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Dynamic and Thermodynamic Properties of Clathrate Hydrates*

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Abstract. Vibrational spectra and thermodynamic properties of ices and the cubic structure I (CS-I) clathrate hydrate have been studied by the lattice dynamics method. The phonon density of states for the empty hydrate framework and for xenon hydrate have been determined; the vibrational frequencies of the guest molecules in large and small cavities have been found. The stability of the hydrate with respect to the external pressure at low temperatures and its thermodynamic stability at temperatures around 0°C have been studied. It has been found that the empty hydrate framework is unstable in certain temperature and pressure regions. A definite degree of occupation of the large cavities by the guest molecules is necessary for the hydrate to become stable. It has been found that there is a maximum of the critical temperature at which the hydrate exists, which is a function of the external pressure.

Key words. Clathrate hydrate, clathrate formation, vibrational properties, dynamic and thermodynamic instability.

1. Introduction

To a great extent the present paper has been stimulated by what was, to our mind, a fruitful discussion on the nature of clathrate hydrates with Davidson's school, which began in the mid-seventies [1–3]. On the basis of an analysis of data from the literature (of great help for us was Davidson's review [4]) and of our own experiments on hydrates composition, we have found that the composition of hydrates is constant (within the limits of experimental accuracy) over the whole stability region and corresponds to the full occupation of the large cavities. Full occupation of the large cavities (within the accuracy of X-ray analysis) was pointed out by Jeffrey and McMullan [5]. The degree of occupation of the small (dodecahedral) cavities can vary from 0 to 1, thus explaining variations in the compositions of chlorine [6] and ethylene oxide [7, 8] hydrates. Davidson and Ripmeester [3], however, pointed out that hydrate numbers (*h*) for cyclopropane (8.12, 7.87, 7.76 ([4], Table V)), CH_2ClF (7.98) and CH_3Br (7.89) are such that, even if all the

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* Dedicated to Dr. W. Davidson in honor of his great contributions to the sciences of inclusion phenomena.
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small cavities are empty, some large cavities should also be empty. While we are aware of these results, we consider that determining hydrate compositions is a difficult task, and the development of clathrate chemistry shows that with an increase of accuracy in the determination of composition the 'homogeneity' range of a clathrate phase narrows. A detailed analysis of the data on CS-II hydrate compositions made by Davidson *et al.* [4, 9] shows the most probable value of filling the degree of the large cavities to be of the order of 0.99975, i.e. it does not differ significantly from 1. The data on CS-I hydrates that had been obtained prior to the appearance of papers [10, 11] were less definite: the most probable degree of filling the cavities was evaluated as 0.94–0.96. In the papers cited the problem of the guest molecules (^{129}Xe) distribution between T- and D-cavities was solved for the first time, and then [11], when hydrate composition was determined precisely enough, the degrees of occupation, y_T and y_D, and also the maximum hydrate number for a hydrate with only large cavities filled (7.76) were found. The degrees of occupation turned out to be significantly different (0.9809 and 0.7161 for large and small cavities, respectively). Thus, as the experimental precision increased, the maximum hydrate number for CS-I hydrate decreased from 8.47 in 1959 [12], 8.12 (1978) [3] and 7.85 (1984) [13], to 7.76, and the last value is close to the ideal number 7.67, corresponding to the full occupation of the large cavities. The complexity of determining hydrate compositions explains the fact that Stackelberg's idea [14] of the possibility of partial occupation of the cavities, developed quantitively by van der Waals and Platteeuw [12], and Barrer and Stuart [15] was enthusiastically accepted by experimentalists. In many cases this was also prompted by the confirmation of the theory provided by investigations of hydroquinone compounds [12]. The theory, based on a supposition that the clathrate β-framework is metastable with respect to the initial host α-modification, has been extended to clathrate hydrates. But water clathrates turned out to be much more complex. It has been found that, in addition to two cubic frameworks, a number of other types of framework may be constructed, with at least four types of cavities [5, 16, 17], and that a number of hydrates with closely similar compositions may be formed in one guest-host system. Thus, four hydrates with hydrate numbers 24, 26, 32 and 36 [18] and with different structures [19] have been found in the system Bu_4NBr-H_2O, i.e. there are four hydrates in the region 96.0–97.3 mole % of water and high resolution, together with new ideas about clathrate formation, are necessary to distinguish between these clathrates. A smooth change of equilibrium conditions leads to a jump-like variation of hydrate composition as a result of the construction of new frameworks, rather than a smooth filling of the cavities in the same framework. Comparing the composition with the structural data confirms the fact that large cavities are fully occupied. An analogous situation is found in the Br_2-H_2O system, where four hydrates form: $Br_2 \cdot 7\,H_2O$, $Br_2 \cdot 8.3\,H_2O$, $Br_2 \cdot 10\,H_2O$ and $Br_2 \cdot 12\,H_2O$ [2]. Moreover, all these hydrates have a fixed composition over the whole stability region, as is also the case with peralkylonium salt hydrates. Thus, the data on the composition are insufficient to judge whether frameworks with unoccupied large cavities are metastable, but have a large absolute value of $\Delta\mu$ (and, consequently, $y \to 1$ from below), or labile, i.e. they cannot exist under the conditions considered, if the cavities are empty (and, strictly, $y = 1$).

