03

Peculiarities of Determining the Specific Energy of Hydrate Formation

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The paper presents methods for determining the heat of formation of clathrate hydrates. The methods for calculating the specific energy of hydrate formation are analyzed. An energy description of the hydrate formation process in the systems is presented: solid hydrate former solid phase of water (ice), hydrate former — solid phase of water (ice), hydrate former — liquid phase of water, hydrate former under critical conditions — liquid phase of water. A comparison is made of the values of the specific heat of formation (dissociation) of gas hydrates from liquid water, ice, hydrates of liquefied gases, as well as mixed systems of hydrate formers, obtained experimentally and by calculation. The discrepancies in the values are in the range from 0 to 4.98 % and average 2.14 %, which allows us to state that the mathematical description proposed in the article is sufficiently reliable

Keywords: hydrate formation, hydrate former, clathrate hydrates, dissociation, specific heat.

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Introduction

The clathrate hydrates (hereinafter referred to as hydrates) are crystalline compounds that are formed under certain temperature and pressure conditions from ice-like associates of water molecules and hydrate former molecules absorbed by them.

The natural hydrates in the Earth's interior are a promising source of hydrocarbon raw materials, whose resources exceed known stock of the natural gas in two orders by various estimates. Therefore, studying thermodynamics and kinetics of processes of formation/dissociation of the hydrates is an important field of research, which is designed to provide a resource base of the world energy industry for the long-term period.

Hydrate formation heat belongs to enthalpy characteristics. Hydrate formation is an exothermic process, while their dissociation is a endothermic process [1]. At the same time, the values of heat of formation and dissociation are assumed to be equal.

The hydrate formation heat is determined experimentally, using semi-empirical methods as well as computationally [1,2].

Experimental determination of a thermal effect of the process of hydrate formation as well as hydrate dissociation is complicated by considerable difficulties [1]. It is more difficult to determine specific energies of the nonstoichiometric compounds, since it is necessary to exactly know a quantity and a composition of process substances that are often unstable, to fix its start and finish as well as to thoroughly measure an amount of released and absorbed heat. It is also difficult to produce homogeneous samples without macroscopic defects (inclusions, microbubbles, etc.).

The semi-empirical methods that include the said uncertainties and assumptions are limited by narrow ranges, their applicabilities and, moreover, give significant discrepancies and in most cases do not provide correct understanding and interpretation.

In this regard, it is relevant to develop a unified method of determining the specific energy of hydrate formation under various phase conditions, a wide range of the temperature and pressure conditions, which allows obtaining accurate results.

1. Methods of calculating the specific energy of hydrate formation

The heat of hydrate formation (dissociation) in the gas–liquid water system is often calculated by using the Clapeyron–Clausius equation:

$$\Delta H = T\frac{dP}{dT}\Delta V = T\frac{dP}{dT}\frac{zRT}{P} = zR\frac{d(\ln P)}{d(1/T)}, \qquad (1)$$

where P — the pressure; T — the temperature, [K]; dP/dT — the derivative at the hydrate–gas phase equilibrium line; ΔV — the variation of the system volume during hydrate formation; z — the compressibility factor; R — the universal gas constant, $[\mathrm{J}/(\mathrm{mol}\cdot\mathrm{K})]$.

At the same time, a gas nature is taken into account in the equation (1) only through its compressibility factor. However, many various gases and their mixtures have the same numerical values of z, but different equilibrium

conditions, thereby resulting in uncertainties. Using the parameter of variation of the system volume during hydrate formation (that is mandatorily experimentally-determined) makes it difficult to use this method, whose extreme simplifications make the obtained results inconsistent and unreliable.

For hydrate formation heat at the line of pressure and temperature equilibrium of the gas–water hydrate, the study [3] proposes a correlation of the equation (1) in the following form

$$\Delta H = -0.189T\,\frac{\lg P_1 - \lg P_2}{T_1^{-1} - T_2^{-1}}, \qquad (2)$$

where (P_1, T_1) and (P_2, T_2) are coordinates of the points at the equilibrium line.

For approximate calculations of hydrate formation heat of the multi-component (natural) gases at the temperature above 273.16 K, the study [4] presents the formula

$$\Delta H = 33.44n\left[(1 + 2475\overline{\rho})t + 282.5 - 42.12\overline{\rho}\right], \qquad (3)$$

where $\overline{\rho}$ — the air relative density of the gas, t — the hydrate formation temperature, [°C]; n — the hydrate number.

