Review Article
Theory of Clathrates

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Abstract. A review is presented of the theory of clathrate compounds, starting with the first quantitative theory suggested by van der Waals and Platteeuw and ending with the current ideas. A brief description is given of the theory of ideal and non-ideal solid clathrate solutions and of the theory allowing us to describe clathrates with an unstable, empty host lattice. The review is composed of results obtained by the different methods based on various approximations.
  In the concluding section predictions are made of the further development of the theory.

Key words. Clathrate, ideal and non-ideal clathrate solutions, phase diagrams, guest–guest interaction, instability of empty host framework.

1. Introduction

Some of the first compounds which are today called inclusion compounds were apparently observed by Kronstedt in 1776 and by Priestley in 1778 [1, 2]: the former placed a stone in a burner flame, observed expansion and named it 'zeolite' because of this property (from Greek – 'boiling stone'); the latter observed a strange ice which was denser than a saturated aqueous solution of sulphurous gas and sank it in. Later Karsten and Pelletier [3] described an experiment in which they obtained greenish-yellow crystals of 'murium oxide' while cooling its vapour down to −40°C. Davy, in 1811 [4] showed, firstly, that 'murium oxide' was a simple substance (which he called chlorine) and, secondly, that dry chlorine does not crystallize under these conditions, while the humid gas does give the observed crystals, hence he concluded that these crystals must be chlorine hydrate. Its composition – $Cl_2 \cdot 10\,H_2O$ – was determined by Faraday [5]. de la Rive showed the 'abnormal ice' of Priestley to be the hydrate of composition $SO_2 \cdot 10\,H_2O$. Subsequently such well known scientists as Wöhler, Berthelot, Le Châtelier, Roozeboom, Alekseyev, Hofman and Nikitin [7, 8] examined compounds of this type, but in spite of these investigations inclusion compounds remained a mystery, as if they lay outside chemistry. The reason may be the following: none of the developing theories of the chemical bond could explain the formation of these compounds and this made them 'outlaws' [7]. A new stage in the study of these compounds started with the basic paper of Powell [9] who, on the basis of an X-ray structural investigation of hydroquinone compounds with volatile substances [10], discovered the 'nature of the bond' between the components in the compounds and introduced new concepts and terminology (clathrates – for the compounds formed by the inclusion of molecules of one type (the guests) into the cavities of the crystal frame formed by the molecules of the other component (the host)). Thus, Powell revealed

a new way of organizing chemical matter, taking away the halo of mystery from such 'adducts' and 'legalizing' their existence. Somewhat later (1949) the German scientists von Stackelberg [11] and Schlenk [12] came to the same conclusion. Schlenk called such compounds 'inclusion compounds'.

Understanding the nature of these hitherto mysterious compounds gave an impetus to their experimental and theoretical study. At present a wide class of compounds is referred to as inclusion compounds, in which inclusion phenomena play several roles. There are lattice clathrates such as the gas hydrates, compounds of hydroquinone with volatile components, and compounds of urea with paraffins ('clathrates' according to Weber and Josel's classification [13]). There are also monomolecular inclusion compounds like those of cyclodextrins with iodine or naphthalene ('cavitato-clathrates' according to [13]), complex compounds like the compounds of crown ethers or cryptands with metal ions (clathratocomplexes [13]), the so called 'inclusion phases' such as hafnium and tantalum carbides and nitrides, covalent lattices like the clathrasils and zeolites, and there are also numerous classes of biocompounds which are especially referred to as 'clathrins'.

In this review we shall consider theoretical models only of the lattice clathrates, although the basis of these models may, eventually, be applied to some extent to the other types of inclusion compounds.

The first variants of the statistical-thermodynamic theories of forming clathrates were proposed by van der Waals [14] (the particular case of the clathrates with one type of cavity and one type of guest), Platteeuw and van der Waals [15] (clathrates with two types of cavities and one type of guest), Barrer and Stuart [16] (clathrates with two types of cavities and different types of guest), and then van der Waals and Platteeuw extended these views to the general case [17] (clathrates with different types of cavities and different types of guest). These theories gave a good quantitative description of the clathrate systems in the simplest cases (e.g., systems of the noble gas–hydroquinone type), but agreement with experiment became worse as both the guest (e.g. with transition to diatomic molecules) and the host subsystems (e.g. aqueous systems) became more complex. Attempts to improve the description were made both by perfecting the calculation of the guest-host interactions, and by creating better theoretical models.

In this review we shall try to show the development of the theory of formation of clathrates from the first models to the current ones.

2. Theory of Ideal Solid Clathrate Solutions

The theory is derived assuming the inclusion of the guest molecules into an empty metastable frame of the host (β-modification of the host) which becomes stable at a definite degree of filling of the cavities.

2.1. THERMODYNAMICS OF CLATHRATES

The theory includes a set of assumptions:

(1) the contribution of the molecules of the host to the free energy of the clathrates does not depend on the way of filling the cavities (if the guest does not distort the host framework),

(2) nonpolar guests are placed in the cavities, which cannot contain more than one molecule;

(3) interaction of the included molecules is negligible;

(4) classical statistics are valid.

There are two additional important assumptions in this theory (although authors [17] do not single them out):

(5) the empty β-frame of the host is stable, but, as we have already mentioned, it is metastable with respect to the stable α-modification of the host;

(6) the stable α-phase of the host does not include the guest. (This last condition is fulfilled in most cases, but not with α-hydroquinone [28, 30], which was most often used by the authors of the theory [17] as an example of the host component.)

The theory of ideal clathrate solutions is based on a model of a liquid, derived by Lennard-Jones and Devonshire [18], in which the behaviour of a liquid is modelled by the behaviour of the molecules, each of which lies in a cavity formed by neighbouring molecules. The potential field in which the molecule moves is found in a self-consistent way. In the case of clathrates the molecules of the host form the cavity and the potential field, in which the guest moves, is deduced not from a self-consistent equation, but by summing the potential energies of the intermolecular (interatomic) interactions of the molecules of the host, forming the walls of the cavity, with the guest being in the cavity. The calculation of the value of the potential field is based on the atom–atom approximation, in which the energy of interaction of the molecules is defined as the sum of the pair potentials of interactions of the atoms constituting the molecules, not taking into account three body interactions.

The model notions of Lennard-Jones and Devonshire are more suited to a description of clathrates than the liquid state. However, in both cases the molecules forming the cavity are considered to be fixed. Such an approximation for clathrates may be applicable to the case when the molecules of the host interact more strongly with each other than with the guest molecules. The above considerations allowed the authors to describe the clathrate approximately as a system consisting of two subsystems: the subsystem of the host molecules and the subsystem of the guest molecules. The molecules of the guest are considered to be a system of noninteracting molecules, each of which may stay in one of the cavities of the host lattice. Thermodynamic functions of such systems are found after calculation of the number of states of the system of the guest possessing one and the same energy. Let us write out here the free energy for the general case of the clathrate, the host molecules of which form the structures with m types of cavities, including n types of guest:

$$F_{\text{ideal}} = F^\beta - kT \sum_{i=1}^{m} N_t \sum_{l=1}^{n} y_{lt} \ln h_{lt} +$$

$$+ kT \sum_{t=1}^{m} N_t \left[\left(1 - \sum_{l=1}^{n} y_{lt} \right) \ln \left(1 - \sum_{l=1}^{n} y_{lt} \right) + \sum_{l=1}^{n} y_{lt} \ln y_{lt} \right] \tag{1}$$

where F^β is the free energy of the empty frame of the host, k is the Boltzmann

constant, T is the absolute temperature, $y_{lt} = N_{lt}/N_t$ is the degree of filling of the cavity of type t by the guest of type l, N_t is the number of cavities of type t, N_{lt} is the number of guests of type l being in the cavities of type t, h_{lt} is the distribution function of the guest of type l included in the cavity of type t. In (1), as well as in the review [17] the first index denotes the molecule type, and the second one the cavity type. The free energy for the case of clathrates with one type of cavity and one type of guest is obtained from (1) by omitting the indices and the corresponding summation signs.