Thus, in addition to the available classical approach, another consideration of clathrates with thermodynamically unstable (labile) frameworks is possible, and there are a number of other clathrate compounds (urea and thiourea compounds [20, 21]), which also belong to the same type of clathrates. A simple logical argument may be given confirming this point of view:

(1) Ice I_h at low pressures is the most stable water phase. Any other structure (and hydrate framework too) is less stable and should melt at lower temperatures.
(2) Numerous experimental data show that solids may be overheated to temperatures only slightly exceeding their melting point, this difference being much less than the assumed difference between the melting point of ice and that of the hypothetical hydrate framework. Thus, at 0°C, i.e. at temperatures at which the thermodynamics of hydrates are usually considered, the empty hydrate framework should be labile. Only at a certain temperature $T_c < 0°C$ can this framework be metastable and may then be described by Van der Waals and Platteeuw, and the Barrer and Stuart theories.

In principle, experimental data on composition and thermodynamics permits the determination of $\Delta\mu_{\alpha\beta}$ for clathrates whose β-framework is stable but metastable with respect to the α-modification. If the β-framework is labile, there is no such possibility and another approach to the description of this type of clathrates is the calculation of its thermodynamic functions, starting from the calculation of its dynamic properties. At present, we know of no calculations of the dynamic properties of crystals, the complexity of whose structure is comparable with that of the structure of CS-I hydrates – one of the most simple hydrate structures. A series of papers on the molecular dynamics of hydrates has been published by Tse *et al.* [22–25]. The vibrational spectra and thermodynamical properties of hydrates are discussed in these papers. We believe that lattice dynamical investigations of ices and ice-like crystals extends our capabilities and will permit us to supplement molecular-dynamical calculations, thereby allowing us to approach the problem of the dynamic and thermodynamic stability of these compounds on a more fundamental basis.

Thus, in the present paper we propose to solve the following problems: to calculate the dynamic properties of the CS-I hydrate framework and those of the framework occupied by guest molecules (xenon); to calculate the thermodynamic properties of these compounds; to establish the boundaries of the thermodynamic stability of ice and hydrate; to establish the reasons for their instability; and to clarify the role of the guest molecules in the stabilization of a clathrate framework.

2. The Dynamic Properties of Ice and Hydrates

To calculate the phonon spectra of molecular crystals on the basis of selected intermolecular interaction potentials, one needs to construct the dynamic matrix and to calculate its eigenvalues. Formulae for the elements of the dynamic matrix of molecular crystals were first presented in [26]. They permit the calculation of both short-range and long-range Coulomb sections of the dynamic matrix. However, in [27], where the dynamical properties of proton-ordered ice phases were calculated, it was pointed out that some formulae given in [26] are incorrect. In [27], correct formulae are given without proof only for $\mathbf{q} = 0$ ($\mathbf{q}$ is the wave vector). Therefore in [28, 29] we derived correct formulae for short-range and electrostatic parts of those elements of the dynamic matrix which are incorrectly given in [26]. Thus a technique for calculating the vibrational spectra of molecular crystals has been developed, and this permitted us to study the dynamics of ices and ice-like crystals, proceeding from well developed potentials of intermolecular interaction of the water molecules.

