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Dynamics of Hydrogen Bonds in Hydrogen Compounds of Period II Elements

G. I. Novikov

Belarussian State Technical University, Minsk, Belarus

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Abstract—The correlation energy diagrams of hydrogen compounds of Period II elements show that the hydrogen bond energy varies nonmonotonically along the period, passing through a minimum for CH_4, which is consistent with the fact that this compound exhibits the properties of neither carbon hydride nor hydrogen carbide and is a "parent" compound for the organic chemistry. The degree of polymerization of liquid hydrogen fluoride was estimated from the correlation diagrams. The estimated degree of polymerization of thawed ice is consistent with the known clathrate model of its structure.

Among hydrogen compounds of Period II elements, compounds of the first three elements are classed with hydrides (hydrogen in them is electronegative), whereas in the other compounds hydrogen is electropositive. Therefore, it is interesting to analyze the characteristics of hydrogen bonds in these compounds from the energy viewpoint.

The most obvious manifestation of hydrogen bonding is interaction between gaseous monomeric molecules. Therefore, we will attempt to estimate the energy parameters of reactions (1) and (2).

$$(\mathrm{LiH}) = 1/2(\mathrm{Li_2H_2}),\ \Delta H_1^0,\ \Delta S_1^0, \qquad (1)$$

$$(\mathrm{BeH_2}) = 1/2(\mathrm{Be_2H_4}),\ \Delta H_2^0,\ \Delta S_2^0. \qquad (2)$$

Here and hereinafter, the formulas of gaseous molecules are given in parentheses. The third member of the series, boron hydride, has been comprehensively studied, with the required tabulated data available [1, 2].

$$(\mathrm{BH_3}) = 1/2(\mathrm{B_2H_6}),\ \Delta H_3^0\ \mathrm{kJ}\ -58,\ \Delta S_3^0\ -72\ \mathrm{J\,K^{-1}}. \qquad (3)$$

As for LiH and BeH_2, for estimating $\Delta H_{1,2}^0$ and $\Delta S_{1,2}^0$ we used the tabulated quantities [1, 2] and estimated the unknown quantities according to [3]. The results are given in Table 1. The hydrogen bond energies (E_{hb}) and entropies of their formation (ΔS_{hb}), which characterize processes (1)–(3) (the estimated values are marked with asterisks), and also the molar volumes of the hydrides are given in three bottom rows of Table 1.

Among the quantities given in Table 1, attention should be given to very large negative values of E_{hb}, ranging from –58 to –115 kJ and considerably exceeding in the absolute value the known energies of hydrogen bond dissociation, not exceeding 30–40 kJ mol^{-1}. This suggests a different nature of interactions in the dimers under consideration and common hydrogen-bonded species. Namely, gaseous LiH, BeH_2, BH_3, and their derivatives are compounds with strong (ionic in LiH crystals and polymeric in BeH_2 crystals) bonds. Among the dimeric species given in Table 1, only B_2H_6 has been found experimentally and extensively studied. The gaseous hydride dimers Li_2H_2 and Be_2H_4 have not yet been detected experimentally. Since the solid polymer $(BeH_2)_n$ irreversibly decomposes above 200°C, we can only estimate the partial

Table 1. System of published [1, 2] and estimated (*) thermodynamic characteristics of hydrides MH_m [M = Li (m = 1), Be (m = 2), B (m = 3)] (ΔH_f^0, kJ mol^{-1}; S^0, J mol^{-1} K^{-1}) and hydrogen bonds in them (E_{hb}, kJ; ΔS_{hb}^0, J K^{-1}), and molar volumes of the hydrides (V, cm^3 mol^{-1})

Form, parameter	Li	Be	B
$[MH_m]$,[a] ΔH_f^0	–90	125	–58*
$[MH_m]$, S^0	20	25	44*
(MH_m), ΔH_f^0	140	300*	75
(MH_m), S^0	171	180*	188
$1/2(M_2H_{2m})$, ΔH_f^0	25	210*	17
$1/2(M_2H_{2m})$, S^0	95	106*	116
E_{hb}	–115*	–90*	–58
ΔS_{hb}^0	–76*	–74*	–72
V	10	21*	32

[a] Here and hereinafter, the formulas of species in the solid phase are given in brackets.