The expression for the free energy of the clathrate allows one to obtain all the remaining thermodynamic functions with the help of differentiation with respect to the corresponding variables: energy (enthalpy), heat capacity, entropy, and chemical potentials of the molecules of the host and guest.

The essential advantages of this theory are its simplicity, the possibility of calculating the thermodynamic functions of the clathrates, of constructing the phase diagrams knowing the potentials of the interatomic interaction of the molecules of the guest and the host, and the thermodynamic functions of the empty lattice of the host, i.e. to find the thermodynamic conditions under which the clathrates exist.

Below we suggest a description of methods of calculating the potential energy of the guest–host interaction and the corresponding distribution function h_{lt}.

2.2. THE GUEST–HOST INTERACTION

The first term in (1) is considered to be known. The second term is defined by the behaviour of the guest in the cavity. The guest is in the potential field of the host lattice. Knowing the potential energy $W_{lt}(\mathbf{r})$ of the guest of type l which is at the radius-vector $\mathbf{r}$ from the cavity centre of type t (i.e. the energy of the guest–host interaction), we may state the distribution function h_{lt}:

$$h_{lt} = 2\pi a_t g_{lt} \Phi_{lt} \exp[-W_{lt}(0)/kT], \tag{2}$$

where

$$g_{lt} = \frac{1}{2\pi a_t^3} \int d^3\mathbf{r} \exp\{-[W_{lt}(\mathbf{r}) - W_{lt}(0)/kT\} \tag{3}$$

is the part of the distribution function connected with the influence of the potential field of the host lattice on the guest; Φ_{lt} is the part of the distribution function connected with the translational movement and internal degrees of freedom of the guest in the cavity.

To calculate the function g_{lt} the authors of reference [17] used the method suggested in the model of the cellular liquid of Lennard-Jones and Devonshire which was based on the assumption that the host molecules are evenly distributed on a surface of radius a_t (interaction of the guest only with the nearest neighbours was taken into account). In this case the guest is in a potential field of spherical symmetry, the value of which depends only on the distance between the guest cavity centre. Having chosen the potential energy of the guest-host interaction to be of the form:

$$\varphi(R) = 4\varepsilon\left\{\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6\right\} \tag{4}$$

they obtained

$$W_{lt}(0) = Z_t \varepsilon \{ \alpha^{-4} - 2\alpha^{-2} \} \tag{5}$$

$$g_{lt} = \int \exp \left[\frac{Z_t \varepsilon}{kT} \left(-\frac{l(y)}{\alpha^4} + \frac{2m(y)}{\alpha^2} \right) \right] y^{1/2} \, dy \tag{6}$$

where Z_t is the number of molecules forming the cavity of type t, $\alpha = a_t^3 / \sigma^3 2^{1/2}$; $l(y)$ and $m(y)$ are functions.

2.2.1. Hydroquinone Clathrates

For the hydroquinone clathrates, as the authors of review [17] have already mentioned, the agreement between theory and experiment is reasonable. The checking of the validity of the theory was carried out in a series of papers [19–22]. The authors compared the theoretically calculated part of the heat capacity, connected with the guest, with the experimental one, found by extrapolating from the heat capacity of the hydroquinone clathrates containing one type of guest. Argon, krypton, methane, nitrogen and oxygen were chosen as the guest. The theory is in reasonable agreement with experiment given the definite choice of the parameters of the guest–host interaction in the range of temperatures where classical statistics can be applied. An attempt to extend the theory into the domain of low temperatures was not successful. In their opinion, this is connected with the fact that in this domain of temperatures it is not possible to neglect the influence of the guests on the host lattice. van der Waals [23] has also pointed out the difficulty of describing the movement of a diatomic guest in clathrates, observing that the rotational freedom of the guest depends on its vibrational state.

2.2.2. Hydrates

Hydrates of structures I and II have two types of cavities, and this allows one to check the theory for the more general case. In review [17] it is pointed out that hydrates possess an important distinction in the structure of the cavities in comparison with the hydroquinone clathrates, and this requires a careful choice of the potential parameters of the guest interaction with the host molecules forming the cavity. A detailed comparison of the observed and calculated dissociation pressures has shown that agreement of theory and experiment is good for monatomic gases and for spherical molecules like methane, but good agreement is not achieved for nonspherical molecules.

   Thus, in studies [24, 25], developing the ideas of [16], the authors have considered theoretical aspects of the stabilizing influence of a gas filling the small cavities and have carried out calculations of the energies of the guest–host interaction for argon, krypton, xenon and methane in the small cavities.

   In [26] the dissociation pressures of hydrates with the elongated guests (C_2H_6, CO_2, N_2, O_2, C_2H_4) were calculated using the Kihara potential. This potential, unlike the Lennard-Jones potential, takes account of the influence of the molecular length, its form and symmetry on the interaction energy. A core (in the case of a diatomic molecule it is a segment binding the atoms) is ascribed to each

molecule. The energy of the molecular interaction is of the usual Lennard-Jones potential type (4), but the distance between the molecules is taken to be the shortest distance between their nuclei. For all the guests studied the results of calculations using the Lennard-Jones potential (4) are worse than the results of calculations using the Kihara potential. The detailed bibliography of studies using the Kihara potential is presented in [27].

2.3. THE PHASE EQUILIBRIA

Knowledge of the thermodynamic functions of clathrates allows the construction of the phase diagrams, if the thermodynamic functions of the other phases are known. Equations describing these equilibria are obtained by equating the chemical potentials of the components in the different phases. In [17] the consideration of the phase diagrams for the hydroquinone clathrates and hydrates with one or two types of guest was initiated. The quantitative and qualitative analysis was carried out for the case of the hydroquinone argon clathrate. The quantitative analysis was carried out for the equilibrium in which the gas phase of the guest, the solid, stable α-phase of hydroquinone (let us remind ourselves that the authors of [17] considered α-hydroquinone to be a phase unable to dissolve the guest) and the clathrate phase take part. For this case the equations for the host and guest chemical potentials in the corresponding phases lead to the following formula:

$$\Delta\mu^{\alpha\beta} = \mu_Q^\alpha - \mu_Q^\beta = \nu^\beta kT \ln(1 - y) \tag{7}$$

$$P_{\text{ideal}} = \frac{kT}{2\pi a^3 g} \cdot \frac{y}{1 - y} \exp[W(0)/kT] \tag{8}$$

where ν^β is the ratio of the cavity number to the host molecule number in the β-phase, $\Delta\mu^{\alpha\beta}$ is the difference of the chemical potentials of the host molecules in the clathrate phase and the α-phase. The clathrate phase at a given temperature T is formed with the degree of filling of the cavities, y, defined by Equation (7) at the pressure which may be found from Equation (8), i.e. these equations define the curve of the monovariant equilibrium $P(T)$. As seen from Equations (7, 8), for the calculation we have to know the dependence of $\Delta\mu^{\alpha\beta}$ on T and P, and also the parameters of the intermolecular interaction of the guest with the host lattice, which allows the calculation of W and g. It is essential that while deducing (7) the guest solubility in the α-phase was neglected. The curve of the monovariant equilibrium, calculated by these formulae, described two experimental points obtained at 60°C and 120°C. The remaining monovariant equilibria were studied at the qualitative level.

For the case of hydrates with two types of guests the calculation of the equilibrium curves of the gas–hydrate–ice system at −3°C for the H_2O–CH_4–C_3H_8 system, reported in [17], agrees well with experiment. The authors also considered at the qualitative level the phase diagrams for the systems H_2O–H_2S–CCl_4, H_2O–H_2S–C_3H_8, H_2O–CH_4–CHF_2CH_3 and H_2O–H_2S–$CHCl_3$.

Thus, the proposed theory correctly described the phase diagrams and its value was recognized by other investigators.

2.3.1. *Phase Diagrams for Inclusion of the Guest into the α-Phase*

Structural studies of the hydroquinone α-modification [28, 29] showed the existence of the same cavities as in the β-modification, but with a concentration six times lower. Guests, capable of being included into the β-phase cavities, may also be included into the α-phase. It means that the stable α-phase with included guests may be described in the same way as the β-phase. The expression for the free energy of the α-phase is given by Equation (1) where the index β should be substituted by α.

