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RESEARCH INTO PECULIARITIES OF PHASE TRANSITIONS DURING THE DISSOCIATION OF GAS HYDRATES

Purpose. Analytical study of the dissociation process of gas hydrates taking into account the peculiarities of phase transitions occurring during their dissociation and described by the Clausius-Clapeyron equation.

Methods. The research uses an integrated approach, which includes the analysis and generalization of literature sources devoted to studying the peculiarities and thermobaric properties of gas hydrates; processes of hydrate formation and accumulation; methods for the development of gas hydrate deposits and technologies for extracting the methane gas from them; analytical calculations of phase transitions of gas hydrates.

Findings. The conditions for the formation of gas hydrate deposits have been analyzed and the peculiarities of stable existence of gas hydrates have been revealed. The existing experience in the development of gas hydrate technologies by leading scientists, world research laboratories, advanced design institutes and organizations is summarized. The mechanism of hydration formation in rocks is studied and some classifications of gas hydrate deposits occurring in sedimentary rock stratum are presented. It has been determined that gas hydrates in natural conditions usually occur not only in the form of pure hydrate reservoirs, but most often contain a certain share of rock intercalations, which makes the deposit structure heterogeneous. The mechanisms of hydrate formation and dissociation of gas hydrates have been revealed. It has been determined that the Clausius-Clapeyron equation in a modified form can be used to describe phase transitions both during the formation and dissociation of gas hydrates, taking into account the deposit heterogeneity.

Originality. The Clausius-Clapeyron equation for the analysis of phase transformations in solid phases during hydrate formation and dissociation of gas hydrates is defined more exactly, taking into account the consumption of additional heat due to the influence of the properties of rock intercalations.

Practical implications. The research results are useful for designing the rational thermobaric parameters (pressure and temperature) in the dissociation of natural or technogenic gas hydrates, as well as for optimal control of the kinetics of the process.

Keywords: gas hydrate, dissociation, phase transition, heterogeneity, thermobaric parameters.

Introduction.

Ukraine is one of the largest European countries with a significant industrial potential. Today, the coal industry is a strategic state sector, however, the Ukrainian economy is largely dependent on the import of additional energy resources, in particular natural gas and oil. The availability and timely supply of these liquid hydrocarbons are essential conditions for the proper functioning of the mining and industrial complex not only in Ukraine, but also in most European countries. In the current economic and political conditions, to ensure the economic stability of the country, it is relevant to increase the level of energy independence by introducing and developing alternative fuels [1, 2], innovative technologies for mining of minerals [3-5], in particular coal [6, 7] and iron ore [8], and also introducing the energy-saving technologies [9-11].

Along with methane from coal deposits, shale gas and gas from compacted sandstones, it is promising to recover gas from gas hydrate deposits. Today, the leading countries of the world, such as India, Canada, China, Germany, Norway, the USA, Japan and others, are engaged in the development of technologies for the recovery of gas from gas hydrate deposits. A

significant energy reserve for Ukraine are gas hydrate deposits, which are located in the bottom part of the Black Sea [12-14]. In addition, the possibility of using gas hydrate technologies for the accumulation of coalmine methane, which can be utilized and used as an additional type of fuel, is of particular interest [15, 16].

Gas hydrates are formed by including gas molecules (volatile liquids) in the cavity of the scaffold (crystal lattice) constructed of water molecules under thermodynamic conditions specific for each gas component. In case of their violation, the “guests” molecules, that is, gas molecules held in the skeletal water scaffold by weak Van der Waals forces, leave it, and the hydrate is dissociated into gas and fresh water with significant heat absorption [17]. Since gas hydrates belong to the class of nonstoichiometric clathrate compounds and are molecular crystals, research into crystal hydrates morphology is of great importance and gives an ability to study in depth many properties and characteristics of gas hydrates [18]. The morphology of gas hydrate crystals is influenced by the temperature and pressure of hydrate formation, the composition of the water and gas phases, as well as the rate of water and gas diffusion to the surface of

crystal growth. In this regard, conducting the research on the development of gas hydrate technologies, determining the peculiarities of the gas hydrate formation and dissociation kinetics, as well as studying the effect of gas hydrate self-preservation is an urgent and important task.