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Table 2. Distribution of the hydrogen bond energy (E_{hb}) over kinds of interactions in molecular crystals of NH_3, H_2O, and HF (kJ mol^{-1})

Compound	$\Delta H^0_{subl} = \Sigma E_{o,i,d}$	E_o	E_i	E_d	L	$E_{hb} = E_o/L$
CH_4	9.5	0	~0.5	9	0	0
NH_3	29	17	3	9	~1.7	10
H_2O	50	40	2	8	2	20
HF	40	30	2	8	1	30

pressure of the gaseous dimer at this temperature for the case if there were no dissociation:

$$1/n[BeH_2]_n = 1/2(Be_2H_4),$$

$$\Delta G^0_{473\,K} = 85000 - 473 \times 81 = \frac{-19.14 \times 473}{2} \log P_{Be_2H_4}.$$

This equation gives $P_{Be_2H_4}$ ~10^{-1} atm, i.e., 70–75 mm Hg, which would be quite sufficient for the dimer to be detected tensimetrically. However, the equilibrium pressure of gaseous hydrogen under these conditions, corresponding to the reaction $1/n[BeH_2]_n = (H_2) + [Be]$, $\Delta G^0_{473\,K}$ ~$125\,000 - 473 \times 115 = -19.14 \times 473 \log P_{H_2}$, will be P_{H_2} ~10^{+20} atm, i.e., decomposition of BeH_2 is irreversible, and against its background the gaseous dimer can hardly be detected.

The partial pressure of the dimer (Li_2H_2) at 416°C (when the saturated vapor pressure P_{LiH} 1 atm) was calculated from the following equilibrium:

$$[LiH] = 1/2(Li_2H_2),$$

$$\Delta G^0_{690\,K} = 115000 - 690 \times 75 = \frac{-19.14 \times 690}{2} \log P_{LiH}.$$

The expected value is $P_{Li_2H_2}$ ~10^{-10} atm, i.e., it cannot be measured experimentally.

Thus, it seems impossible to determine experimentally the thermodynamic characteristics of the gaseous hydrides LiH and BeH_2, but the specific features of hydrogen bonds in lithium, beryllium, and boron hydrides can be illustrated to a first approximation by the estimates given in Table 1.

The next members of the series of hydrogen compounds of Period II elements are CH_4, NH_3, H_2O, and HF. The three latter compounds are classical representatives of compounds with hydrogen bonding.

Polymerization of HF and H_2O in the vapor via hydrogen bonding was discussed previously [3, 4]. The neighboring members of the series are NH_3 and CH_4. In the series CH_4, NH_3, H_2O, HF, the hydrogen bond energy grows from the value close to zero in $\{CH_4\}$ (here and hereinafter, the formulas of species in the liquid phase are given in braces) to tens of kilojoules in liquid and polymeric gaseous HF; in HF, the hydrogen bond energy becomes comparable with the valence bond energy. The main factors responsible for this trend are an increase in the nucleus charge and in the number of lone electron pairs and a decrease in the number of valence-bonded hydrogen atoms. An increase in the strength of hydrogen bonds is also manifested in the tendency to polymerization, which is the most pronounced in HF, very weak in water vapor (the mean molecular weight of water vapor of 18.64 in the normal boiling point, reported in [5], is apparently overestimated), and seems to be absent in gaseous NH_3 and CH_4. However, there are also other well-known data qualitatively characterizing the tendency to form hydrogen bonds: abnormal boiling and melting points of H_2O, NH_3, and HF, clathrate properties of ice, etc.

From this standpoint, it is interesting to consider formalized sublimation of crystalline compounds of this series to monomeric vapor, $[EH_m] = (EH_m)$. The enthalpy of this process, $\Delta H^0_{subl} = \Delta H^0_{f(v)} - \Delta H^0_{f(cr)}$, is largely associated with the enthalpy of cleavage of hydrogen bonds in molecular crystals (kJ mol^{-1}): $[CH_4]$ $-74.9 + 84.4 = 9.5$; $[NH_3]$ $-46.2 + 75.2 = 29$; $[H_2O]$ $-241.8 + 291.9 = 50$; and [HF] $-268.6 + 308.6 = 40$, as follows from Table 2 [4, 5].