Equations describing the phase equilibria for the case of clathrates with one type of cavity and one type of guest when the α-phase may also include the guest are presented in [30–32]. These equations allow the consideration of actual equilibria. The hydroquinone–noble gas system is best suited for the description. In the cases of the monovariant equilibrium analyzed above, consideration of the guest solubility in the α-phase leads to the substitution of Equation (7) by the equation:

$$\Delta\mu^{\alpha\beta} = (v^{\beta} - v^{\alpha})kT \ln(1 - y) \tag{9}$$

where v^{α} is the ratio of the cavity number to the host molecule number in the α-phase. In the case of hydroquinone $v^{\beta} = 1/3$ and $v^{\alpha} = 1/18$. Equations obtained in [30–32] for the hydroquinone clathrates which are in equilibrium with the solid α-phase of hydroquinone and the gas phase of the guest, become much simpler because of the practical identity of the cavities, the low volatility of hydroquinone and the similar energy of the guest–guest interaction in the α- and β-structures and they allow us to deduce [30, 33] the non-, mono- and divariant equilibria. So, the temperature of the nonvariant equilibrium T_0 may be found from the equation:

$$T_0 = T_m \left[1 + \frac{v^{\alpha}}{v^{\alpha} - v^{\beta}} \cdot \frac{\Delta\mu_0^{\alpha\beta}}{\Delta H_m^{L\alpha}} \right] \tag{10}$$

where T_m is the melting point of hydroquinone, $\Delta\mu_0^{\alpha\beta}$ is the difference of the chemical potentials in the nonvariant point, $\Delta H_m^{L\alpha}$ is the enthalpy change at the transition from the α-phase to the liquid phase. It follows, in particular, from this equation that $T_0 > T_m$, provided that $\Delta\mu_0^{\alpha\beta} < 0$.

In [30, 33, 34] the calculation of the phase diagrams was carried out and a comparison made with experiment (Figure 1) where possible.

3. Theory of Nonideal Solid Clathrate Solutions

Assumptions in the theories analyzed above correspond to assumptions applied in the models of ideal solutions. Accordingly, the extent of their application coincides with the extent of application of the theories of ideal liquid solutions, i.e. it may be used either at very low concentrations, when the guest–guest interaction is not substantial, or when the nature of the dissolved molecules is such that interaction with each other is extremely small. In clathrate systems the first condition is not apparently observed as the guests are situated sufficiently close to each other. That is why, when the energy of the guest–guest interaction is considerable the influence of the guests on each other is rather appreciable. For instance, estimation of the energy of the guest–guest interaction in hydroquinone according to Lennard-Jones
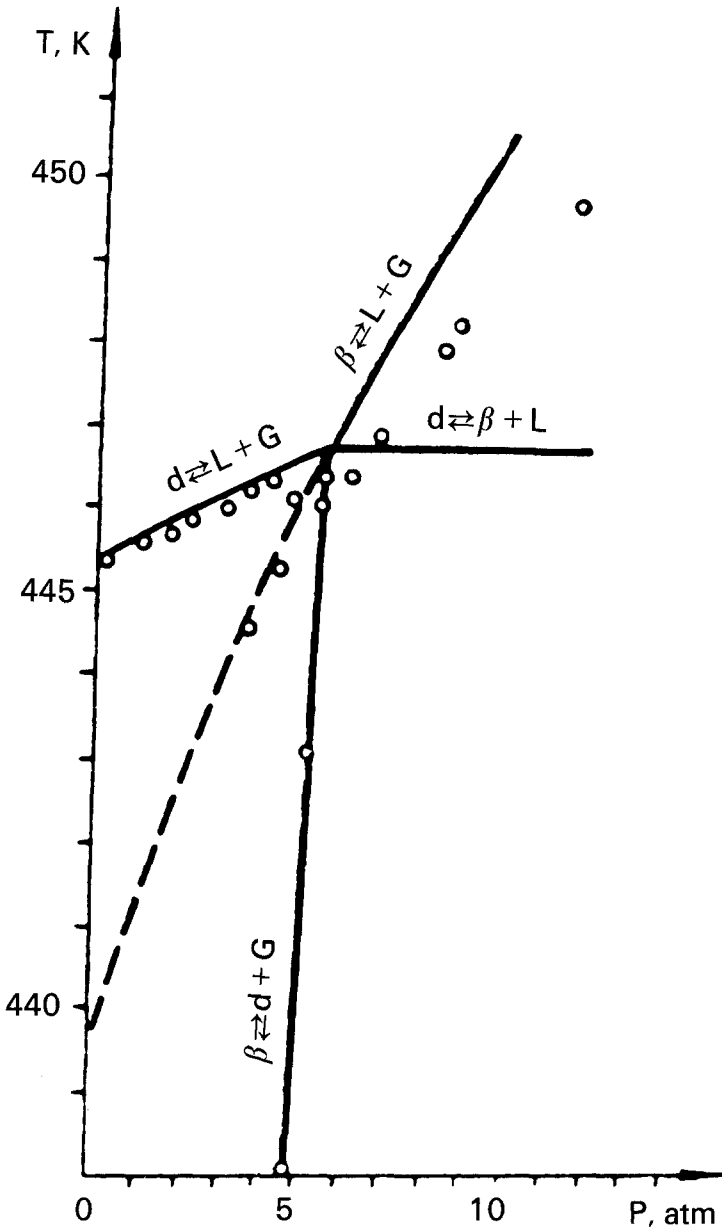
Fig. 1. *P,T* phase diagrams of the hydroquinone–xenon systems. Calculation: continuous lines – stable equilibria, dotted lines – metastable equilibria. Experimental data [65] are represented by dots.

gives $E \simeq -1.2$ kJ/mol for Xe, $E \simeq -0.23$ kJ/mol for Ar, and even more in hydrates: $E \simeq -2.6$ kJ/mol for Xe and $E \simeq -0.48$ kJ/mol for Ar. These values are comparable with the $\Delta\mu^{\alpha\beta}$ value, which is -0.33 kJ/mol for hydroquinone and $\simeq -1$ kJ/mol for hydrates. That is why it is evident that neglect of this interaction should lead to the appreciable divergence in comparison with experiment. These experiments, for instance, may be included with those in which two clathrate phases were shown to exist with one and the same host lattice, but different degrees of filling of the cavities by the guest under similar thermodynamic conditions. Experiments have also revealed the existence of phase transitions involving a change of the order of the guest dipole moments [35, 36]. The theory of ideal clathrate solutions cannot describe the cooperative behaviour of the guest. In [37] an attempt was made to calculate the statistical sum of the clathrate taking into account interaction of the guests with each other. The guest–guest interaction was considered as additive to the guest–host interaction by including the potential field of the guests, which are in the centers of nearby cavities, into the potential field of the cell. This approach, naturally, allowed the author to get a new expression for the chemical potential of the guest molecules, and – as a consequence – a new expression for the sorption isotherms. This study did not consider possible phase transitions or the influence of the guest–guest interaction on stoichiometry.

In the following papers [30–33, 38–40] the guest–guest interaction was considered as equally important to the guest–host interaction. A theory of non-ideal clathrate solutions was proposed. The main statements of this theory differ from the theory of ideal clathrate solutions by including guest–guest interactions.

3.1. THE GUEST–GUEST INTERACTION

In statistical physics the free energy of a system is found from the formula:

$$F = -kT \ln \sum_n \exp(-E_n/kT) \tag{11}$$

where E_n is the energy of the system's nth level; n is a set of quantum numbers defining the system state. The summation in (11) is carried out over all of the system states.

