

Features of Understanding and Describing the Hydrate Formation Process

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Abstract

Clathrate hydrates are not only a huge source of energy, but also potentially interesting from a technological point of view due to their ability to bind water. According to generally accepted modern concepts, hydrates formed by individual hydrate-formers or their mixtures are non-stoichiometric inclusion compounds of a cellular type with the crystal lattice built of water molecules held by hydrogen bonds. The molecules of the hydrate-former are located in the internal cavities of the crystal lattice and are held in them by van der Waals forces. The article presents a formalized description of the hydrate formation process. A model of hydrate formation in gas-water systems is proposed. The model describes the processes occurring during hydrate formation in structures. It contains equations for calculating the main energy and molecular parameters of the hydrate-former, as well as the kinetics of the process.

Keywords: Hydrate; Hydrate-former; Crystal lattices; Structures; Energy

1. INTRODUCTION

Clathrate hydrates are crystalline compounds formed under certain thermobaric conditions from hydrate-forming molecules (with characteristic sizes in the range of 0.38–0.92 nm) and water [1,2]. Hydrates are solid solutions, non-stoichiometric inclusion compounds of the cellular type. Many gases (nitrogen, noble gases, hydrogen, oxygen, acidic, hydrocarbon, alkaline), organic liquids (mainly volatile), individual solids (for example, adamantane), as well as their and multicomponent mixtures have the ability to form hydrates.

The structural features of the water molecule and the weak bonds caused by electrostatic forces and donor-acceptor interactions between neighboring hydrogen and oxygen atoms in water molecules create favorable opportunities for the formation of directed intermolecular hydrogen bonds with neighboring molecules, linking them into spatial intermolecular associations [3]. The formation of hydrogen bonds is caused by weak electrostatic forces and donor-acceptor interactions with charge transfer.

Molecules of hydrate-formers are held in the cavities by hydrogen bonds from water molecules through relatively weak Van der Waals forces (which are several orders of magnitude weaker than covalent bonds). These forces are a type of interatomic attraction that is additive, and they are responsible for the cohesion of gas atoms in solid and liquid states, as well as for the physical adsorption of molecules on the surfaces of solid bodies when normal chemical bonds are absent. Unlike conventional chemical, ionic, and covalent bonds, van der Waals forces also act when the atoms are still some distance apart. Despite the fact that the atoms inside a hydrogen or methane molecule are bound to each other by covalent forces that are saturated inside the molecule and cannot hold them together, in a liquid state the same methane exists precisely due to van der Waals forces [3].

Since the hydrate-forming agent molecule rotates freely surrounded by water molecules, and the electrical forces of interaction of the charges included in both dipoles tend to cause rotation of the dipole axes, attractive forces arise between the water molecules and the hydrate-forming agent.

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In cases where the molecules of hydrate-formers are not dipoles, the positive and negative charges within the nonpolar hydrate-former molecule are displaced in opposite directions under the influence of the electric forces of water molecules, resulting in polarization. In this case, the charge displacement always leads to the situation where charges of the opposite sign from the hydrate-former molecules approach the closer end of the water molecule dipole, and vice versa. As a result, attractive forces arise between the two molecules, which contributes to the formation of hydrates. The water dipoles located outside the hydrate complex polarize the hydrate-forming agent molecule located in the hydrate complex.

Crystallographic studies [4] revealed that molecular-sized cavities (Fig. 1) in hydrate structures can be 12-, 14-, 15-, 16- and 20-tihedrons (the vertices are oxygen atoms, and the edges are hydrogen bonds).

Molecules with small characteristic dimensions of the order of 4–5.5 Å are placed in all types of cavities, larger molecules with characteristic dimensions of 5.5–7 Å are placed only in T, T', P, H, E cavities [1]. The most characteristic crystal lattices for hydrates are cubic structures CS-I and CS-II, less common is the hexagonal GS-III (structure H). The CS-I structure is a body-centered cubic lattice of 46 water molecules, containing 2 small and 6 large cavities (see Fig. 2). The CS-II structure is a face-centered cubic lattice of the cubic syngony of 136 water molecules, containing 16 small and 8 large cavities. The structure of GS-III is built from 34 water molecules, has 3 small cavities, 2 medium ones and 1 large cavity (for example, 3 small cavities of the D-type, 2 medium T'-type and one largest—E-cavity).