Table 2 shows that the major contribution to the dissociation energy of hydrogen bonds is made by the orientation interaction (E_o), whereas the other kinds of nonvalent interactions, induction (E_i) and dispersion (E_d), only additionally hinder the egress of molecules to the gas phase and affect the melting point of the crystals. Therefore, by dividing E_o by the number L of hydrogen bonds per molecule (columns 6 and 7 in Table 2), we obtain E_{hb} in the crystalline state.

For hydrogen fluoride, the model of linear polymers $(HF)_n$ with alternation of valence and hydrogen bonds is commonly accepted; therefore, for the HF fragment in polymers we assume $L = 1$ and $E_{hb} = E_o/L = 30$ kJ mol^{-1}.

Each quadrupole water molecule can form four hydrogen bonds in diamond-like ice crystals, i.e., for H_2O as a polymer fragment $L = 2$; hence, $E_{hb} = E_o/L = 40/2 = 20$ kJ mol^{-1} (Table 2).

In NH_3 molecules, the nitrogen atom bears one lone electron pair and three hydrogen atoms; in these molecules, additional possibilities may arise for enhancement of hydrogen bonding, i.e., $2 > L \geq 1$. By interpolating the E_{hb} values in the series CH_4 (E_{hb}

~0), NH_3 (E_{hb} ?), H_2O (E_{hb} = 20), and HF (E_{hb} = 30 kJ), we obtain for $E_{hb}(NH_3)$ the tentative value of 10 kJ, i.e., L can be taken equal to 1.7 (E_o/L = 10 kJ, Table 2).

In CH_4 molecules in the gaseous and condensed state, the orientation interaction energy can be considered to be zero to a first approximation, i.e., $E_{hb} = 0$.

In view of the aforesaid, we refined and supplemented (Table 3) the previously made graphic correlation of the ΔH^0_f and S^0 values for polymeric gaseous species of CH_4, NH_3, H_2O, and HF [3, 4, 6, 7].

From the $\Delta H^0_f/n$ values (n is the degree of polymerization) given in Table 3 for H_2O, we can calculate that, at the boiling point (T = 100°C, P = 1 atm), the partial pressure of dimeric water molecules (H_4O_2) in the saturated vapor will be about 0.5 mm Hg, that of trimeric molecules, about 10^{-4} mm Hg, and that of tetrameric molecules, 10^{-7} mm Hg. The above-mentioned value given in [5] for the content of dimeric molecules (~3.5%, i.e., 27 mm Hg) is apparently overestimated, which may be due to problems with accurate determination of the density of saturated water vapor.

In saturated NH_3 (at –33.5°C and P = 1 atm) and HF (at +33°C and P = 1 atm) vapors, the partial pressure of the dimer is about 0.7 mm Hg). The HF vapor, however, mainly consists of the hexamer molecules (partial pressure ~737 mm Hg).

In saturated CH_4 vapor (at –161.5°C and P = 1 atm), the expected partial pressure of the dimer does not exceed 0.08 mm Hg, with the dimerization being due to dispersion interaction rather than hydrogen bonding (E_{hb} ~0).

Let us consider in more detail the correlations $\Delta H^0_f/n = f(1/n)$ (Fig. 1).