Calculations of the dynamic properties of low pressure ice phases and CS-I clathrate hydrates were performed using the SPC potential. This potential was developed especially for describing the properties of condensed water phases [30] and includes the short-range interaction between oxygen atoms, described by a Lennard–Jones formula:

$$V_{\mathrm{O-O}}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \qquad (1)$$

where $\sigma = 3.16$ Å; $4\varepsilon = 2.60$ kJ/mole, and the Coulomb interaction of the charges placed on oxygen and hydrogen atoms are $q_{\mathrm{O}} = -0.82|e|$, $q_{\mathrm{H}} = 0.41|e|$ (e is the charge of the electron). The solid line in Figure 1 is the result of our calculations of the translational vibration spectrum of D_2O-ice I_h in comparison with experimental data provided by inelastic neutron scattering (points) [31]. It is clear from the figure that a quite satisfactory agreement with the experiment in the whole frequency region is obtained, thus confirming the validity of the SPC potential for the calculation of the dynamic properties of solid water phases. This permitted us to calculate the vibrational frequencies of the empty host CS-I framework. Because there are 276 eigenfrequencies of translational and librational vibrations of water

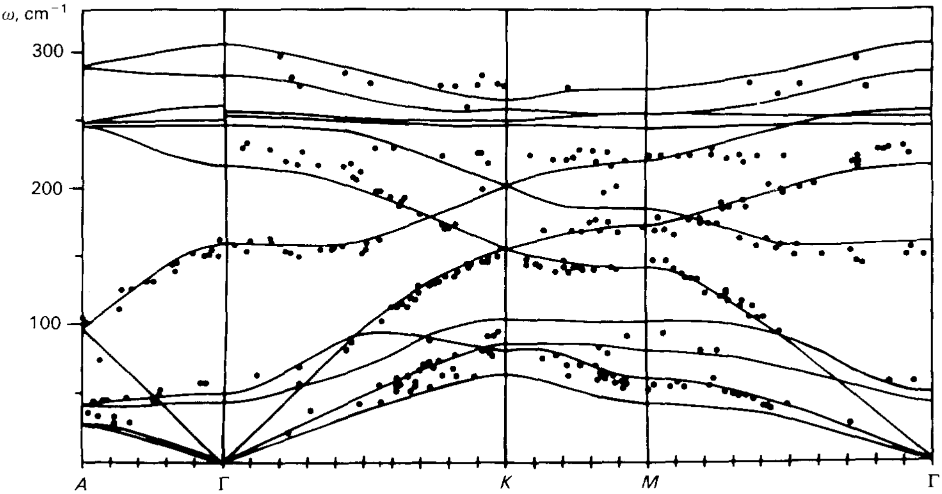

Fig. 1. Dispersion curves of translational vibrations of D_2O-ice I_h (solid lines our calculations, points experimental [31]).

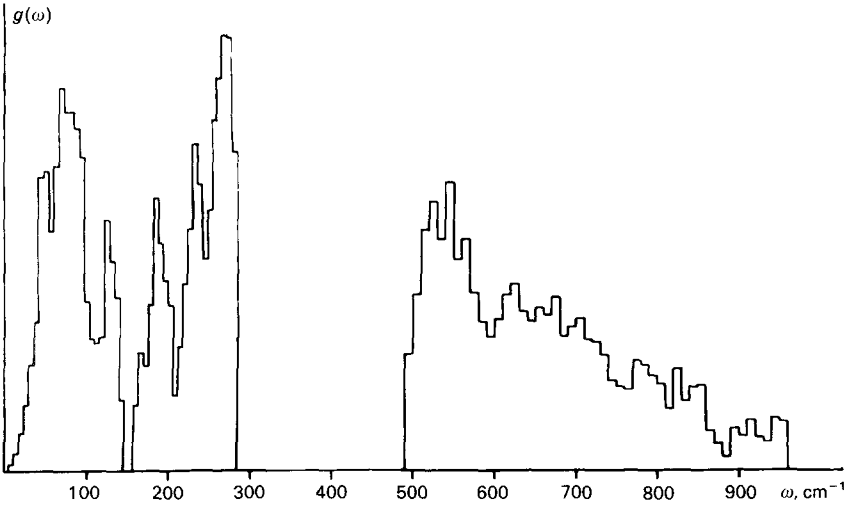

Fig. 2. Phonon density of states of CS-I empty hydrate framework.

molecules for each value of the wave vector, it is not expedient to draw the dispersion curves for different $\mathbf{q}$ directions. In Figure 2 a histogram of the density of phonon states of the framework is given. The histogram was constructed using eigenfrequencies according to 35 values of the wave vector in 1/48th part of the Brillouin zone. As in the case of ices the frequency region of molecular vibrations is divided into two zones. In the lower zone (0–280 cm^{-1}) water molecules mainly undergo translational vibrations, whereas in the upper one (490–960 cm^{-1}) the vibrations are mostly librational. In comparison with I_h and I_c ices, the frequency spectrum of the CS-I framework is shifted towards lower frequencies, which may be explained by a greater porosity of the structure of the hydrate framework compared to ices.