Actual scientific research and publications analysis.

Today, in many countries of the world, prospecting programs and research centers for the study of gas hydrates have been created, since the production of gas hydrate can help in solving the world energy problem. However, it is extremely important to create and apply methods and technologies for the development of gas hydrate deposits and methane gas extraction [19]. The technologies for the development of gas hydrate deposits and the production of methane gas from them are related to the physical-chemical properties of these clathrate compounds and are based on dissociation, due to which gas hydrates are dissociated into gas and water. It is possible to release the gas contained in the hydrates by shifting the equilibrium constants of their stable existence. Today, there are three main methods for extracting the gas from gas hydrates [20, 21]:

- thermal method based on heating the deposit;
- depression method, which is aimed at reducing the pressure in gas hydrate;
- method of replacing or adding chemical substances, which are catalysts for the dissociation process of a gas hydrate deposit.

The main features of each of the methods will be discussed below [22].

The thermal method for the gas hydrate deposits development can be used for strata with high content of hydrates with a small share of rocks inclusions. When applying this method, it is necessary to take into account the total energy consumption for dissociation of crystal-line hydrates and the amount of energy that can be obtained from the extracted gas.

The method of the pressure reduce is suitable for gas hydrate layers, in which the saturation of hydrates is low, and gas or water have not lost their mobility. The technology is most effective when gas hydrates are located near the free gas formation. When the volume of free gas decreases, there is a constant change in the equilibrium between hydrate and gas, which causes the gas hydrate continues to emit

a gas that fills the lower layer. The main disadvantage of the pressure reduce method is the formation of gas hydrates in the borehole zone, which complicates the gas extraction process.

The method of substitution or addition of chemicals is based on a shift in the phase equilibrium of gas hydrate, which leads to its decomposition. The substitution is to displace methane from the “cells” of the clathrates by filling them with another gas, such as carbon dioxide. Methanol, glycol, ethanol and saline solutions can be used as chemical substances used in the development of gas hydrate deposits.

The greatest success in studying the potential of gas hydrate deposits has been achieved by Japan. Back in the early 2000s, the country began implementing a gas hydrate development program. Japan is developing research cooperation with Canada and the United States. There is an extensive research program in Canada; wells at the mouth of the Mackenzie River (Mallik field) were drilled together with Japanese specialists [23, 24]. Research projects to study gas hydrates in the United States are concentrated in the permafrost zone in Alaska and in the deep-water part of the Gulf of Mexico [25].

This paper [19] provides the results of geological studies of gas hydrates and carbonate deposits in the Northern Gulf of Mexico. The main directions of the Joint Industry Program further development are presented, including the results of deep-water drilling of hydrate zones, which have been selected as the most promising for the future successful production of gas hydrate.

Significant successes in the study of gas hydrates have been achieved in the countries such as South Korea, China and India. South Korea is engaged in assessing the gas hydrate potential in the Sea of Japan. Studies have shown that the Ulleung field is the most promising for further development [26, 27]. India developed its national research program to study gas hydrates back in the mid-1990s. Its main research object is the Krishna-Godavari Basin in the Bay of Bengal [28, 29]. The Chinese program includes exploration of the South China Sea shelf near Guangdong Province and permafrost on the Qinghai Plateau in Tibet [30, 31].

Scientists from Nigeria (University of Lagos) have conducted a number of studies, including the development of a technology for transporting the natural gas in the gas hydrate

state, which can be considered economically feasible compared to the usual method of transporting the liquefied natural gas under certain conditions, given the distance of transportation [32].

American and Chinese scientists [33] have determined the optimal storage parameters for gas hydrates at atmospheric pressure and subzero temperature using Romanov spectroscopy. As a result, the researchers have managed to describe the mechanism of not only the gas hydrate formation and dissociation, but also the long-term storage of this product at a subzero temperature.