For analytical evaluation of heat of hydrate formation from a gas and ice similar to the Trouton's rule, the formula [5] was proposed

$$\Delta H = AT, \qquad (4)$$

where A is the constant equal to 125 J/(mol · K) for all hydrate formers with accuracy of up to 15 %; $T(K)$ — the temperature, at which the dissociation (formation) pressure is 0.1 MPa.

The following relationship was proposed in the study [6] for ten individual gases:

$$\Delta H = z\,\frac{R}{M_i}\,B, \qquad (5)$$

where M_i is the molecular mass of the i-th gas; B — the empirical coefficient.

The results of calculations according to (5) provide an error of about 10 % at the high equilibrium pressures. It should be noted that the relationship (5) is unsuitable for calculating heat of hydrate formation of the multi-component gases and, especially, of the liquified gases.

The heat of formation of hydrates of the five individual gases (methane, ethane, propane, ethylene and carbon dioxide) [J/(mol · K)] is determined by the developed dependence [7]:

$$\Delta H = \exp(A + BT), \qquad (6)$$

where T — the temperature, [K]; A, B — the empirical coefficients.

The known analytical dependences are developed for calculating the heat of formation (dissociation) of the gas hydrates are limited in use, while the results of calculations with their use differ from the experimental data for about 10 %.

2. Energy description of the hydrate formation process

The process of formation of hydrate structures with absorption of the hydrate former molecules by the crystal lattice is similar to the process of adsorption of molecules on a solid surface, which is represented by the ice-like associates of water molecules [8]. When the crystal lattice is formed in cavities at the hydrate formation temperature, the pressure increases to the value of saturated vapor of the absorbed components. At the same time, the hydrate former in the structure is in a pseudo-liquified state. If the temperature and pressure conditions of hydrate formation correspond to the supercritical temperatures and the subcritical pressures of an absorbed component, then its saturated vapor in the hydrate cavity is condensed with release of heat energy. If the temperature and pressure conditions of hydrate formation correspond to the supercritical temperatures and the pressures of an absorbed component, then with its absorption the heat energy is released and this energy is equal to a change of enthalpy or the internal energy. The process of absorption of the molecules is in energy (dynamic) equilibrium with a reverse process (desorption) [9].

The energy processes during formation of clusters and lattice cells of the crystal lattices of the hydrates are caused by release of energy (kJ/mol) and according to the Hess's law they can be determined in the systems:

— hydrate former–solid phase of water (ice)

$$\Delta H_1 = Q_s \pm L_{i-h}n, \qquad (7)$$

— hydrate former–liquid phase of water

$$\Delta H_2 = Q_s + (H_i \pm L_{i-h})n = H_1 + H_i n, \qquad (8)$$

— hydrate former under the critical conditions–liquid phase of water

$$\Delta H_3 = Q_s + (H_i \pm L_{i-h})n + Q_c = H_2 + Q_c = H_1 + H_i n + Q_c. \qquad (9)$$

In the equations (7)–(9): L_{i-h} — the specific energy of restructuring ice into the hydrate lattice (the sign „+" means

Table 1. Data on the heats of formation of the crystal lattice from the ice-like associates of water molecules

T, K	H_i, kJ/mol	C_i, kJ/mol·K	κ, kJ/mol
223.15	3.98246	0.03154	3.05675
233.15	4.38978	0.03275	3.24629
243.15	4.79711	0.03390	3.44683
253.15	5.20443	0.03500	3.65675
263.15	5.61933	0.03603	3.86212
273.15	6.01909	0.03693	4.06871

Table 2. Comparison of the values of the specific heat of formation of hydrates from ice in the first quadrupole point, which are obtained experimentally and computationally