Phonon spectra of $6\,\text{Xe}\cdot46\,H_2O$ and $8\,\text{Xe}\cdot46\,H_2O$ hydrates (in the first type of hydrate the only big cavities are occupied, in the second type both big and small cavities are filled) are given in Figure 3. Calculations are performed with a unit cell parameter $a = 12$ Å. Lennard–Jones interaction parameters for xenon atoms were taken as follows: $\sigma_{\text{Xe}} = 4.069$ Å, $4\varepsilon_{\text{Xe}} = 1.87$ kJ/mole. Xenon–oxygen interaction parameters were calculated using usual combinational rules: $\sigma_{\text{Xe—O}} = (\sigma_{\text{Xe}} + \sigma_{\text{O}})/2$, $\varepsilon_{\text{Xe—O}} = (\varepsilon_{\text{Xe}} \cdot \varepsilon_{\text{O}})^{1/2}$. Vibrational frequencies of xenon atoms in large cavities lay in the region 15–18 cm^{-1} and 23–29 cm^{-1}. The higher frequencies may be ascribed to atomic vibrations along the axis perpendicular to six-angled chains of water molecules; lower frequencies to vibrations in the plane parallel to these chains. Vibrational frequencies of xenon atoms in small cavities are in the region 36–43 cm^{-1}, and inclusion of xenon atoms into small cavities lowers its vibrational frequencies in large cavities by 1–3 cm^{-1}. Guest atoms influence the vibrational spectrum of host frameworks, slightly raising the phonon frequencies, and this effect occurs mainly in the lower (translational) part of the framework spectrum. Inclusion of xenon does not influence the frequencies of librational vibrations.

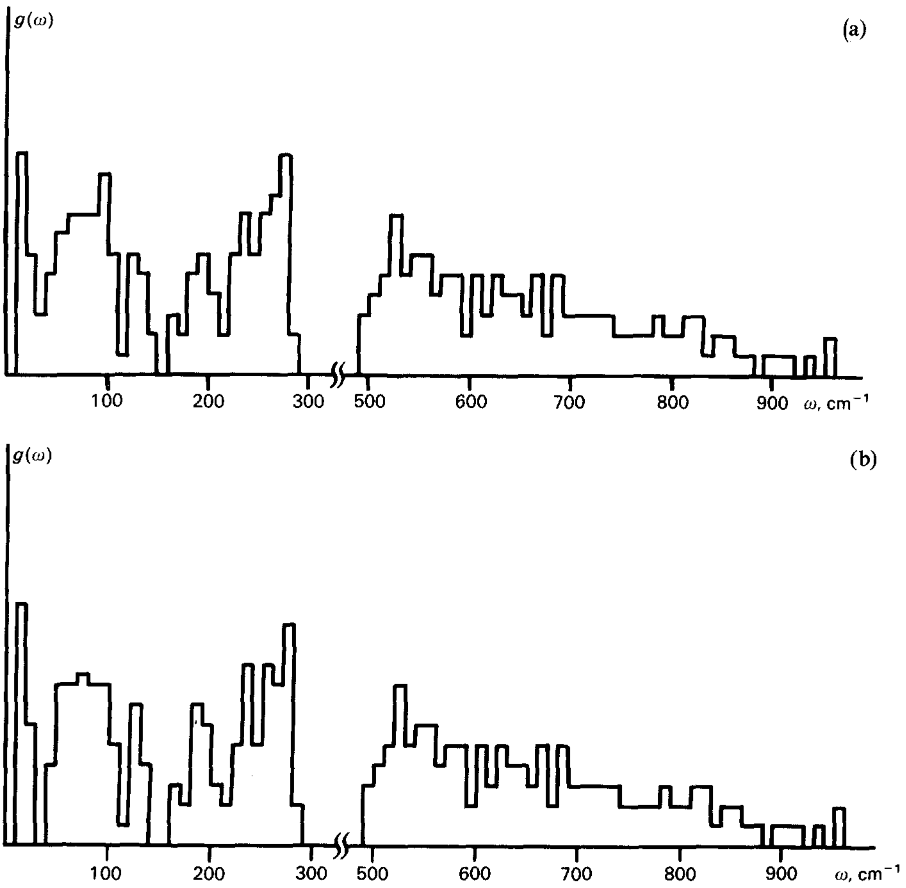

Fig. 3. Phonon density of states of hydrates 6 Xe·46 H_2O (a) and 8 Xe·46 H_2O (b).