Figure 1 shows that, in the intervals from n = 1 to n = 5–6, the correlation plots are gently sloping and correspond to the linear variation of the polymerization characteristics until, probably, cyclic polymeric species are formed. In the region of higher degrees of polymerization, the curves inevitably become steeper, so as to come to the points corresponding to the crystalline state ($\Delta H^0_{f,298\,K}$ of crystals). Such a “break” of the correlation may be due to the fact that, in cyclic polymers, the further “block” copolymerization with significant contributions of E_i and E_d (Table 1) becomes energetically favorable, yielding three-dimensional structures. This “break” of the correlation is shown in Fig. 1 at the points corresponding to the polymers $(NH_3)_5$ and $(H_2O)_5$ (portions *BC*), as in these structures the bond angles HOH (104.3°) and HNH (107.4°), close to those characteristic of the sp^3-hybridized central atom, approximately fit the geometry of a flat regular pentagon (angle 108°). The same “break” of the correlation is also inevitable for the CH_4 molecules, which do not polymerize in the gas phase because of virtual lack of hydrogen bonding (ΔH^0 of polymerization was taken equal to zero), but the contributions from E_i and E_d (Table 2) provide condensation and crystallization. In Fig. 1, the above-mentioned “break” is illustrated by two straight lines drawn between the points for the gaseous monomer, gaseous pentamer, and crystalline form (portions *AB* and *BC*). Also, horizontal lines are drawn in Fig. 1 from the points corresponding to $\Delta H^0_{f,298\,K}$ of liquid CH_4, NH_3, H_2O, and HF to interceptions with the *BC* portions. The interception points correspond to $n \approx$ 20–25 for H_2O, $n \approx$ 12–14 for NH_3 and HF, and $n \approx$ 50 for CH_4. The latter result is surprising, as CH_4 tends to polymerize neither in gas nor in liquid phase. We can explain this result as follows.

Table 3. System of published [1, 2] and estimated (*) thermodynamic characteristics (ΔH^0_f, kJ mol^{-1}; S^0, J mol^{-1} K^{-1}) of hydrogen compounds of carbon (CH_4), oxygen (H_2O), nitrogen (NH_3), and fluorine (HF) (for oligomeric species, per monomeric unit); melting points (T_m, °C), boiling points (T_b, °C), and molar volumes (V, cm^3 mol^{-1}) of the compounds

Form, parameter	C ($m = 4$)	N ($m = 3$)	O ($m = 2$)	F ($m = 1$)
$[MH_m]$, ΔH^0_f	–84.4	–75.2	–291.9	–308.6
$[MH_m]$, S^0	99.4	66.2	44.0	35.0
$\{MH_m\}$, ΔH^0_f	–83.4	–69.5	–285.8	–304.0
$\{MH_m\}$, S^0	109.8	95.1	69.9	57.0
(MH_m), ΔH^0_f	–74.9	–46.2	–241.8	–268.6
(MH_m), S^0	186.2	192.5	188.7	173.5
$1/2(M_2H_{2m})$, ΔH^0_f	–74.9	–51.0	–252.0	–283
$1/2(M_2H_{2m})$, S^0	150	144	129	115
$1/3(M_3H_{3m})$, ΔH^0_f	–74.9	–52.0	–255	–293
$1/3(M_3H_{3m})$, S^0	134	127	110	97
$1/4(M_4H_{4m})$, ΔH^0_f	–75	–53	–257	–294
$1/4(M_4H_{4m})$, S^0	129	120	100	87
$1/5(M_5H_{5m})$, ΔH^0_f	–76	–57	–261	–
$1/5(M_5H_{5m})$, S^0	125	102	94	–
$1/6(M_6H_{6m})$, ΔH^0_f	–	–	–	–299
$1/6(M_6H_{6m})$, S^0	–	–	–	67
T_m	–182.5	–77.8	0	–83
T_b	–161.5	–33.5	100	33.2
V	37.2	21.0	19.1	19.4

According to our model, the crystalline state corresponds to $1/n = 0$, or $n = \infty$. Therefore, in the liquid