While finding the free energy of the clathrate it is convenient to single out the guest–guest interaction from E_n. In the case of clathrates with one type of cavity and one type of guest E_n is presented as [38]:

$$E_n = E_m^Q + \sum_{a=1}^{N_1} [\varepsilon_{k_a}(\mathbf{P}_a) + P_{a/2m}^2 + W(\mathbf{r}_a)] +$$

$$+ \sum_{i \neq j} (U_{ij}^\delta + S_i S_j U_{ij}^D)\sigma_i \sigma_j \tag{12}$$

The expression for E_n follows from the main statements of clathrate chemistry. Thus, the first term in (12) describing the energy of the mth level of the host molecules (where m is a set of quantum numbers and variables defining the host lattice state), is based on the assumption about the weak influence of the guest on the host lattice. The second term, describing the energy of N_1 noninteracting guests,

is connected with the idea that the interaction of the guest with the host lattice is weaker than the interaction between the host molecules. It gives an opportunity to consider the guest behaviour to be defined by the fixed potential of the host frame. This approximation is analogous to the adiabatic approximation used to describe an electron movement in the nuclear field. In the second term under the summation sign appear the energies ε_{k_a} of the inner kth level of the ath molecule, the kinetic energy of motion of the ath molecule having a momentum $\mathbf{P}_a$ and the potential energy of this molecule in the lattice field $W(\mathbf{r}_a)$. This idea is based on the fact that the guest conforms to classical statistics.

The third term in (12) describes the energy of the interaction of the guest, possessing a dipole moment. The case is considered when the dipole moments of the guest can be aligned along or against some direction in the crystal. This term is summed from the energy of the dispersive interaction U_{ij}^{δ} of the ith and jth molecules and the energy of the interaction of their dipole moments. If the dipole moments are aligned in one direction their interaction energy is equal to U_{ij}^{D}. If the dipole moments have different directions the energy changes sign and it is taken into account by the product $S_i S_j$ ($S_i = 1$, if the dipole is directed in one direction and $S_i = -1$, if the dipole is directed the opposite way). Not all the cavities may be occupied by the guest and we take this into consideration by introducing the variables σ_i. If in the ith cavity there is a guest, $\sigma_i = 1$, if it is absent, $\sigma_i = 0$. The indices in (12) are: a numbers the guest, i and j number the cavities.

In references [41–44] the authors generalized the theory for the case when the guest may occupy more than two positions. The interaction energies of the host lattice with the guest molecule, which are in different positions, are different, i.e. the positions of the guest in the cell are not equivalent. As presented in [40] the energy (Hamiltonian) of the guest is a generalization of Equation (12) and is an example of the expression for the energy in the lattice model. In these models the space is divided into cells, and to each there is ascribed a variable, equal to unity if a guest is in the cell, and to zero if it is not there. The energy of the guest–guest interaction, if the molecules are in the cell in different positions, is described by other discrete variables. Calculation of the statistical sum in the lattice models leads to consideration of the configurations $\{S, \sigma\}$ differing from each other by the different sets of values S_i and σ_i.

3.2. FREE ENERGY OF THE CLATHRATE

After substitution of (12) into (11), summation over n is substituted for summation over a set of quantum numbers m, k_a, integration over $\mathbf{P}_i$ and $\mathbf{r}_i$ and summation over all the configurations $\{S, \sigma\}$. The term depending on m is apportioned into the free energy of the empty framework. The second and the third terms depend on $\mathbf{r}_i$, i.e. it is impossible to integrate independently over $\mathbf{r}_i$ and sum over the configurations $\{S, \sigma\}$. However, as far as the guests are limited in their motion by the cavity, then in a first approximation we shall describe the energy of the guest–guest interaction by the energy of the interaction of the guest fixed in the centers of the cavities. In this approximation the third term in (12) does not depend on $\mathbf{r}_i$, which allows us an integration over $\mathbf{r}_i$ independently from the summation over $\{S, \sigma\}$.

Integration over $\mathbf{r}_i$ apportions in the free energy, a term which describes noninteracting guests and, in common with the first term, gives expression (1) for the free energy F_{ideal} of an ideal model. Summation over the configurations $\{S, \sigma\}$ defines a part of the free energy connected with the interaction of the guests with each other. It is possible to carry out an exact summation over the configurations in the lattice models only in a limited number of cases (two-dimensional models of Ising and models reducible to them). However, the approximate models for solving such problems have been worked out. The simplest and most approximate method is the method of the self-consistent field [38, 40]. Its essence is that the variables S_i and σ_i on finding the statistical sum are substituted for the mean $S = \langle S_i \rangle$ and $\sigma = \langle \sigma_i \rangle$ which are found by the self-consistent method.

Thus, for F we obtain [32, 33]:

$$F = F_{\text{ideal}} + \frac{1}{2} \sum_{l,t} \sum_{l',t'} N_t y_{lt} y_{l't'} U_{ll'}^{tt'} +$$

$$+ \frac{1}{2} kT \sum_{l,t} N_t y_{lt} \left[(1 - S_{lt}) \ln \frac{1 - S_{lt}}{2} + (1 + S_{lt}) \ln \frac{1 + S_{lt}}{2} \right] \tag{13}$$

where

$$S_{lt} = \langle S_i^{lt} \rangle = N_{lt}^{-1} \sum_{i=1}^{N_{lt}} S_i^{lt}$$

is found from the equation of self-consistency

$$2kT \ln[(1 - S_{lt})/(1 + S_{lt})] = \sum_{l',t'} y_{l't'} S_{l't'} U_{lt,l't'}^{D} \tag{14}$$

The expression for $U_{ll'}^{tt'}$ is defined by the energies of the dispersive $U_{lt,l't'}^{\delta}$ and dipole–dipole $U_{lt,l't'}^{D}$ interactions of the guest of type l, which is in the cavity of type t with the guest of the type l' which are in the cavities of type t' under the condition when all the dipoles are directed in one direction, from the following expression:

$$U_{ll'}^{tt'} = U_{lt,l't'}^{\delta} + S_{lt} S_{l'} t' U_{lt,l't'}^{D} \tag{15}$$

After substitution in (13) of the solution $S_{lt}(T)$ of Equation (14) the free energy of the clathrate $F(T, \{y_{lt}\})$, depending both on T and all the set of the filling degrees $\{y_{lt}\}$, can be found. For the more complex models thermodynamic functions of the clathrates were calculated both in the self-consistent field approximation [41–43], and in the cluster approximation [44]. The cluster approximation, unlike the self-consistent field approximation, allows one to take into account not only the long-range order in the dipole orientations, but also the short-range order. This is important when the theory is used to describe the actual systems. The authors in their study [44] have described the hydroquinone clathrates with the nearest distances between the cavity centers which are on a line parallel to the c axis, less than the distances between the centers of the nearby cavities, which are on the line perpendicular to the c axis. This is the reason for the anisotropy of the interaction of the guest with each other. The cluster approximation allows one to take into account such anisotropic interactions.

In the self-consistent field approximation [45] a thermodynamic model was considered for the particular case of a gas hydrate, where, as well as the above interaction, the interaction of the included guests is also taken into account.

3.3. THE PHASE EQUILIBRIA

The chemical potentials of the host molecules μ_Q and the guests $\mu_g^{(l)}$ are obtained from (13) by the corresponding differentiation over the numbers of the host and guests:

$$\mu_Q = \mu_Q^\beta + kT \sum_t v_t \ln\left(1 - \sum_l y_{lt}\right) +$$
$$+ \frac{1}{2} \sum_{lt,l't'} v_t y_{lt} y_{l't'} U_{ll'}^{tt'} \tag{16}$$

$$\mu_g^{(l)} = -kT \ln h_{lt} + \sum_{l't'} y_{l't'} \bar{U}_{ll'}^{tt'} +$$
$$+ kT \ln\left[y_{lt}(1 + S_{lt})/2\left(1 - \sum_r y_{rt}\right)\right] \tag{17}$$

where $v_t = N_t/N_Q$, where N_Q is the number of host molecules,

$$U_{ll'}^{tt'} = U_{lt,l't'}^\delta + S_{l't'} U_{lt,l't'}^D$$

In the particular case considered later in [45] expressions (16) and (17) coincide with the expressions for the chemical potentials of the host and guest obtained in this study.