3. Dynamic Instability of Ice and Hydrates at Low Temperatures and High Pressures

The free energy of a crystal in harmonical approximation is given by a known formula:

$$F = U + kT \sum_i \ln[2 \sinh(\hbar w_i / 2kT)], \tag{2}$$

where U is the energy of the lattice, T the absolute temperature, k Boltzmann's constant, and W_i the eigenfrequency of lattice vibrations. The second term in equation (2) is the vibrational part of the free energy. Summation was performed over a set of 384 eigenfrequencies for ice, 276 for a hydrate framework, and 294 and 300 for a hydrate with large, and both large and small cavities filled, respectively.

Thermal expansion and the effect of pressure on the systems studied were considered within the quasi-harmonic approximation. Vibrational frequencies and the free energy were calculated for a number of values of the lattice parameter. The pressure at a given temperature was then defined as a derivative of the free energy with respect to the volume:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \tag{3}$$

The equilibrium value of the lattice parameter corresponds to the minimum of the free energy as a function of the volume.

It is well known that solids with tetrahedral coordination (group IV elements, A^{III} B^{V} and $A^{II}B^{VI}$ compounds), when compressed, are characterised by a structural instability, leading to melting or to transition into a new crystal modification [32]. Theoretical calculations confirming that phenomenon were performed, for example, for Si–Ge solid solutions [33]. There are only a few investigations on the effect of pressure on the stability of systems constructed of a tetrahedral network of water molecules. Thus, in [34] the transition of ice I_h into an amorphous phase after its compression through an extrapolated melting curve (at pressures ~10 kbar, $T = 77$ K) was observed experimentally. In [25] this result has been confirmed by molecular dynamics investigations, the transition parameters being $T = 80$ K, $P = 13$ kbar.

We have investigated the pressure dependence of volume of the systems studied and their frequency spectrum at $T = 0$. There are two terms in the free energy under these conditions: lattice energy and the energy of zero vibrations. The last term is about 20–25% of the free energy and thus essentially affects the equilibrium volume and its dependence on the external pressure. In Figure 4 we show plots of $V(P)/V_0$ obtained, where V_0 is the volume at zero pressure. As a certain critical pressure is approached, imaginary frequencies appear in the vibrational spectrum, i.e. the crystals become dynamically unstable. The basis of this instability, as in the case of

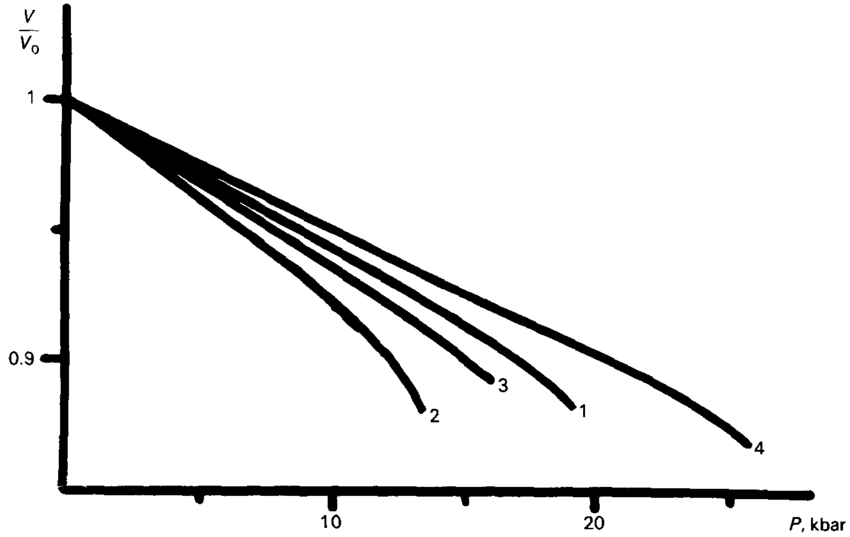

Fig. 4. $V(P)/V_0$ as a function of P for ice (1), CS-I empty framework (2), 6 Xe·46 H_2O (3) and 8 Xe·46 H_2O (4) hydrates.

other tetrahedral compounds, is the decrease of the frequency of transverse acoustic phonons with the decrease of the size of the unit cell. The critical pressure of ice I_c is $P_c = 19.5$ kbar, which agrees with the value of P_c of ice I_h at 80 K given above, thus confirming the validity of our calculations.