The hydrate crystal lattice itself (4 cubic, 5 hexagonal, 4 tetragonal and 3 rhombic) differs from the 17 modifications of ice (hexagonal, trigonal, cubic, tetragonal, rhombic) in that it is thermodynamically metastable unless filled with a minimum number of hydrate-forming molecules. For example, the lattice of ice XVI, obtained by removing neon molecules from the lattice in vacuum at temperatures below 147 K, turned out to be thermodynamically unstable under experimental conditions [6].

2. FORMALIZATION OF THE PROCESS

Due to the electrical interaction of the permanent dipole moments in the water molecule and the induced moments in the hydrate-forming agent molecule, a hydrate molecule is formed. Consequently, the higher the polarizability of the hydrate-forming agent molecules, the higher the stability of the hydrates, the smaller the size of the hydrate-forming agent molecules and the greater the heat of hydrate formation. Van der Waals forces increase with

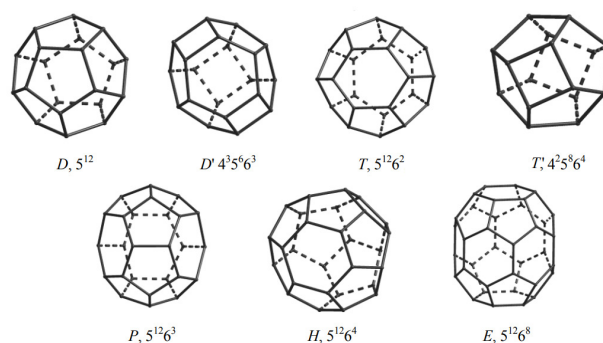


Fig. 1. Polyhedrons of hydrated frameworks – cavities ($m\gamma - \gamma$ faces with the number of edges m).

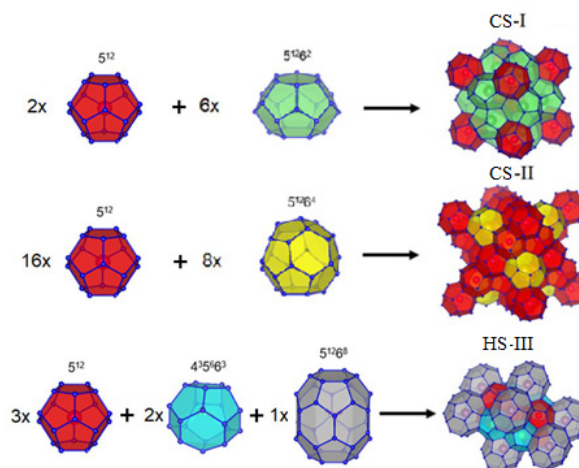


Fig. 2. Elementary cells of hydrate crystal lattices (modified after Ref. [5]).

the number of electrons in the molecules. The number of electrons in the hydrate-forming agent molecules is a measure of the magnitude of the van der Waals forces, which can be used to qualitatively determine their effect on the stability of hydrates. Among the many hydrate-forming substances, inert gases are the simplest hydrate-forming substances, since their molecules consist of one atom and are the most symmetrical both geometrically and electrostatically and do not have a permanent dipole moment. The more electrons a molecule has, and the lower the ionization potential, the greater its atomic weights, melting and boiling points, molecular sizes, and polarizability. With an increase in the number of electrons in a molecule, the heat of hydrate formation and dissociation temperature increase, but the decomposition pressure decreases.

The cavities of hydrates are conventionally divided into small and large and can be filled with hydrate-former molecules either partially or completely. Cavities free of hydrate-forming agents can be filled with water molecules, which was mathematically substantiated and verified by author of Refs. [2,7] and is confirmed by observations [8].