The process of natural gas transformation into gas hydrate state with the subsequent formation of gas hydrate structures on the basis of using the self-preservation effect has also been studied [34]. Several stages of gas hydrate formation, the formation of pellets from it, their transportation by land transport and controlled dissociation of the finished product are described.

The paper of [35] considers the possibility of using the self-preservation effect of gas hydrates as an economically feasible method of storing and transporting the natural gas at higher temperature and lower pressure as compared to the usual method of transporting the liquefied gas. The authors have performed laboratory experiments on methane hydrate dissociation in order to reveal its potential for use when storing and transporting the hydrocarbon gases. It has been determined during the research that extremely slow dissociation is observed in the range of subzero temperatures. The obtained results are promising for the practical application of the self-preservation properties of gas hydrates for storage and transportation of natural gas.

Specificity of the hydrate formation and accumulation processes.

With regard to the formation of gas hydrate deposits in the seas and oceans, it should be noted that gas hydrate is accumulated, as a rule, not in free space – sea water, but in the bottom rock mass. An important role in the process of natural gas hydrate formation is assigned to the parameters of pressure and temperature, as well as to the properties and peculiarities of the environment, in which the processes of hydrate formation and subsequent hydrate accumulation actually take place [36]. Since gas hydrates accumulate in sedimentary rocks, these rocks become

impermeable. A closed space is formed, capable of self-compaction, in which gas accumulates, tending to rise upward. The more free gas penetrates into the hydrate formation zone, the stronger the gas hydrate reservoir becomes. After complete saturation of the gas hydrate layer, free gas can be accumulated already under it.

To assess the energy potential of gas hydrates, it is important to determine the possible variants of their location in the sedimentary stratum and to determine the properties of hydrate-containing reservoirs. Having analyzed the existing data on the occurrence of gas hydrates within the Earth's interior, it can be concluded that gas hydrates exist in rocks in the form of minor intercalations, clusters, veins and massive reservoirs (Fig. 1) [37].

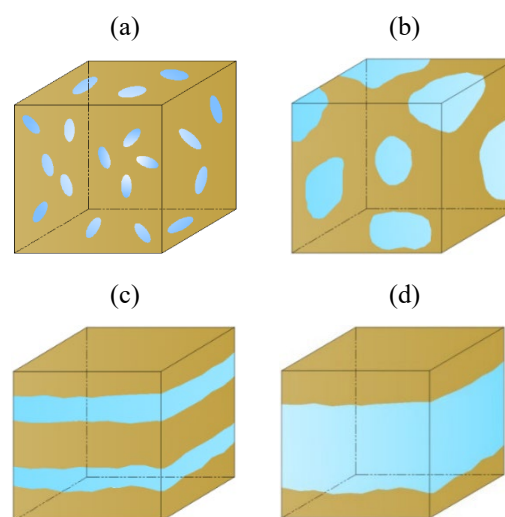


Fig.1. Occurrence of gas hydrates in the sedimentary rock stratum: (a) minor intercalations; (b) clusters; (c) veins; (d) massive reservoirs

Geological and geophysical characteristics of gas hydrate deposits occurring in sedimentary rocks can be a sign, according to which these deposits are divided into three types (Fig. 2) [38]. The first type includes gas hydrate deposits, under which there is natural gas in a free form. The equilibrium line of hydrate formation for type I coincides with the bottom of the gas hydrate deposit. The second type is gas hydrate deposits, under which there is an aquifer. The third type includes deposits occurring between the rocks, under which there is neither free gas nor free water.

Gas hydrate deposits within the Black Sea bottom occur not only in the form of pure hydrate reservoirs, but, most often, with rock

intercalations, which makes the deposit structure heterogeneous [39].