The CS-I hydrate framework is dynamically stable at $T = 0$, and its critical pressure is $P_c = 13.5$ kbar. On filling large and small cavities with xenon the hydrate becomes more stable with respect to pressure. The critical pressure for $6\,Xe{\cdot}46\,H_2O$ hydrate is 16 kbar and for $8\,Xe{\cdot}46\,H_2O$ it is 26 kbar. Guest molecules, interacting with the hydrate framework, as has just been mentioned, cause the frequencies of lattice vibrations to increase, thus increasing the region of hydrate stability. In [16] on the basis of experimental data on the pressure dependence of CS-I hydrate temperatures (at pressures up to several kbar) a hypothesis has been proposed that there is an upper limit of hydrate formation at pressures of 15–20 kbar. Our results confirm this hypothesis and simultaneously show a sufficient rise of the dynamic stability of a fully occupied hydrate compared with partially occupied hydrates.

4. Thermodynamic Instability of Ice and Hydrates at High Temperatures

At low pressures and low temperatures all the crystal lattices investigated are dynamically stable. We believe, that the cause of their destruction at increasing temperature is the increasing amplitude of vibrations of water molecules, leading at certain temperatures to the loss of thermodynamic stability of the crystal. We will call these temperatures 'high' for a given type of crystal. As a criterion of the thermodynamic stability of ice and hydrate framework at finite temperatures, we choose the ratio of root-mean-square amplitude of vibrations of water molecules to the nearest-neighbour distance:

$$\eta = \langle U^2 \rangle^{1/2}/a. \tag{4}$$

This ratio is widely used as a criterion of the thermodynamic stability of solids that melt with a decrease or increase of volume [35, 36]. Thus, this ratio may be used to describe the destruction of the hydrates with both types of behaviour in different regions of the phase diagram.

The critical value of η, at which the crystal becomes labile, depends on its structure and the atoms of which it is composed. Having assumed, that η_c is the same for tetrahedrally-coordinated networks constructed of water molecules, we have calculated the value of this parameter at the melting point of ice ($P = 0$, $T = 273$ K). The value of η_c turns out to be $\eta_c = 0.289$. Using this value, we calculated the region of thermodynamic stability of ice and hydrates on the $P-T$ phase diagram (Figure 5).

The empty CS-I hydrate framework is the most unstable of the structures studied. The temperature at which it becomes labile is −13°C at low pressures. Inclusion of guest molecules increases this temperature up to +3°C for $6\,Xe{\cdot}46\,H_2O$ hydrate and +12°C for $8\,Xe{\cdot}46\,H_2O$ hydrate. Thus, at temperatures around 0°C the CS-I hydrate framework is thermodynamically unstable and full occupation of at least the large cavities is necessary for the hydrate to become stable.

The pressure dependence of the critical temperature T_c is different for ice and the hydrate framework on the one hand, and for the hydrate with partially or fully

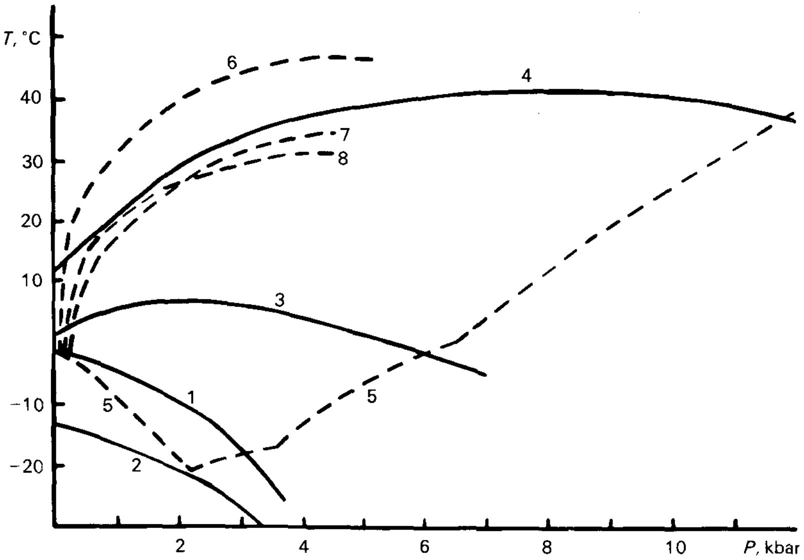

Fig. 5. Calculated curve of thermodynamical instability of ice (1), CS-I empty framework (2), 6 Xe·46 H_2O (3) and 8 Xe·46 H_2O (4) hydrates and experimental melting curve of ice (5) and curves of decomposition of hydrates of CH_4 (6), N_2 (7) and Ar (8).