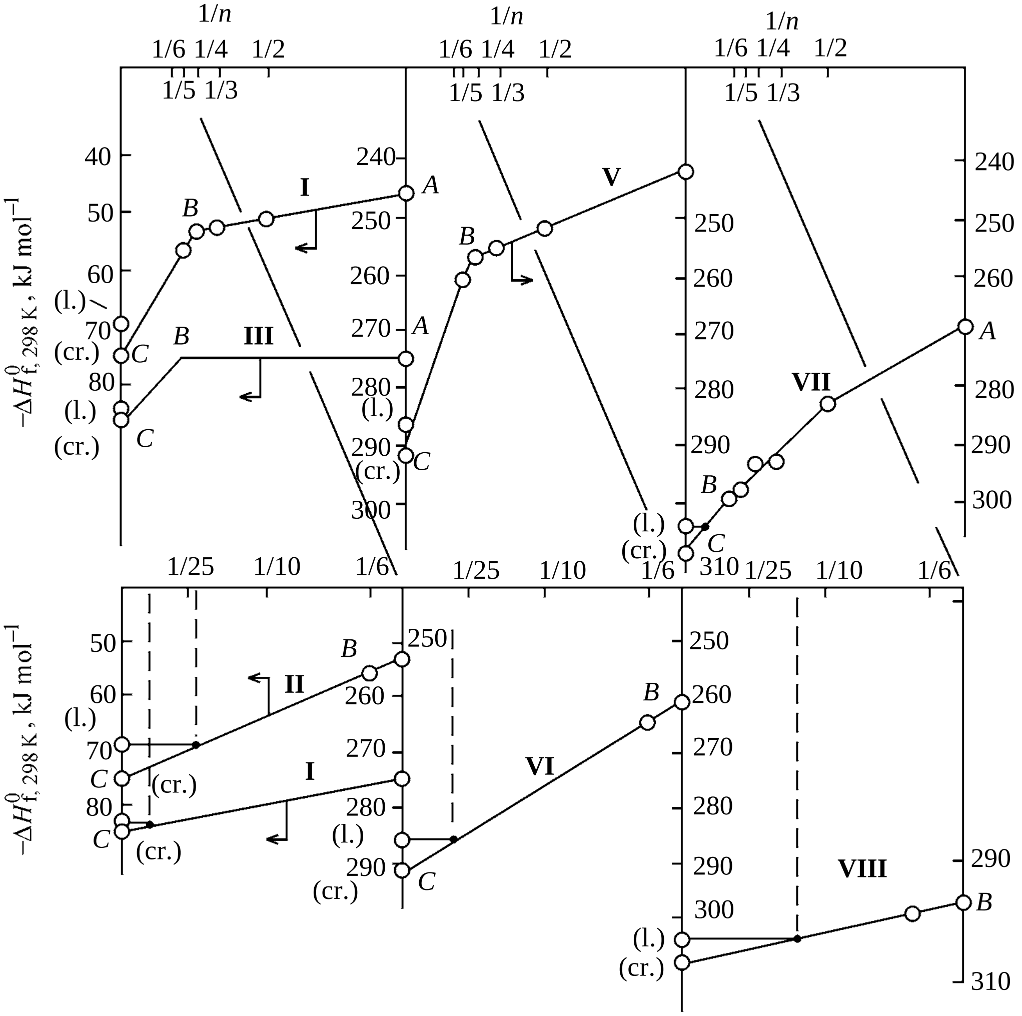

Fig. 1. Correlations of the $\Delta H^0_{f,298\,K}$ values for monomeric (*A*), crystalline (*C*), liquid, and gaseous polymeric forms of (**III, IV**) CH_4, (**I, II**) NH_3, (**V, VI**) H_2O, and (**VII, VIII**) HF with $1/n$ (n is the degree of polymerization) in the range from 0 (crystalline compounds) to 1 (gaseous monomer).

(molten) state there should be $n << \infty$. If a substance is polymerized in the liquid state, the model gives the n values having a real sense. For example, the calculation gives $n \approx 50$ for liquid sulfur and $n \approx 5$ for liquid NO_2, which seems quite reasonable. A lot of other similar examples can be given. Turning back to the diagram for CH_4 (Fig. 1, **III**, **IV**), we should, apparently, interpret the value obtained not as a certain specific degree of polymerization but as an effective quantity corresponding to the weak van der Waals interactions, the only interactions possible in this system.