Hydrate former	Reference	Experimental values ΔH_1, kJ/mol	Calculated values ΔH_1, kJ/mol	Δ, %
CH_4	[10]	18.13	17.98	0.83
	[11]	18.01		0.17
C_2H_6	[10]	25.70	26.51	3.1
	[12]	26.38		0.49
C_3H_8	[13]	26.6	26.89	1.08
	[14]	26.97		0.30
	[15]	26.54		1.31
	[10]	27.00		0.41
	[16]	26.50		1.46
i-C_4H_{10}	[10]	31.07	31.56	1.56
	[1]	32.28		2.26
	[17]	31.00		1.79
CO_2	[17]	24.30	24.85	2.24
	[11]	24.30		2.24
H_2S	[18]	28.97	27.56	4.23
N_2	[19]	15.97	15.85	0.75
	[19]	15.95		0.63
O_2	[19]	13.36	13.39	0.22
Kr	[20]	19.54	20.11	2.88
Xe	[20]	25.27	25.20	0.28

the exothermic process, the sign „–“ means the endothermic process); H_i — the specific energy of formation of ice from liquid water; Q_s — the specific energy of absorption of hydrate former molecules by clusters of the lattice cell of the hydrates; Q_c — the specific energy of ab of hydrate former molecules under the critical conditions.

The specific energy of absorption of hydrate former molecules by clusters of the lattice cell of the hydrates can be approximately evaluated through a dependence with the boiling temperature [9] found by the formula developed by the authors [8]:

$$Q_s = \frac{\sum\limits_i m_i r_i}{\sum\limits_j b_{1_j}}, \tag{10}$$

where r_i — the specific heat of absorption of the i-th hydrate former (it the first approximation it is equal to the heat of condensation); m_i — the number of absorbed molecules of the i-th hydrate former by clusters of the lattice cell of the hydrates [2]; b_{1_j} — the number of cavities of the lattice cell of the hydrates.

The specific energy of formation of the crystal lattice from the ice-like associates of water molecules can be determined from reference data or by the dependences developed by the author [9] in the temperature and pressure conditions of the hydrate formation process.

$$H_i = C_i T_W - \kappa, \tag{11}$$

$$H_i = H_{i_0} - 0.16554 P_w - 0.00045 P_w^2, \tag{12}$$

where C_i — the heat capacity of ice, [kJ/(mol · K)]; κ — the specific heat of the crystal lattice (Table 1); H_{i_0} — the specific heat of formation of the ice-like associates of water molecules at the temperature of 273.15 K; P_w — the pressure of hydrate formation, [MPa].

The process of restructuring of the ice lattice into the hydrate one can be exothermic or endothermic. For example, based on analysis of the experimental data (see below), it was determined by the author that at the temperature of hydrate formation in the first quadrupole point the value of L_{i-h} is 1.10 kJ/mol for

Table 3. Comparison of the values of the specific heat of formation of hydrates from water in the first quadrupole point, which are obtained experimentally and computationally

Hydrate former	Reference	Experimental values ΔH_2, kJ/mol	Calculated values ΔH_2, kJ/mol	Δ, %
CH_4	[11]	53.50	53.34	0.30
	[10]	54.19		1.58
	[14]	53.81		0.88
	[21]	53.32		0.00
C_2H_6	[12]	68.24	68.95	1.04
	[10]	71.80		3.63
	[14]	71.34		3.41
C_3H_8	[22]	133.98	139.20	3.82
	[15]	134.20		3.66
	[23]	137.00		1.59
	[23]	134.00		3.81
i-C_4H_{10}	[22]	138.00	139.28	0.92
	[1]	137.60		1.21
	[10]	133.20		4.46
C_2H_2	[24]	62.80	62.77	0.05
CO_2	[22]	60.37	62.14	2.89
	[1]	59.90		3.67
	[25]	63.60		2.32
H_2S	[18]	62.37	64.32	3.08
SO_2	[24]	69.50	69.74	0.34
N_2	[19]	49.58	52.11	4.98
O_2	[19]	49.57	49.97	0.80
Cl_2	[24]	66.99	67.09	0.15
Ar	[26]	55.10	53.06	3.77
Kr	[24]	58.20	56.12	3.64
Xe	[20]	61.77	61.54	0.37

methane, 0.88 kJ/mol for ethane, 1.28 kJ/mol for ethylene, 1.20 kJ/mol for hydrogen sulfide, 0.33 kJ/mol for sulfur dioxide, 0.8 kJ/mol for nitrogen, 0.75 kJ/mol for oxygen, minus 0.59 kJ/mol for propane, minus 0.32 kJ/mol for isobutane.

3. Results and discussion

A quite large amount of experimental data is accumulated for gaseous and liquid hydrate formers. The values of the specific heat of formation (dissociation) of the gas hydrates from liquid water, ice hydrates of liquified gases as well as mixed systems of the hydrate formers, which are experimentally and computationally obtained, are shown in Tables 2–5.