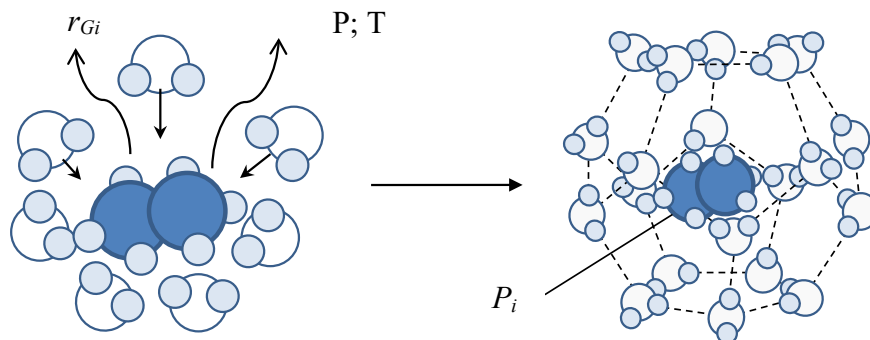


Fig. 3. Scheme of the process of absorption of gas molecules by associates of water molecules.

The process of forming hydrate structures with the sorption of hydrate-forming molecules by the crystal lattice is similar to the process of adsorption of molecules on a solid surface, which is represented by ice-like associates of water molecules (Fig. 3). During the formation of the crystal lattice in the cavities at the hydrate formation temperature, the pressure increases to the value of saturated vapors of the adsorbed components (P_i). In this case, the hydrate-former in the structure is in a liquefied state. If the thermobaric conditions of hydrate formation correspond to supercritical temperatures and subcritical pressures of the absorbed component, its saturated vapors in the hydrate cavity condense with the release of thermal energy. If the thermobaric conditions of hydrate formation correspond to supercritical temperatures and pressures of the absorbed component, then during its absorption, thermal energy is released equal to the change in enthalpy or internal energy. The process of absorption of molecules is in energy (dynamic) equilibrium with the reverse process (desorption).

When a hydrate is formed in the hydrate-former-liquid water system, a simultaneous exothermic process of crystallization with the construction of a hydrate lattice occurs. When a hydrate is formed in the gas-ice system, the formation of hydrate structures occurs through the transformation of the ice crystal lattice into a hydrate lattice. According to the Gibbs phase rule, hydrates can consist of CS-I structures or CS-II structures or structure H, or their combinations.

In addition, the water component in the systems is always present in the form of vapor and, if necessary, either by successive condensation and crystallization or by desublimation, participates in the construction of the lattice.

For systems of liquid hydrate-formers, in contrast to gaseous ones, the process is accompanied by an increase in the volume of the system and, vice versa: as is known, for completely condensed systems, an increase in pressure is a consequence of the tendency of one of the phases to pass into another and thereby increase the volume of the system.

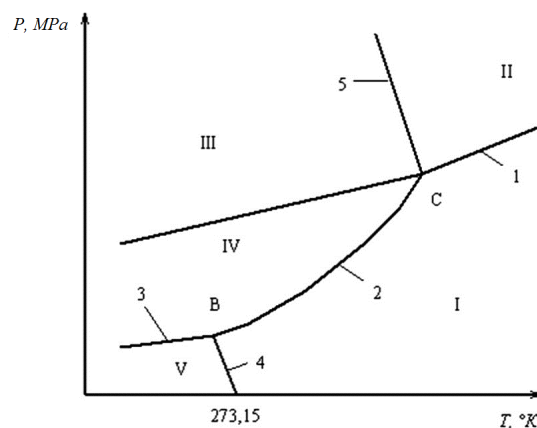


Fig. 4. Basic diagram of equilibrium conditions of a hydrate-forming system: 1 – vapor pressure of a hydrate-former; 2 – equilibrium conditions for hydrate formation in a gas-liquid water system; 3 – equilibrium conditions for hydrate formation in a gas-ice or supercooled water system; 4 – change in the crystallization temperature of water freezing; 5 – dependence of the critical temperature of hydrate-former. The following regions of the system state are limited by the indicated lines: I – gas-water; II – supercritical gas-water; III – hydrate-liquefied gas; IV – hydrate-gas; V – gas-ice.