Chemical potentials (16) and (17) in common with the chemical potentials of the other studied phases allow one to construct the phase diagrams. Let us write out the equation of the monovariant equilibrium of three phases: the gas phase of the guest, the α-phase and the clathrate phase. If we consider the simplest case of the clathrate with one type of cavity and one type of guest, then it is possible to omit from expressions (16) and (17) the indices l and t and the summation signs over them. The equations of the chemical potential of the host and guest in the different phases are reduced to the following equations, defining $P(T)$:

$$\Delta\mu^{\alpha\beta} = v^\beta kT \ln(1 - y) - v^\beta y^2 U/2kT. \tag{18}$$

$$P = P_{\text{ideal}} \frac{1 + S}{2} \exp\{y\bar{U}/kT\} \tag{19}$$

where P_{ideal} is defined by Equation (8). As can be seen, Equations (18) and (19) differ from Equations (7) and (8) by the existence of the terms depending on U and $\bar{U}$ and connected with interaction of the guest. The guest–host interaction from Equations (8) and (9), as well as for the ideal model, depends only on the clathrate stability, i.e. it defines the equilibrium pressure at which the clathrate forms. The guest–guest interaction, as seen from Equation (18), can affect the clathrate stoichiometry, if it is comparable with the relatively small difference $\Delta\mu^{\alpha\beta}$. So, for the hydroquinone clathrates [30, 32, 34], even if the guest–guest interaction is small, its inclusion improves the description of the composition and, more importantly,

allows the difference $\Delta\mu^{\alpha\beta}$ in (18) to become independent of the nature of the guests, unlike the ideal model, where this dependence is observed [30, 32, 34] in contradiction of the theory. Inclusion of the guest–guest interaction allows one to calculate the stoichiometry more exactly (for example, for Xe at $T = 328$ K in the ideal model $y = 0.32$; taking into account the guest–guest interaction, $y = 0.39$; experiment gives $y = 0.40$ [30]). Apparently, the high degree of filling in the case of CH_4, CH_3F, etc. [30] is explained by this actual guest–guest interaction. Besides, an opportunity has appeared which explains the results of experiments which could not be explained at all in terms of the ideal model. These are the experiments on the phase transitions connected with the guest subsystem of the order–disorder type, and also the transitions analogous to the condensation of the guest subsystem in the host lattice [30, 39]. The problem is that Equations (18) and (19), unlike Equations (7) and (8), are nonlinear and this fact, as shown in [30, 39], leads to the phase transition of the type 'liquid–gas of the guest component' in the host lattice and to the ferroelectric phase transition connected with the ordering of the dipole moments of the guest at decreasing temperature. The detailed analysis of Equations (18) and (19) is in [39].

The model deduced above allows one to explain at the qualitative level the existence, under the same thermodynamic conditions, of clathrates with different degrees of filling and phase transitions connected with the ordering of the dipole molecules. The models for the quantitative description of the phenomena considered are suggested in [41–44]. The authors of these studies, both in the self-consistent field approximation and in the cluster approximation with a definite choice of parameters, have obtained good agreement between theory and experiment in the composition and anomalies of the dielectric susceptibilities connected with ferroelectric phase transitions.

4. Theory of Clathrates with an Unstable Empty Framework of the Host

Analysis of the composition of gas hydrates and guest distribution in cavities of different types has shown that the degree of filling of the big cavities in hydrates does not differ significantly from unity [46–48] and that the packing of the guests in the channels of urea and thiourea is the most dense, i.e. in the latter case the clathrates are of a constant composition, corresponding to complete filling of the channels, in all the regions of stability [61], while for the hydrates, even if they have a variable composition, it is only owing to the variable degree of filling of the small cavities. On the basis of the composition data only it is impossible to say whether the degree of filling of the big cavities (y_B) equals unity strictly or approaches asymptotically to it. With respect to the hydrates of cubic structure II, y_B was shown some time ago not to differ significantly from unity. For the hydrates of cubic structure I with the experiment exactness enhancement the maximum hydrate number 'was changing' from 8.47 [17] via intermediate values up to 7.85 [63] and, finally, to 7.76 [64], and it is now not far from the ideal value of 7.67 with all large cavities filled. Thus, nowadays the experimental situation allows the investigations to follow two different viewpoints: the first one suggested by us above, and the classical one developed by the authors of studies [63, 64]. The answer to this question is given by the calculations deduced below (to some extent). These results

contradict the theory of both ideal and nonideal solid solutions. The degree of filling may approach unity both in the case of large values of $|\Delta\mu^{\alpha\beta}|$ and in the case of strong attraction of the guests to each other. However, in both cases it follows from the theory that the degree of filling cannot be strictly equal to 1, and in the case of the clathrates of urea and thiourea with n-paraffins the guest molecules cannot be placed in the channels more densely than they are packed in the crystalline n-paraffins, as observed by experiment [62]. It is natural to assume that the host lattice is unable to exist without complete filling of the cavities, even as a metastable one. This assumption contradicts the 5th assumption of the theory for a number of clathrates (see Section 2). It is necessary to consider a variant where an empty host lattice is unstable and may become metastable or stable at the complete occupancy of a definite type of cavity. This statement appears to be insufficient for a quantitative description in every concrete case and knowledge of the mechanisms leading to the framework destruction is necessary. In studies [47, 49, 50] the theory was derived for the clathrates of the cellular and channel types with a labile framework.

4.1. CLATHRATES OF THE CELLULAR TYPE (CRYPTATO-CLATHRATES)

It is clear intuitively that a friable crystal structure containing a large number of cavities may readily be destroyed by external forces. However, the basis of the above suggested theory of clathrates is an assumption of a metastable empty host framework with respect to the solid and liquid phases. The empty framework is stable and its thermodynamic functions, which are considered to be given, change insignificantly when filling the cavities by the guest. To prove the metastability of the empty host framework it is necessary to consider the conditions of the mechanical equilibrium of the atoms and molecules forming the frame, the conditions of the dynamic stability (i.e., lattice vibrational frequencies should be real) and the conditions of the thermodynamic equilibrium. In order that the framework may exist, it is necessary for the total force acting on every atom or molecule of the framework to be equal to zero (this defines the equilibrium position of the atoms), the eigenfrequencies of the vibrations of the empty framework to be real (this provides the atomic vibrations near the equilibrium position) and the conditions of the thermodynamic stability to be fulfilled. Knowing the equilibrium position of the atoms and the vibrational frequencies it is possible to find the thermodynamic functions of the frame. If the chemical potential of the framework is more than the chemical potential of the solid or liquid phase ($\Delta\mu^{\alpha\beta} < 0$) it will be the proof of metastability of the empty framework.

The guests, filling a mechanically, dynamically or thermodynamically unstable framework restore its stability. A question arises – which cavities should be filled to make the framework metastable or stable? The answer may be found by experiment or considerations at the microscopic level of the empty framework or the framework with partially (or completely) occupied cavities.

In [47, 49] the model of the clathrate with the framework having two types of cavities was considered. The framework is thought to become stable at the minimum with complete filling of one of the two types of cavities (the cavities of this type we shall call 'the labile cavities'). Nonpolar guest molecules of one type are

considered for simplicity. Side by side with the assumptions used for building the nonideal theory of clathrate solutions and excluding the assumptions on metastability of the empty host framework the following is suggested:

(a) In the case of mechanical instability of the framework the guests appearing in the 'labile' cavities change the equilibrium position of the host molecules insignificantly and in association with this corrections of the clathrate free energy are small.

(b) In the case of dynamic and thermodynamic instability the real vibrational frequencies of the empty host framework change insignificantly on including the guest into the 'labile' cavities and mainly contribute to the free energy of the host framework.

These assumptions allow us to consider the framework with the included guest as being metastable, and filling the cavities of the second type ('stable' ones) to be described as in the above analyzed theories of forming the clathrates. The free energy of the metastable lattice with the guests included into the 'labile' cavities is presented as:

$$\bar{F} = \tilde{F}_Q - kTN_1 \ln h_1 + \tfrac{1}{2}N_1 U_1 \tag{20}$$

where $\tilde{F}_Q$ is the part of the free energy depending on the host molecules, N_1 is the number of 'labile' cavities. The second term describes the guest behaviour in the 'labile' cavity, where h_1 is defined, as usual, by equations (2) and (3). The third term describes the interaction of the guests with each other, which are in the 'labile' cavities.

