STRUCTURE OF SOLID AMORPHOUS PHASES OF WATER AND CAPTURE OF MOLECULES CH_4, H_2 IN MULTISTRUCTURES OF AN ICE

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Introduction

In conditions enough fast cooling at T <133K water forms amorphous phases [1]. In the field of low pressure the amorphous phase of low density is formed, and at increase of pressure there is an amorphous phase of higher density. At change of pressure or temperatures in amorphous phases occur jumps of density (> 20 %).

Amorphous phases of an ice can be of interest for creation on their basis of stores hydrogen fuel in the form of CH_4, H_2 adjustable pressure and in temperature. A structure of cryogenic phases of water, mechanisms of their transformations, properties to accumulate methane and hydrogen are a subject of studying in the given work.

Within the limits of new theoretical concepts thermo field dynamics [2] and quantum-field chemistry [3] we offer models of a structure of cryogenic solid amorphous glasses of water and computer modeling receives power barriers of transport CH_4 and H_2 inside of their cellular multistructures.

Results and discussion

Quantum-field approaches [2,3] treat structures of the condensed phases of water as system of multiparticles of water $(H_2O)_n$. The internal structure of each such supermolecule $(H_2O)_n$ is described with some spatial grid of intramolecular hydrogen (O–H–O) α–bonds. Grids form a cellular structure of multiparticles of water. Walls of cells are formed by ring fragments (O_6H_6).

Intermolecular hydrogen (O–H----O) β– bonds of adhesion between multiparticles $(H_2O)_n$ define stability of various phases of water. Share distribution of quantity hydrogen α–bonds of cohesion and β– bonds of adhesion of molecules of water define a structure of the condensed phases of water. In view of existence of physical γ–bonds of molecules in a gas phase of water within the limits of thermo field dynamics share distributions of three types of bonds of molecules of water it has been received by methods of statistical thermodynamics with use of minimization of Gibbs energy:

$$G(\alpha,\beta,\gamma) = U(\alpha,\beta,\gamma) - \tau \bullet \sigma(\alpha,\beta,\gamma) + p\Omega(\alpha,\beta,\gamma)$$

where $U(\alpha,\beta,\gamma)$ is internal energy of a phase of water, $\sigma(\alpha,\beta,\gamma)$ is its entropy, $\Omega(\alpha,\beta,\gamma)$ is its volume, p, τ denote pressure and temperature accordingly. We notice, that, $\tau = \kappa T, S = \kappa\sigma$, where κ is constant by Boltsman.

Considering $\alpha + \beta + \gamma = n$, where α , β , γ - denote quantity of corresponding types of bonds, and n is the total of bonds, in pair approach internal energy has form:

$$U(a,\beta,\gamma) = N_{H_2O}\varepsilon_{H_2O} + \alpha\varepsilon_\alpha + \beta\varepsilon_\beta + \gamma\varepsilon_\gamma,$$

where ε_{H_2O} is an energy of water molecule, and ε_α, ε_β, ε_γ denote energies of corresponding types of bonds.

Expression of an entropy has next form:

$$\sigma(\alpha,\beta,\gamma) = \ln\frac{n!}{\alpha!\beta!\gamma!}$$

For ideal solutions, volume of a phase of water we shall present in an additive kind:

$$\Omega(\alpha,\beta,\gamma) = N_{H_2O}\Omega_{H_2O} + \alpha\Omega_\alpha + \beta\Omega_\beta + \gamma\Omega_\gamma$$

Here Ω_{H_2O} is a volume of single water molecule, there are effective volumes Ω_α, Ω_β, Ω_γ of corresponding types of bonds.

The waters average on various calculated multistructures energy of α–bonds and the β– bonds have made: $\varepsilon_\alpha \sim -32$ kJ/mol, and $\varepsilon_\beta \sim -26$ kJ/mol, accordingly. According to our calculation for temperature T = 133K and pressure P=5 10^8 Pa equilibrium share distribution of hydrogen α–bonds and β– bonds in a solid amorphous phase has made: ν_α =99,47%, ν_β =0,53%. At temperature T = 273K and P = 10^5 Pa in liquid water the share of β– bonds of adhesion between molecules of water increases: ν_α =91,8%, ν_β =8,2%.=91,8, =8,2.