The region of thermodynamic stability of hydrates covers both negative and positive (on the Celsius scale) temperatures (Fig. 4).

3. MATHEMATICAL MODELING

Hydrates are formed from multi-component hydrate-forming compositions

$$\sum_{i=1}^k Y_i = 1, \tag{1}$$

where Y_i is the mole fraction of the i -th component, k is the number of hydrate-former components in the mixture with the individual components most often forming two types of crystal lattices of structures, which contain small, medium and large cavities.

This process can be formalized in the form of equations that describe the energy exchange (measured in kJ/mol) in hydrate-former–water systems:

$$H_1 = E_h + E_s, \quad (2)$$

$$H_2 = E_{i-h} + E_s, \quad (3)$$

where H_1 is the energy released during the formation of a hydrate in a hydrate-former–liquid water system; H_2 is the energy released during the formation of a hydrate in a hydrate-former–ice system; E_h is the energy released during the formation of the hydrate crystal lattice from liquid water; E_{i-h} is the energy of the formation of the hydrate crystal lattice from ice; E_s is the energy released during the adsorption of hydrate-former and water vapor by the hydrate crystal lattices.

The specified energies are determined from the equations:

$$E_h = \left(H_i + \sum Y_i \frac{m_{G_i}}{\sum m_{G_i}} \cdot L_{i-h,i} \right) \cdot n, \quad (4)$$

$$E_s = \sum \frac{m_{V_j} \cdot r_L + m_{G_i} \cdot r_{G_i}}{\sum b_{t.c.,j}}, \quad (5)$$

$$E_{i-h} = L_{i-h} \cdot n, \quad (6)$$

$$H_i = H_0 - 0.16554 \cdot P + 0.00045 \cdot P^2, \quad (7)$$

where H_i is the energy of a crystalline lattice formation from ice-like associates of water molecules varies depending on the pressure P of system; L_{i-h} is the energy of transformation of ice into the hydrate crystal lattice; n are the hydrate numbers of the structures; r_L , r_{G_i} are the adsorption energies of water and the i -th hydrate-former (in the first approximation, they can be taken as equal to the condensation energies); $b_{t.c.,j}$ are the numbers of cavities in the unit cells of the structures; m_{G_i} and m_{V_j} is the possible number of molecules of the i -th hydrate-former and adsorbed water that can be absorbed by the cavities of the structures. The latter is given as

$$m_{G_i} = \sum b_{t.c.,j} \cdot \theta_{t.c.,j}, \quad (8)$$

$$m_{V_j} = \sum b_{t.c.,j} \cdot (1 - \theta_{t.c.,j}), \quad (9)$$

where $\theta_{t.c.,j}$ are the degrees of filling of cavities with the i -th hydrate-former

$$\theta_{t.c.,j} = \frac{C_{t.c.,j} \cdot P_i}{1 + C_{t.c.,j} \cdot P_i}, \quad (10)$$

where $C_{t.c.,j}$, are the Langmuir constants of cavities; P_i (see Fig. 1) is the partial pressure (in Pa) of the i -th hydrate-former according to Dalton's law

$$P_i = Y_i \cdot P. \quad (11)$$

The hydrate number can be determined by the formula:

$$n = \frac{m_{L_j} + m_{V_j}}{\sum b_{t.c.,j} \cdot \theta_{t.c.,j}}, \quad (12)$$

where m_{L_j} , are the number of water molecules in the unit cell of the hydrate crystal lattice.