For liquid NH_3 and HF (Fig. 1, curves **I**, **II** and **VII**, **VIII**, portions *BC)*, the obtained values of n = 12–14 provoke no objections, as the numbers of hydrogen bonds in these compounds are similar, and for HF the polymerization to high degrees in the gas and liquid phases is well known and comprehensively studied. The anomalies in the melting and boiling points of NH_3 and HF are also similar but considerably less pronounced as compared to water.

For example, as judged from the melting points, ammonia (–77.8°C) shows an even greater structural anomaly than HF (–83°C). This fact is one more indirect evidence that NH_3 and HF have much in common (see also Fig. 2b). Indeed, the degrees of polymerization of liquid HF (at –83°C) and NH_3 (at –77.8°C), according to our model, are approximately equal and relatively high ($n \approx$ 10–14), although the NH_3 polymers are less stable because of considerably weaker hydrogen bonds.

A striking feature of “thawed ice” is the very high degree of polymerization ($n \approx$ 20–25), which can be accounted for [8] by formation (in going from the

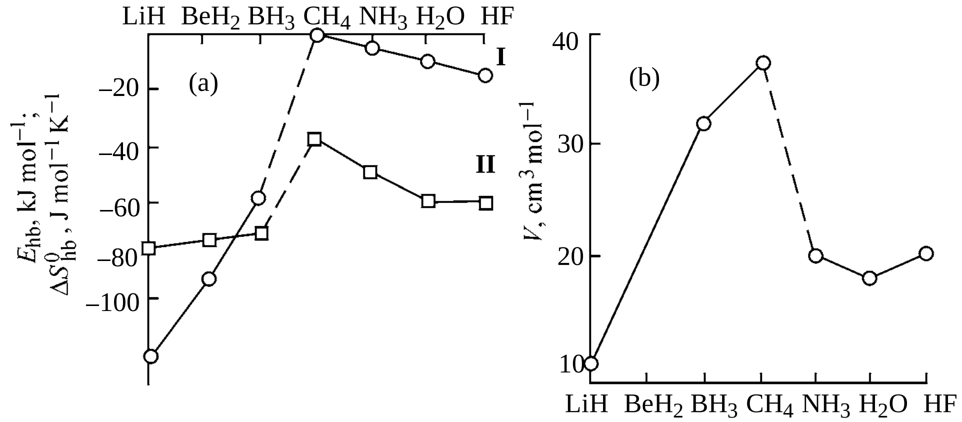

Fig. 2. Correlation diagrams for (a) (**I**) energy ($E_{E_{hb}}$) *and (***II**) entropy (ΔS^0_{hb}) of hydrogen bonding in gaseous hydrogen compounds of Period II elements and for (b) molar volumes V of the corresponding compounds EH_m.

liquid to crystalline state) of polyhedral polymeric species, pentagonododecahedra and pentagonododecahexagonodihedra, with the oxygen atoms of the water molecules presumably located in the vertices. Combinations of such polyhedra can correspond to any n from 20 to 24 (range characteristic of “thawed iced”).

In this context, it is appropriate to mention well-known molecular compounds, gas hydrates, having in most cases the composition $X \cdot 5.75H_2O$ [8] and the above-indicated polyhedral structure. Passing to integer coefficients, we obtain $4X \cdot 23H_2O$. This formula corresponds to a superposition of two polyhedra incorporating four molecules of X. A similar compound can presumably form from “fragment” water molecules, i.e., $4H_2O \cdot 23H_2O$ seems to be a reasonable composition of the “thawed ice” polyhedron, and ice can be considered in terms of this model as a “hollow” (at P = 1 atm) form of the polyhedron with the molecular weight $M_L = 23 \times 18/4 = 103.5$. The “thawed ice,” in terms of this model, should have the molecular weight $M_W = (1 + 5.75) \times 18 = 121.5$, which corresponds to the limiting capacity of the clathrate polyhedron under standard conditions.

The real (equilibrium) capacity will be characterized by the molecular weight M'_W, which can be calculated from the relationship $\rho_{water}/\rho_{ice} = 1/0.94 = M'_W/M_L = M'_W/103.5$; hence, $M'_W = 103.5/0.94 = 110.1$.