occupied cavities on the other hand. In the case of ice and an empty hydrate framework the derivative dT_c/dP is always negative (Figure 5). This means that, at all pressures, ice and a hypothetical empty CS-I framework melt with a decrease of volume. The thermodynamic instability lines for 6 Xe·46 H_2O and 8 Xe·46 H_2O hydrates at low pressures have a positive derivative dT_c/dP and go through a maximum, the pressure and temperature values at the maximum being points: 2 kbar, +9°C for 6 Xe·46 H_2O hydrate, and 8 kbar, +41°C for 8 Xe·46 H_2O hydrate. We have no experimental data on the phase diagram of xenon hydrate at high pressures. However, we can compare the results obtained with the phase diagrams of methane and other gas hydrates, which are given in [16] (Figure 5). All the experimental phase diagrams have $dT_c/dP > 0$ at $P = 0$, and as the pressure increases, the absolute value of the derivative decreases almost to zero (at least, for methane and argon hydrates). The maximum temperatures at which hydrates exist are about 45°C (or, according to other data, up to 55°C [37]), and are in agreement with our calculations. The point of the maximum on the $T_c(P)$ curve has been found experimentally only for SO_2 hydrate, because most systems have been studied only at low pressures (up to 4 kbar). Thus, our results are in agreement with experimental data and confirm the fact that there is a maximum on the pressure dependence line of the destruction temperature of gas hydrates.

5. Conclusions

The dynamic and thermodynamic properties of the CS-I clathrate hydrate framework, and hydrates with compositions 6 Xe·46 H_2O and 8Xe·46 H_2O have been studied using the lattice dynamic method. It has been shown that inclusion of the guest molecules increases the stability of the hydrate with respect to external pressure. At zero pressure and temperatures above −13°C the empty framework is thermodynamically unstable. For the clathrate to become stable it is necessary to have full occupation of at least large cavities by the guest molecules. The pressure dependence of the critical temperature of hydrate destruction has a maximum, which is in agreement with the available experimental data.

The results reported, together with numerous experimental data on other clathrate compounds, permit us to define three types of clathrate formation:

(1) The α-modification can solve the guest component, i.e. there is clathration by the stable phase (as, for example, α-hydroquinone [38], Dianin compounds and others). In such compounds the degree of occupation may change from 0 to 1, as in Dianin compounds, or from 0 to some $y^* < 1$, when the β-modification becomes stable, as in the hydroquinone-guest system [38]. However, from the point of view of the theory of heterogeneous equilibria, these phases are solid solutions of the guest-component in the initial host modification, rather than new compounds.

(2) The classical case, when the β-framework is stable, but metastable with respect to the α-modification. At a certain degree of occupation the β-framework becomes stable. Such a compound is a real clathrate compound, because it has a new quality (e.g., structure) that is not common to the initial compounds. From the point of view of the phase rule, it is a new phase.

(3) The case where the β-framework is labile in the temperature and pressure region under consideration and becomes thermodynamically stable when some (labile) type of cavity is fully occupied. In this case there may be some variants; e.g. only partial filling of these cavities may be necessary, but with ordered distribution of the guest molecules in them.

Such a division of clathrate compounds is meaningful only when temperature and pressure are taken into consideration. When the thermodynamic conditions are changed, a transition of the clathrate from type 2 to type 3, and *vice versa*, is possible.

Finally, let us point out that there are different reasons leading to clathrate destruction at low and high temperatures. In the first case the reason for the destruction is the dynamic instability of the hydrate framework; in the second case there is thermodynamic instability when the amplitudes of water molecule vibrations are increasing. One may expect that a transition from one case to the other should occur in an intermediate region.

The authors would not like to overestimate the results obtained since the choice of the simplest potential of intermolecular interaction as well as the approximations made in the process of calculations decrease their accuracy. However, even in this case the results obtained indicate the instability of the host water framework which, from our point of view, is fundamental to an understanding of this class of clathrates.