Densities (in kg/m³) and molar masses (in kg/mol) of hydrates of structures:

$$\rho = \frac{[M_L \cdot \sum (m_{L_j} + m_{V_j}) + \sum (m_{G_i} \cdot M_{G_i})] \cdot 10^3}{N \cdot h^3}, \quad (13)$$

$$M = \frac{[M_L \cdot \sum (m_{L_j} + m_{V_j}) + \sum (m_{G_i} \cdot M_{G_i})] \cdot 10^3}{m_L + \sum b_{t.c.,j}}, \quad (14)$$

where N is Avogadro's number; M_L and M_{G_i} are the molar masses (in g/mol) of water and i -th hydrate-former, respectively; h is the lattice parameter of hydrates (in Å):

$$h = A \cdot T^2 + B \cdot T + C, \quad (15)$$

where T is the temperature (in K); A , B , C are coefficients for components determined experimentally. The values of the coefficients obtained by processing experimental data for some hydrate-formers are listed in the Table 1.

Rates of formation (in mol/s) of hydrate structures:

$$W = \frac{K \cdot f \cdot (T - T_s)}{H_{1,2}}, \quad (16)$$

where f is the area (in m²) of contact of gas with water or ice; T_s is the temperature (in K) of the system when the heat is removed; K is the heat transfer coefficient measured in kJ/(s·m²·K).

4. RESULTS AND DISCUSSION

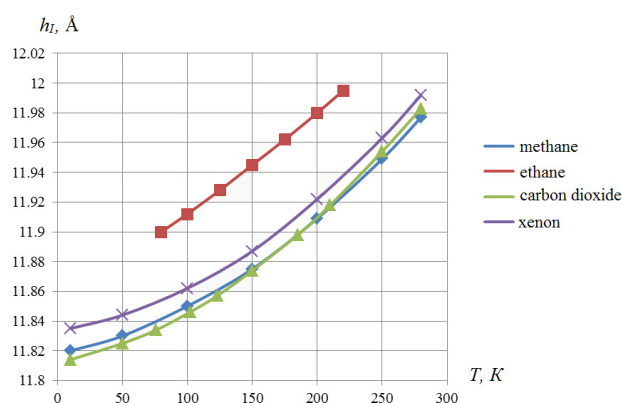
The calculated values of the hydrate number, density and heat of hydrate formation from water and ice were compared with the experimental ones. The comparison was performed for various binary gas systems that form hydrates in

Table 1. Values of the coefficients for some components in equation (15).

Hydrate-former	Temperature range of hydrate formation, K	A	B	C
CH ₄	10–280	10 ⁻⁶	2·10 ⁻⁴	11.818
C ₂ H ₆	80–220	5·10 ⁻⁷	5·10 ⁻⁴	11.855
CO ₂	10–280	2·10 ⁻⁶	2·10 ⁻⁴	11.812
Xe	10–280	2·10 ⁻⁶	10 ⁻⁴	11.834
C ₃ H ₈	40–250	2·10 ⁻⁶	8·10 ⁻⁵	17.085
N ₂	10–280	2·10 ⁻⁶	8·10 ⁻⁵	17.074

Table 2. Values of hydrate parameters obtained by calculations and experimental methods.

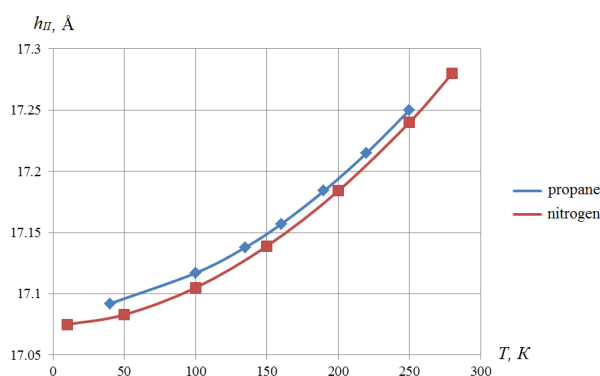
Gas mixture	Thermobaric conditions	Parameter	Calculated values	Experimental values	Source	Discrepancy
98.8% CH ₄ + 1.2% C ₂ H ₆	$P = 7.03$ MPa; $T = 282.99$ K	n H_2 , kJ/mol	6.07 66.81	6.09 66.47 ± 0.50	[9]	0.3 % 0.5 %
98.8% CH ₄ + 1.2% C ₂ H ₆	$P = 0.1013$ MPa; $T = 224.66$ K	ρ , kg/m ³ H_1 , kJ/mol	952.4 22.12	942.0 22.14	[9]	1.1 % 0.0 %
65% CH ₄ + 35% C ₂ H ₆	$P = 0.1013$ MPa; $T = 201.61$ K	ρ , kg/m ³ H_1 , kJ/mol	978.1 23.97	968.4 24.45	[9]	1.0 % 2.0 %
95% CH ₄ + 5% CO ₂	$P = 0.1013$ MPa; $T = 205.20$ K	H_1 , kJ/mol H_2 , kJ/mol	18.30 55.55	17.30 53.40	[10]	5.5 % 3.9 %
90% CH ₄ + 10% CO ₂	$P = 0.1013$ MPa; $T = 208.01$ K	H_1 , kJ/mol H_2 , kJ/mol	17.24 54.37	16.90 53.00	[10]	2.0 % 2.5 %
95.6% CO ₂ + 4.4% C ₃ H ₈	$P = 1.64$ MPa; $T = 274.95$ K	n	6.33	6.40	[11]	1.1 %
81% C ₂ H ₆ + 19% C ₃ H ₈	$P = 0.49$ MPa; $T = 274.2$ K	n	8.13	8.20	[12]	0.9 %