The average sizes of compact multiparticles $(H_2O)_n$ in a cryogenic dense phase makes: L ~18 nanometers that corresponds n ~ 10^5 molecules of water. In other phase received from liquid water under normal conditions the average size $(H_2O)_n$ L ~0,9 нм that corresponds approximately n ~ 30. These distinctions in the sizes of compact multiparticles explain observable jumps of density.

Transport of molecules CH_4 and H_2 through cellular grids of water is blocked by the barriers laying in a direction of an axis of a ring (O_6H_6) of a cell. Between walls of a cell of water and molecules of fuel forces of intermolecular adhesion operate. Potential energy of adhesion was calculated by density functional method [3].

Potential curves of transport for CH_4 and H_2 through a ring (O_6H_6) are shown on fig. 1, 2.

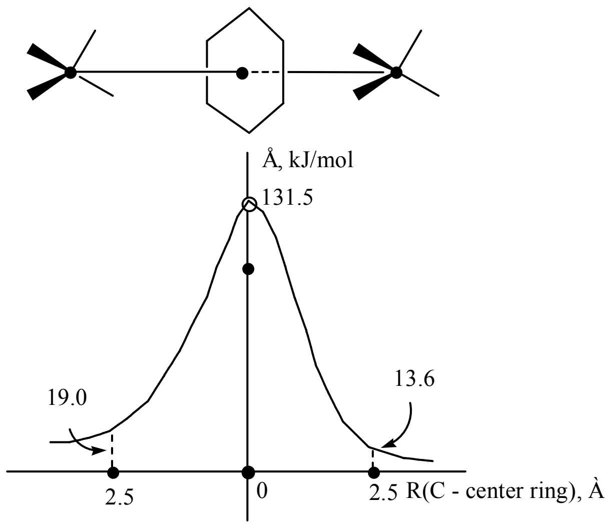

Fig. 1. Potential curves of transport CH_4 through a ring (O_6H_6).

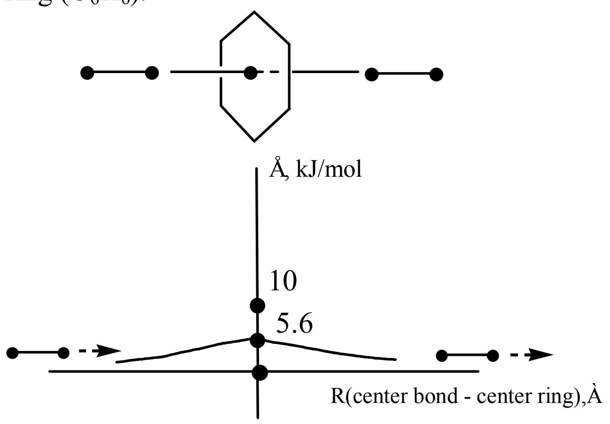

Fig. 2. Potential curves of transport H_2 through a ring (O_6H_6).

In case of carry of metane through a cyclic fragment the barrier is high (132 kJ/mol). For H_2 the barrier is very small (6 kJ/mol). In case of metane the barrier is connected with forces of pushing away of atoms H from a ring at attempt to pass through it. In the second case the barrier of pushing away is weak because of the big remoteness between atoms of hydrogen and atoms of a ring.

Conclusions

On the basis of the set forth above calculations clearly, that the power barrier of carry of a molecule of hydrogen through cellular multistructure of water lays considerably below similar barriers CH_4. It causes the effective mechanism of carry H_2 in phases of water. Carry of molecules of methane inside of the ordered cells of multistructures of water is small, as they are locked inside of cells of water $(H_2O)_n$. Therefore it is necessary to expect, that amorphous phases of an ice can be of interest for creation on their basis of stores CH_4.

As have shown our calculations essential distinction in the sizes of compact multiparticles $(H_2O)_n$ in dense and friable amorphous phases of an ice allows to change a share of accumulation of methane inside of multiparticles. In a dense amorphous phase a molecule of water are collected in tens times in the sizes nanoparticles.

Mechanisms of jumps of density of amorphous phases allow reversible to accumulate CH_4 inside of cellular structures of multiparticles of water. Thus the degree of accumulation can be adjusted pressure and in temperature.

References

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