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References

1. Yu. A. Dyadin, I. S. Terekhova, T. M. Polyanskaja, and L. S. Aladko: *Zh. Struct. Khim.* **17**, 655 (1976).
2. Yu. A. Dyadin and L. S. Aladko: *Zh. Struct. Khim.* **18**, 51 (1977); *C. A. 87*, 12297m (1977).
3. D. W. Davidson and J. A. Ripmeester: *J. Glaciology* **21**, 33 (1978).
4. D. W. Davidson, in *Water – A comprehensive treatise*. Vol 2, p. 115, 1973.
5. G. A. Jeffrey and R. K. McMullan: *Prog. Inorg. Chem*, **8**, 43 (1967).
6. D. N. Clew and N. S. Rath: *J. Chem. Phys.* **44**, 1710 (1966).
7. D. A. Wilms and A. A. Van Houte: *Desalination* **12**, 373 (1973).
8. R. K. McMullan and G. A. Jeffrey: *J. Chem. Phys.* **42**, 2725 (1965).
9. S. R. Gough and D. W. Davidson: *Can. J. Chem.* **49**, 2691 (1971).
10. J. A. Ripmeester and D. W. Davidson: *J. Mol. Struct.* **75**, 67 (1981).
11. D. W. Davidson, Y. P. Handa, and J. A. Ripmeester: *J. Phys. Chem.* **90**, 6549 (1986).
12. J. H. Van der Waals and J. C. Platteeuw: *Adv. Chem. Phys.* **2**, 1 (1959).
13. D. W. Davidson, S. K. Garg, S. R. Gough, Y. P. Handa, C. I. Ratcliffe, J. S. Tse, and J. A. Ripmeester: *J. Incl. Phenom.* **2**, 231 (1984).
14. M. Von Stackelberg: *Z. Electrochem.* **58**, 104 (1954).
15. R. M. Barrer and W. I. Stuart: *Proc. Roy. Soc.* **A242**, 172 (1957).
16. Yu. A. Dyadin and K. A. Udachin: *Zh. Struct. Khim.* **28**, 75 (1987).
17. J. A. Ripmeester, J. S. Tse, C. J. Ratcliffe, and B. M. Powell: *Nature* **325**, 135 (1987).
18. Yu. A. Dyadin, I. I. Yakovlev, I. V. Bondaryuk, L. S. Aladko, and L. S. Zelenina: *Dokl. Akad. Nauk SSSR* **203**, 1068 (1972).
19. L. A. Gaponenko, S. F. Solodovnikov, Yu. A. Dyadin, *et al.*: *Zh. Struct. Khim.* **25**, 175 (1984).
20. M. Yu. Lavrentiev, V. R. Belosludov, Yu. A. Dyadin, and G. N. Chekhova: *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **2**, 15 (1987).
21. Yu. A. Dyadin, V. R. Belosludov, G. N. Chekhova, and M. Yu. Lavrentiev: *J. Incl. Phenom.* **5**, 195 (1987).
22. J. S. Tse, M. L. Klein, and I. R. McDonald: *J. Chem. Phys.* **78**, 2096 (1983).
23. J. S. Tse, M. L. Klein, and I. R. McDonald: *J. Phys. Chem.* **87**, 4198 (1983).
24. J. S. Tse, M. L. Klein, and I. R. McDonald: *J. Chem. Phys.* **81**, 6146 (1984).
25. J. S. Tse and M. L. Klein: *Phys. Rev. Lett.* **58**, 1672 (1987).
26. G. Venkataraman and V. C. Sahni: *Rev. Mod. Phys.* **42**, 409 (1970).
27. G. Nielson and S. A. Rice: *J. Chem. Phys.* **80**, 4456 (1984).
28. V. R. Belosludov, M. Yu. Lavrentiev, S. A. Syskin, and Yu. A. Dyadin: Preprint No. 87–4, Inst. Inorg. Chem. Sib. Otd. Akad. Nauk SSSR. Novosibirsk, 1987.
29. V. R. Belosludov, M. Yu. Lavrentiev, and S. A. Syskin: *Phys. Stat. Sol. B* 149, 133 (1988).
30. H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, and J. Hermans: in *Intermolecular Forces*, p. 331, Holland, 1981.
31. B. Renker, in *Phonons*, p. 167, Paris, 1971.
32. A. F. Goncharov: *Uspekhi Fizicheskikh Nauk* **152**, 317 (1987).
33. T. Soma, H. Iwanami, and H. Matsuo: *Solid State Commun.* **42**, 469 (1982).
34. O. Mishima, L. D. Calvert, and E. Whalley: *Nature* (*London*) **310**, 343 (1984).
35. C. Malinowska-Adamska: *Phys. Stat. Sol.* (*B*) **143**, 63 (1987).
36. T. Soma and H. Matsuo: *Solid State Commun.* **42**, 447 (1982).
37. Yu. F. Makogon: *Gidraty Prirodnyh Gazov* (in Russian), 1974.
38. V. R. Belosludov, Yu. A. Dyadin, G. N. Chekhova, B. A. Kolesov, and S. I. Fadeev: *J. Incl. Phenom.* **3**, 243 (1985).