The free energy of the clathrate is:

$$F = \bar{F} - kTN_2[-y \ln h_2 + \tfrac{1}{2}y^2 U_2/kT + (1-y)\ln(1-y) + y \ln y] \tag{21}$$

where N_2 is the number of 'stable' cavities, y is the degree of filling of these cavities; the expression for h_2 is also obtained from (2) and (3), in which the interaction of the guest with the guests in the 'labile' cavities should be included into the guest–guest interaction.

The suggested model includes in part the assumptions accepted in the theory of the clathrate solutions. It allows us to use the methods developed in this theory. But if, previously, the variables describing the degree of filling of two types of cavities were used to describe the hydrates, then in the given model there is only one variable describing the degree of filling of the 'stable' cavities.

The model suggested above can be easily adapted for the more general case of clathrates with different types of cavities and different types of guests.

As mentioned, the experiment allows us to say something about the complete filling of large cavities of hydrates with the structure CS-II. Consideration at the microscopic level of empty and filled frameworks of the hydrates with the structure CS-I was carried out by the methods of lattice dynamics and molecular dynamics. These methods based on the numerical calculations allow us to investigate the dynamic and thermodynamic properties of the clathrates and give an opportunity to study the stability of the clathrate lattices.

4.1.1. *Lattice Dynamics*

Studies [48, 51] present the results of the numerical calculation of the dynamic and thermodynamic properties of the empty framework of the clathrate hydrate CS-I

and the framework occupied by guests. The unstable character of the host lattice was established and the role of the guest molecules was revealed in stabilization of the clathrate framework.

The method of lattice dynamics used the potentials of the intermolecular interactions which contained for the considered case the interaction of the Lennard-Jones type between the oxygen atoms:

$$V_{O-O} = 4\varepsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right] \tag{22}$$

where $\sigma = 3.16 \text{ Å}$, $4\varepsilon = 2.60 \text{ kJ mol}^{-1}$ and the Coulomb interaction of the charges situated on the oxygen and hydrogen atoms were $q_O = -0.82 |e|$ and $q_H = 0.41 |e|$ (e is the electron charge). The selected potential (the so-called SPC potential), as established in [52], adequately describes the intermolecular interactions in the condensed phases of water.

In Figure 2a, b, c the histograms are presented of the phonon density of states of: (a) the empty hydrate CS-I framework; (b) the hydrate CS-I with the large cavities filled by xenon ($6 \text{ Xe·46 H}_2\text{O}$); (c) the hydrates CS-I with the large and small cavities filled by xenon ($8 \text{ Xe·46 H}_2\text{O}$). The range of the vibrational frequencies of the empty framework is shown to be divided into two zones. In the lower one ($0-280 \text{ cm}^{-1}$) the molecules of water perform mainly translational vibrations, in the upper zone ($490-960 \text{ cm}^{-1}$) it performs librational ones.

It is interesting to note that the spectrum in the low zone consists of two domains divided by a gap. This may apparently be connected with the existence of the stronger hydrogen bonds forming pentagonaldodecahedra. Thus, even in such complex crystal lattices we may single out the pentagonaldodecahedron as a stable molecular system which is found not by coincidence in most clathrate hydrate structures. The phonon spectra of the hydrates with the compositions $6 \text{ Xe·46 H}_2\text{O}$ and $8 \text{ Xe·46 H}_2\text{O}$ are obtained using the Lennard-Jones potential of the interatomic xenon–oxygen interaction. Its parameters were calculated according to the usual combination rules (details in [48, 51]). The xenon vibrational frequencies in the large cavities are $15-18 \text{ cm}^{-1}$. The dynamic properties revealed allow us to construct the crystal thermodynamic functions in the usual way. In Figure 3 the equation of state $V(P)/V_0$ is presented at $T = 0$ (V_0 is the volume value at zero pressure) of the empty CS-I hydrate lattice (curve 2), the CS-I hydrate with the large cavities filled by xenon (curve 3) and with filling of all the cavities (curve 4). Also shown is the equation of state at $T = 0$ for ice Ih (curve 1). All the curves terminate at the same critical pressure when the crystal becomes dynamically unstable. The empty framework of the CS-I hydrate is dynamically stable at $T = 0$ and $P < 13.5 \text{ kbar}$. When the large cavities are filled by xenon its stability to compression increases. The critical pressure for the $6 \text{ Xe·46 H}_2\text{O}$ hydrate is 16 kbar and for the $8 \text{ Xe·46 H}_2\text{O}$ hydrate it is 26 kbar. (Note that under such pressures xenon is in the solid state, and this may change some of the lines of the phase equilibria).

With increasing temperature the stability boundaries of the hydrate framework may be found using the Lindemann criterion. The empty framework is the most unstable of all the structures studied. At low pressures the temperature at which it loses its stability is $-13°\text{C}$. Inclusion of the guest molecules into the large cavities

increases this temperature to 3°C, but on including xenon into all the cavities the hydrate is stable up to 12°C. Thus the calculations show that at temperatures near 0°C the CS-I hydrate framework is thermodynamically unstable and complete filling of the large cavities is required to restore its stability. In Figure 4 the lines of the $T_c(P)$ dependence are presented, which are the boundaries of the thermodynamic stability for the empty lattice (curve 2), for 6 Xe·46 H_2O (curve 3) and for 8 Xe·46 H_2O (curve 4). There is a maximum in the $T_c(P)$ dependence curve for the hydrates with partial or complete filling of the cavities. It corresponds qualitatively to experiment (curves 6–8). We see that there are two mechanisms leading to the clathrate framework destruction: dynamic instability at low temperatures and great
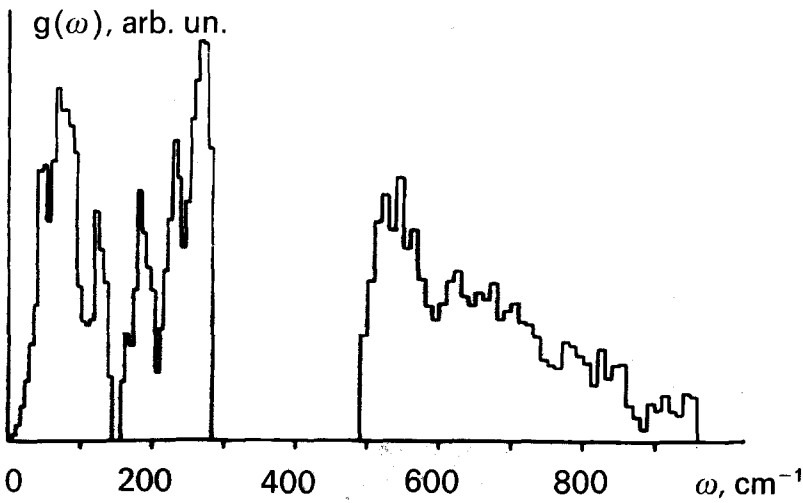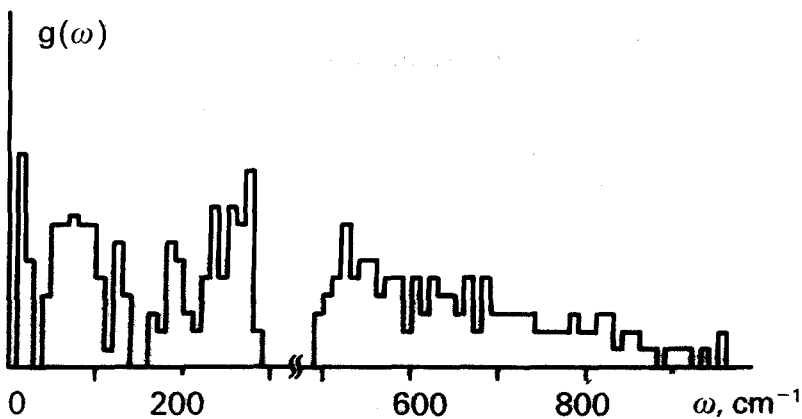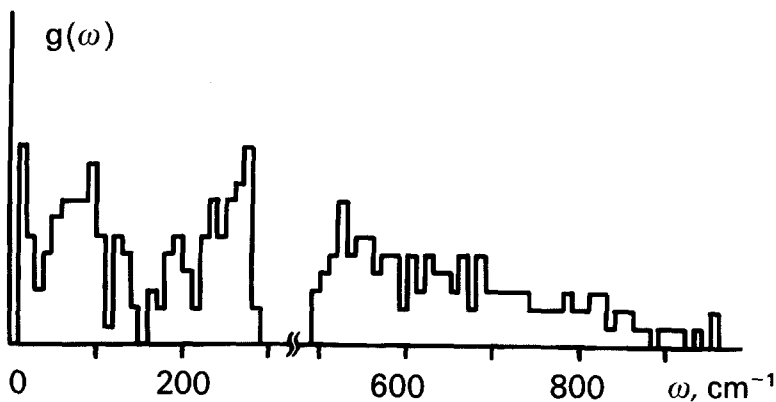

Fig. 2(a).