As it is clear from Tables 2–5, the discrepancies of the values of the parameters, which are calculated according to the developed method and the known experimental data are within the range from 0 to 4.98 % and on average they are 1.96 %. For a number of the hydrate formers (for example, ethane, carbon dioxide) there is a quite significant spread of the experimental values and the causes are not

Table 4. Comparison of the values of the specific heat of formation of hydrates of the liquified gases under various temperature and pressure conditions, which are obtained experimentally and computationally

Hydrate former	Temperature and pressure conditions	Reference	Experimental values ΔH_3, kJ/mol	Calculated values ΔH_3, kJ/mol	Discrepancy, %
i-C_4H_{10}	275.10 K; 0.165 MPa	[27]	197.6	193.1	2.3
CO_2	283.52 K; 9.8 MPa	[28]	52.58	54.90	4.3
	286.15 K; 40 MPa		53.38	53.75	0.7
C_2H_6	288.35 K; 5 MPa		74.79	73.03	2.4
	290.61 K; 20 MPa		62.20	64.46	3.6
C_3H_8	281.00 K; 1.54 MPa	[29]	109.27	107.52	1.6

Table 5. Comparison of the values of the specific heat of formation of mixed hydrates under various temperature and pressure conditions, which are obtained experimentally and computationally

Hydrate former	Temperature and pressure conditions	Reference	Experimental values	Calculated values	Discrepancy, %
98.8 % CH_4+1.2 % C_2H_6	$P = 7.03$ MPa; $T = 282.99$ K	[30]	66.47	66.81	0.5
98.8 % CH_4+1.2 % C_2H_6	$P = 0.1013$ MPa; $T = 224.66$ K	[30]	22.14	22.12	0.0
65 % CH_4+35 % C_2H_6	$P = 0.1013$ MPa; $T = 201.61$ K	[30]	24.45	23.97	2.0
95 % CH_4+5 % CO_2	$P = 0.1013$ MPa; $T = 205.20$ K	[31]	17.30	18.13	4.7
	$P = 0.1013$ MPa; $T = 205.20$ K		53.40	55.55	3.9
90 % CH_4+10 % CO_2	$P = 0.1013$ MPa; $T = 208.01$ K	[31]	16.90	17.24	2.0
	$P = 0.1013$ MPa; $T = 208.01$ K		53.00	54.37	2.5
94.4 % CO_2+5.6 % C_5H_{10}	$P = 0.5$ MPa; $T = 285.10$ K	[32]	68.30	70.17	2.7

always clear. As stated in the introduction, it can be explained by difficulties in determining the specific energies of the nonstoichiometric compounds for preparing tests for homogeneous samples without macroscopic defects, by purity of calorimetric measurements and sometimes by systematic errors. The average discrepancy is 1.41 % (Table 2), 2.17 % (Table 3), 2.48 % (Table 4), 2.29 % (Table 5). This accuracy makes it possible to state that the mathematical description proposed in the present study has a sufficient degree of reliability and to make conclusions about „higher-quality“ results obtained by means of the proposed procedure. Besides, it is necessary to note that more modern experimental studies show high accuracy of the results obtained using the proposed method.

Conclusion

The study has analyzed the methods of determining the heat of formation of the clathrate hydrates. It presents a description of the hydrate formation process, which takes into account the energy processes when forming clusters and lattice cells of the crystal lattices of the clathrate hydrates. And based on it, the physical-mathematical model of the process in the following systems is developed: hydrate former–solid phase of water (ice), hydrate former–liquid phase of water, hydrate former under the critical conditions–liquid phase of water.

It includes comparison of the values of the specific heat of formation (dissociation) of the gas hydrates from

liquid water, ice hydrates of liquified gases as well as mixed systems of the hydrate formers, which are obtained experimentally and computationally as per the proposed procedure. The discrepancies of the values are within the range from 0 to 4.98 % and on average they are 1.96 %, thereby making it possible to state that the proposed method has a sufficient degree of reliability. Unlike the known procedures, using the developed procedure, it is possible to more exactly determine enthalpy parameters of the hydrate formation systems within the wide range of the temperature and pressure conditions for systems of a various state of matter. The accuracy of the results obtained for the clathrate hydrates makes it possible to discuss the prospects of application of the method with certain assumptions and corrections for the other clathrate systems as well, which are studied in terms of condensed matter physics.

Conflict of interest

The author declares that he has no conflict of interest.

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