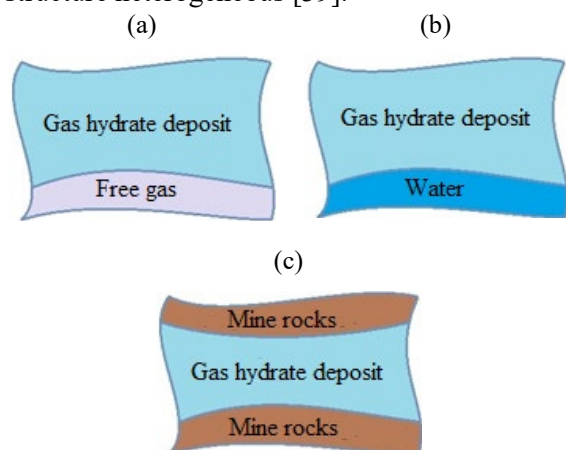


Fig. 2. Types of gas hydrate deposits according to the classification by geological and geophysical peculiarities of occurrence of gas hydrates: (a) first type; (b) second type; (c) third type

Therefore, the study of the dissociation conditions of gas hydrates with a heterogeneous structure, in terms of studying such important characteristics as heat of dissociation, pressure and temperature, is a relevant and important issue.

Specificity of the dissociation process of gas hydrates.

The dissociation of a gas hydrate, which contains a share of rock intercalations, begins at the moment when the energy of the process “gas hydrate → water + gas”, represented in the refined Clausius-Clapeyron $\frac{dT}{dP} = T \frac{\Delta V}{Q - \delta Q}$ equation, where Q is the thermal effect of phase transformations, δQ – the thermal effect of defect relaxation, becomes less than zero with the simultaneous action of two opposite factors – enthalpy ΔH and entropy $T\Delta S$:

$$\Delta G = \Delta H - T\Delta S + P\Delta V < 0, \quad (1)$$

where ΔG – change in Gibbs energy.

A factor that causes a sharp increase in the dissociation temperature of gas hydrates at a relatively low pressure is, as a rule, a sharp decrease in the entropy of the dissociation process ΔS as the gas phase is compressed.

Following from inequality (1), the differences in the behavior of gas hydrates, the dissociation products of which are condensed phases or substances similar in properties to condensed phases, in the range of pressures and

temperatures are determined and varied by the aggregate characteristic $P\Delta V$. In the case of gases, under normal conditions for the presence of guest molecules in the crystal lattice, the $P\Delta V$ index has a significant influence at high pressures. At relatively low pressures, the absolute value of $P\Delta V$ is significant, but slightly different for clathrate compounds with different guest molecules. At the same time, at relatively high pressures, the value of $P\Delta V$ components plays an important role even with insignificant differences in the value of ΔV . When the volume of clathrate is less than the volume of condensed products of its dissociation ($\Delta V > 0$), the stabilization of the clathrate phase occurs due to an increase in pressure according to the Clausius-Clapeyron equation.

The compressibility of the condensed phase is lower than the compressibility of the liquid and fluid phases. Therefore, for gas hydrates of many gases at a certain pressure, the value of ΔV becomes equal to zero or even less than zero, which is represented in the form of a maximum on its dissociation curve. An increase in the gas hydrate density leads to a shift of this maximum towards higher pressures and temperatures. These maxima are typical for the dissociation curves of methane and ethane hydrates.

The presented analysis of the behavior of gas hydrates under high pressures is based on the system of Van der Waals radii determined under normal conditions and is approximate in nature, since the study of the Van der Waals radius system at high pressures has only an illustrative sense. However, even in the conditions of a fairly simple approach, using the available data of analytical and experimental studies, it is possible to conduct a detailed analysis and reveal the patterns of the hydrate formation process at high pressures

The gas hydrate dissociation occurs when thermobaric parameters change, which leads to the clathrate structure destabilization and the release of gas. Given the fact that gas hydrate deposits of a heterogeneous structure contain mineral impurities and intercalations, additional energy should be used for dissociation. Suppose that:

$G_{ice} = \Delta H - T\Delta S + P\Delta V$ – free Gibbs energy for ice;

$G_{rock} = \Delta H - T\Delta S + P\Delta V$ – free Gibbs energy for rock intercalations.