Fig. 2(b).

Fig. 2.   Density of phonon states of (a) empty CS-I hydrate framework, (b) CS-I hydrate with large cavities filled by xenon (6 Xe·46 H$_2$O), (c) CS-I hydrate with large and small cavities filled by xenon (8 Xe·46 H$_2$O).
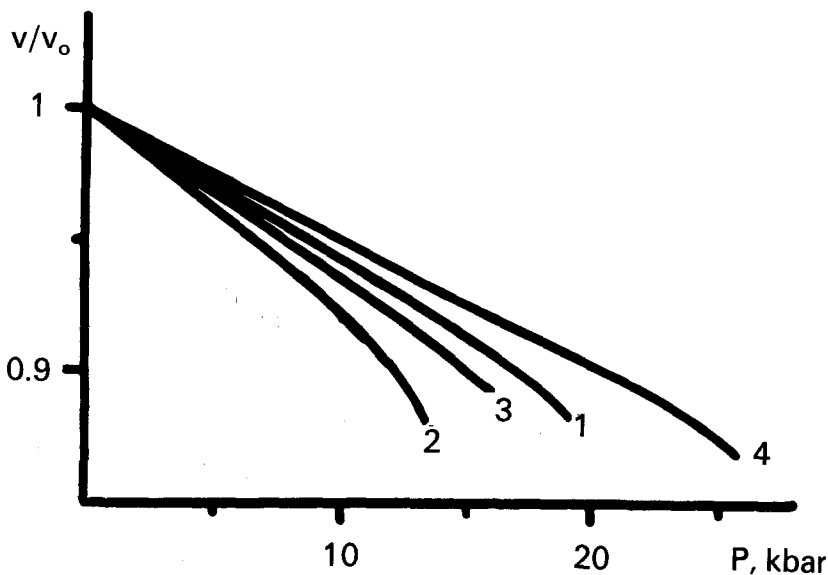

Fig. 3. $V(P)/V_0$ at $T = 0$ for (1) ice Ih, (2) empty CS-I hydrate framework, (3) CS-I hydrate with large cavities filled by xenon (6 Xe·46 H$_2$O), (4), CS-I hydrate with large and small cavities filled by xenon (8 Xe·46 H$_2$O).

pressures, and thermodynamic instability at high temperatures. In the intermediate domain the transition from one mechanism to another should take place.

4.1.2. *Molecular Dynamics*

The molecular dynamics of clathrate hydrates have been considered in studies [53–56]. Investigation of the condensed systems by the molecular dynamics method
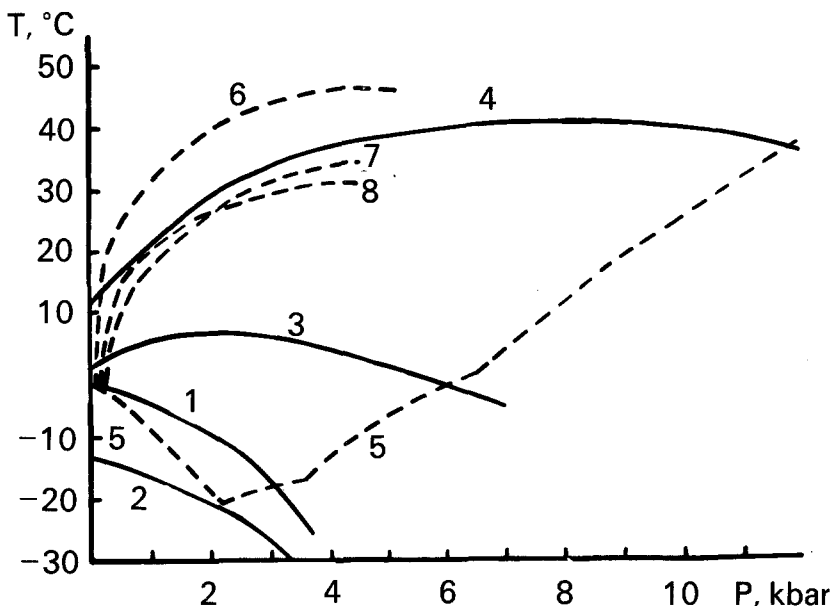
Fig. 4. The instability temperature as a function of pressure.
Theory: (1) Ice Ih; (2) Empty CS-I hydrate framework; (3) CS-I hydrate with large cavities filled by xenon (6 Xe·46 H_2O); (4) CS-I hydrate with large and small cavities filled by xenon (8 Xe·46 H_2O).
Experiment: (5) Ice; (6) CH_4 hydrate; (7) N_2 hydrate; (8) Ar hydrate (structure II).

is the numerical solving of the equations of the molecular motion. Usually a system of several dozen molecules is chosen and then periodic boundary conditions are applied in order to decrease the surface influence on the calculation results. The forces influencing the molecules, as in the lattice dynamics method, are defined by the interatomic interaction potential. By averaging the molecular motion over time it is possible to obtain the structural and thermodynamic characteristics of the system.

In paper [53] the cluster studied consisted of 20 water molecules forming the small cavity of the clathrate hydrate (pentagonaldodecahedron) with the help of the molecular dynamics method. At temperatures higher than 230 K the thermal motion of the molecules was found to increase and the instantaneous structures of the cluster differed greatly from the averaged one over time. In the graph of the $E(T)$ dependence, where E is the inner energy of the system, a discontinuity is observed at $T \approx 200$ K (Figure 5). The cluster changes from the open clathrate to a denser and less ordered structure. The authors connect these changes with a phase transition (possibly the melting of the system). The small dimensions of the cluster assist in the smearing out of this transition. Besides, the essential influence of the surface seems to decrease the transition temperature in comparison with the crystal hydrate.

In papers [54–56] the authors studied the molecular dynamics of the empty CS-I hydrate and of the CH_4, Xe, CF_4, C_3H_6, and $(CH_2)_2O$ hydrates. The study was
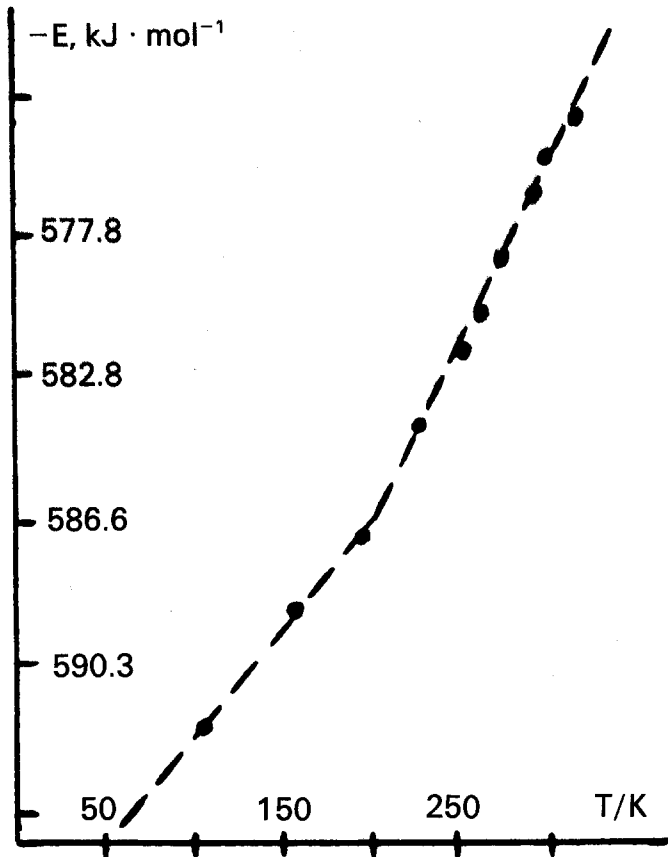
Fig. 5. Energy per molecule vs temperature for the 20-molecule water cluster [53].

