $\phi'(a_0) = 0$ (a_0 is the equilibrium interatomic distance of a one-dimensional chain) and since $\Delta\mu < 0$, always $a < a_0$, i.e. from equation (22) it follows that for the clathrate phase stabilization it is necessary that the guest molecules should be situated in a clathrate in a compressed (in contrast to ideally stretched) state. Thus, the theory made possible to explain not only the dense packing, but even the shortening of the guest molecules, discovered experimentally, though only the supposition of their regular arrangement was included.

The model makes possible the explanation of partial filling the thiourea canal space by the guest molecules at low temperatures (140-160K), observed experimentally [10]: the temperature increase results in the fully occupied metastable host framework becoming labile at the expense of anharmonicity.

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