In this case, in the clathrate structure of “thawed ice,” the degree of filling with “fragment” water molecules will be (110.1 – 103.5)/18 = 0.37; this means that a certain equilibrium clathrate form of “thawed water” at P = 1 atm an 273 K can have the formula $[0.37H_2O] \cdot [5.75H_2O]$. This means that each polyhedron of “thawed ice” can contain, on the average, ~1.5 molecules of “fragment” water, i.e., can have the formula $[1.5H_2O] \cdot [23H_2O]$.

Apparently, the clathrate polyhedra of “thawed ice” and ice can be filled further, but only at elevated pressures. Numerous modification of ice with the density of up to 1.5 g cm^{-3} were obtained at high pressures (up to 25 000 atm) [8]. These modifications may correspond to the clathrate form $[14H_2O] \cdot [23H_2O]$, but the model can hardly be regarded as reliable under the conditions strongly deviating from the standard conditions.

An extremely interesting problem concerning hydrogen bonding is dissipation of the energy associated, in particuilar, with a change in the degree of polymerization of H_2O molecules.

As already noted, in the initial step of polymerization (n from 2 to 5), linear chain propagation can be expected; within these limits, the coordination number of oxygen atoms increases from 2.5 to 3, and the hydrogen bond energy E_{hb}, from 10 to 20 kJ mol^{-1}, as shown in Fig. 3.

It is assumed that the five-membered polymer undergoes ring closure, and further polymerization involves “blocks.” Figure 3 shows that, upon formation of a polyhedron from 20 (or 24) water molecules, the specific value of E_{hb} (per mole of H_2O) becomes equal to 30 kJ mol^{-1}, and upon crystallization of ice (diamond-like structure), E_{hb} reaches 40 kJ mol^{-1}. This example shows that formation of polyhedra as the penultimate stage preceding crystallization is energetically favorable, i.e., the polyhedral model under consideration is justified from the energy viewpoint.

It should be noted in conclusion that the estimated values of E_{hb} and ΔS^0_{hb} for all the hydrogen com-

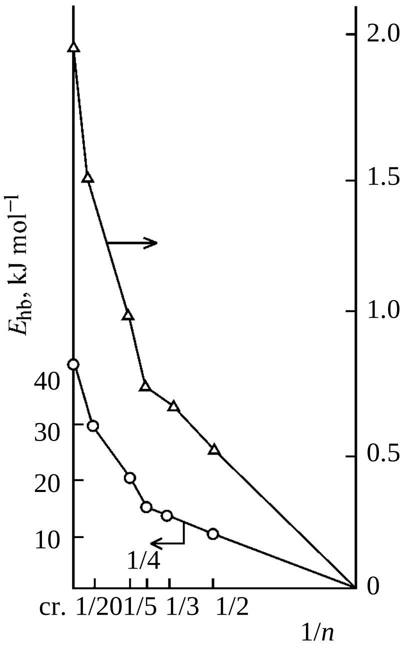

Fig. 3. Correlation of E_{hb} (energy of hydrogen bonds in water) and L (number of hydrogen bonds per water molecule) with 1/n (reciprocal degree of polymerization).

pounds of Period II elements were used to construct a correlation plot (Fig. 2a). This plot shows that, in going from boron hydride BH_3 to hydrogen carbide CH_4, the course of the correlation abruptly changes: from steep ascent of E_{hb} and ΔS^0_{hb} for LiH, BeH_2, and CH_3 to descent for CH_4, NH_3, H_2O, and HF. More precisely, there is a discontinuity between BH_3 and CH_4, associated with a change in the bond nature (BH_3 is boron hydride, and CH_4, hydrogen carbide).

Figure 2b shows the correlation for the molar volumes of all the hydrogen compounds of Period II elements. It is seen that the correlation curve is monotonically ascending from LiH to CH_4, which is followed by an abrupt drop from CH_4 to NH_3. This fact, in combination with data in Fig. 2a, shows that CH_4 can be classed neither with hydrides LiH–BH_3 nor with the series NH_3–HF, occupying a particular place and being the parent compound for the percarbide (organic) chemistry.

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