carried out at temperatures of not more than 200 K. In these papers important information was obtained about the vibrational spectrum and the hydrate structures. Instability of the hydrate structure in the studied temperature range was not found. At the same time, in papers [57, 58] the phase transition in ice under a pressure of 13 kbar and a temperature of 80 K was studied by the molecular dynamics method. The discovery of this transition, also found experimentally [59], proves the possibility of studying phase transitions in hydrates by the molecular dynamics method. That is why investigation of the problem of the thermodynamic stability of the empty hydrate framework and of the hydrate filled by guests by this method would be very useful and could give an opportunity to add information obtained by the lattice dynamics method.

4.2. CLATHRATES OF THE CHANNEL TYPE (TABULATO-CLATHRATES)

An attempt to describe the densest packing of guests in the channels was made by Parsonage and Pemberton [60] who studied the formation of the urea clathrates with the n-paraffins. The equilibrium distance between the terminal carbon atoms in

the channels was found by them from the condition of equilibrium of the repulsion forces between the ends of the guest molecules and the attractive forces acting on the guests from the side of urea, i.e. from the condition of minimum total potential energy. The equilibrium distance between the terminal carbon atoms as obtained by them was close to that found experimentally. However, the authors did not carry out any study of the total free energy of the clathrate which consists, along with the potential energy of the guest, of the part connected with the behaviour of the chain of the guests as a one dimensional system, i.e. the part connected with the interaction of the guests with each other. The equation defining the equilibrium distance between the guests should be found from the equation of the corresponding chemical potentials. The model of the solid solutions considered above is hardly applicable to the given type of clathrates. While constructing a variant of the van der Waals model it is necessary to divide the channel into cells which should correspond to the size of the guest and may be occupied or free. The ratio, y, of the number of filled cells to the total number of cells will tend to 1 (the dense packing) only in the case when the difference between the chemical potentials of the host α- and β-phases $\Delta\mu^{\alpha\beta} \to -\infty$. That is why this model will hardly correlate to the available experimental results.

In papers [49, 50] a model is constructed for clathrates of the channel type with an unstable host lattice. Guest molecules considered are those which are capable of being oriented differently in the channel. Development of the model was based on the expression for the free energy (11). The following were assumed:

(1) the guest stabilize the framework, which is labile without the guests, keeping to closely packed one-dimensional chains;
(2) the channel is considered to be even, i.e. the energy of the guest–host interaction does not depend on the coordinate along the channel axis;
(3) classical statistics is applicable.

These assumptions reveal in the free energy a term depending on the host–host interaction and a term defined by the guest–host interaction. Use of the term depending on the guest–guest interaction is based on the assumption that the energy of this interaction depends only on the coordinates along the channel axis, i.e.:

$$E = \sum_i \varphi(a_i) - \sum_i j(a_i)\sigma_i\sigma_{i+1} + 2j' \sum_i \langle\sigma_i\rangle\sigma_i \tag{23}$$

where a_i is the projection of the distance between the ends of the ith and $(i+1)$th guest molecules on the axis Z, $\varphi(a_i)$ is the potential energy of interaction between them, $\sigma_i = \pm 1$ depending on the orientation of the ith molecule, j and j' are values which take into account the dependence of the interaction energy on the orientation of the guests. In the third term $\langle\sigma_i\rangle$ is used instead of σ_i and is the mean value of the order parameter which is found later by the self-consistent method. The final expression for the free energy of the type of clathrate considered is as follows:

$$F = F_\beta(N_{Q'} T) + N\left\{-\frac{1}{2}kT \ln \frac{2\pi kTh^2}{f(a)} - j(a) + \varphi(a) - \right.$$
$$\left. - kT\left(-\frac{\bar{h}kT}{8f^{-2}} + \frac{g^{-2}kT}{12f^{-3}}\right) - kT \ln \cosh\left[\frac{6j'\sigma}{kT} + A(\sigma)\right]\right\} \tag{24}$$

where N_g is the number of guests,

$$A(\sigma) = \left[\cosh^2 \frac{6j'\sigma}{kT} - 2 \sinh \frac{2j(a)}{kT} \exp\left(-\frac{2j(a)}{kT} \right) \right]^{1/2},$$

$$f(a) = \partial^2 \varphi / \partial a^2 = \varphi''(a), \quad \bar{f} = f(a_0), \quad \bar{g} = \varphi'''(a_0), \quad \bar{h} = \varphi^{IV}(a_0)$$

a_0 is the distance between the carbon atoms of adjacent guests, corresponding to the minimum of the potential energy of the interaction between them. The order parameter σ is defined by the equation:

$$\sigma = \left\{ \sinh \frac{6j'\sigma}{kT} \left(A(\sigma) + \frac{kT}{6j'} \cosh \frac{6j'\sigma}{kT} \right) \right\} \bigg/ A(\sigma) \left[\cosh \frac{6j'\sigma}{kT} + A(\sigma) \right] \tag{25}$$

The guest–host interaction enters (24) as the second term, via h. The expression for h is defined in the usual way according to equations (2) and (3) where it is necessary to carry out in (3) the integration in the plane perpendicular to the channel axis, and instead of the energy of the guest–host interaction it is necessary to substitute $W(\mathbf{r})$ – the energy of the interaction of the guest with the channel walls ($\mathbf{r}$ is the two-dimensional vector of the center of mass of the guest molecule in the plane perpendicular to the channel axis).

In papers [49, 50] the authors investigated the thermodynamic properties of the channel clathrates in regions of low and high temperatures. At low temperatures a phase transition is shown to exist and to be connected with the ordering of the guest positions in the channel. At high temperatures the possible mechanisms of the frame destruction are considered, which are connected with the thermal destruction of the chains of the guest molecules. The theory is shown to describe well the experiment both by the temperature of ordering the guests and by the temperature of decomposition of the urea clathrates.

5. Conclusion

The first models of clathrate compounds created about thirty years ago did not take into account the interaction of the guests with each other and considered the guest and host subsystems to be independent, i.e. they were in fact the theories of ideal solutions. These rather strict limitations allowed us to describe theoretically a fairly narrow selection of clathrate compounds. However, new experimental data on hydroquinone compounds, hydrates, urea and thiourea clathrates required firstly the removal of the limitations connected with neglect of the guest–guest interactions, and then the limitations concerning clathrates with the unstable empty host framework. New ideas suggested for these cases allowed the understanding of the nature of formation of clathrates of a wide class of compounds, to explain such phenomena as the increased value of the degree of filling, segregation of the solid clathrate solutions, and the densest packing of the guest molecules in urea.

The existence of clathrates with a labile host framework led to the statement of the question on the definition of clathrate compounds. In our opinion, as well as in the traditional clathrate compounds, in systems with a labile host framework the host subsystem remains (because of the fact that the host–host interaction is stronger than the guest–guest one). Differences in the bond types in the subsystems

and differences of the characteristic values of the interaction energy leads to the clear differentiation of the subsystem. All this allows us to consider the systems with guest–guest interaction and with an unstable empty host framework, as well as the traditional clathrates, as a unified class of clathrate compounds. The further development of the theory of clathrate formation will lead to more accurate dynamic and thermodynamic calculations, and the specification of the intermolecular interaction potentials.

Acknowledgement

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