**Fig. 5.** Values of the characteristic size of the cells of the crystal lattices of methane, ethane, carbon dioxide and xenon hydrates of structure CS-I.

the range of thermobaric conditions at which all their components pass into the hydrate state. The comparison of the calculated values of the hydrate formation parameters with the experimental data is presented in Table 2.

As can be seen from Table 2, the discrepancies between the parameter values calculated using the developed method and the known experimental ones are in the range from 0 to 5.5% and on average is about 1.7%. Such accuracy allows us to state that the developed model and the calculation method created on its basis have a sufficient degree of reliability.

Figures 5 and 6 show a comparison of the results of experimental data (marked with dots) published in works [13–20] and obtained by the authors using the algebraic type dependence (14) for the crystal lattice parameter of some hydrate-formers.

**Fig. 6.** Values of the characteristic size of the cells of the crystal lattices of propane and nitrogen hydrates of the CS-II structure.

The most important thing in the calculations according to the model is the determination of the Langmuir constants, which can be determined experimentally, by calculation using the equations of statistical thermodynamics or by simplified methods. The physical meaning of this physicochemical parameter takes into account the distribution functions of the hydrate-forming molecules, the interaction potentials between the hydrate-forming molecules and the walls of the cavity.

5. CONCLUSION

The article presents a formalized description of the hydrate formation process. The developed model consistently describes the hydrate formation process as an energetic one. The equations included in the model allow calculating the main energetic and molecular parameters of this process: the energy of hydrate formation in hydrate-

former – water systems, the energy of the hydrate crystal lattice formation from liquid water, the density and molar mass. The crystal lattice parameter for some hydrate-formers in a wide range of conditions is also reflected. The verification of the obtained mathematical description is performed. The model allows estimating the kinetics of the process based on the calculated rate of the hydrate formation process.

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Особенности понимания и описания процесса гидратообразования

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Аннотация. Клатратные гидраты являются не только огромным источником энергии, но и потенциально интересны с технологической точки зрения благодаря способности связывать воду. Согласно общепринятым современным представлениям, гидраты, образованные индивидуальными гидратообразователями или их смесями, представляют собой нестехиометрические соединения включения, кристаллическая решетка которых построена из молекул воды, удерживаемых водородными связями. Молекулы гидратообразователя располагаются во внутренних полостях кристаллической решетки и удерживаются в них силами Ван-дер-Ваальса. В статье непротиворечиво представлено формализованное описание процесса гидратообразования. Предложена модель гидратообразования в системах газ–вода. Модель описывает процессы, происходящие при гидратообразовании в структурах. Она содержит уравнения для расчета основных энергетических и молекулярных параметров гидратообразователя, а также кинетику процесса.

Ключевые слова: гидрат; гидратообразователь; кристаллические решетки; структуры; энергия