The chemical potential of the liquid phase – water, containing impurities in the form of salts present in it, is expressed as follows:

$$\Delta G_{liq}(T) = \Delta G_{liq}^0(T) + RT \ln x_{liq},$$

where x_{liq} – molar fraction of dissolved salts located on the surface of bottom intercalations.

The chemical potential of the solid phase – rock intercalations – is written in the form of an equation:

$$\Delta G_{sol}(T) = \Delta G_{sol}^0(T) + RT \ln x_{sol},$$

where ΔG^0 – standard Gibbs energy of the solid phase.

The equilibrium condition implies:

$$\Delta G_{liq}^0(T) + RT \ln x_{liq} = \Delta G_{sol}^0(T) + RT \ln x_{sol},$$

where ΔG_{liq}^0 and ΔG_{sol}^0 – standard Gibbs energy of liquid and solid phases, respectively; x_{sol} – molar fraction of insoluble intercalations.

Using the ratio of molar quantities ($x_{liq} = k \cdot x_{sol}$, where k – is a function of temperature), the phase temperature T_{ph} can be calculated, at which the transition of an aqueous solution from solid state to liquid (melting), or from liquid state to solid (freezing point) begins:

$$\Delta G_{sol}(T) - \Delta G_{liq}(T) = RT_{ph}(1-k)x_{liq}.$$

For pure water, these two chemical potentials (ΔG_{liq} and ΔG_{sol}) must be equal to zero. Thus, if to assume that T_{ph}^0 is the pure water freezing temperature (273 K), taking into account the refined Clausius-Clapeyron $\frac{dT}{dP} = T \frac{\Delta V}{Q - \delta Q}$ equation, the change in transition temperature of one aggregate state of an aqueous solution to another can be found:

$$\Delta T_{ph} = -\frac{\Delta T_{ph}}{\Delta T_{ph}^0} = -\frac{RT_{ph}^0}{Q - \delta Q}(1-k)x_{sol},$$

where ΔT_{ph} – decrease/increase of freezing temperature depending on the amount of salts.

The physical content of the temperature function is as follows: when $k < 1$, there is a decrease in the freezing point (if the rock intercalations contain water-soluble minerals), and when $k > 1$ (if there are water-insoluble impurities in the rock intercalations), an increase

in the freezing point occurs. Phase diagrams of these two cases are shown in Fig. 3.

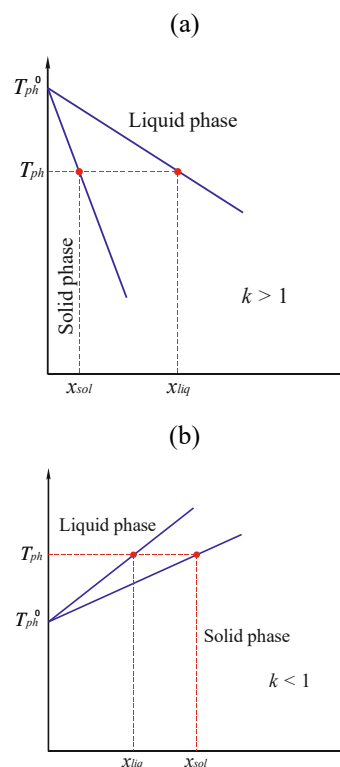


Fig. 3. Transformation of a substance phase state when the freezing point changes

When summarizing the above, it is obvious that the Clausius-Clapeyron equation in the refined form, which is given above, can be used to analyze phase transformations in solid phases during hydrate formation and dissociation of gas hydrates. By influencing the solid phase, it is possible to increase the internal energy of this phase, which, when the system tends to equilibrium under certain conditions, has an effective influence on the processes of phase transformations under pressure, and also changes their kinetics. One of the possibilities of a significant increase in the internal energy in the gas hydrate initial state before the phase transformations is the accumulation of limiting concentrations of various defects and cavities in it. The relaxation energy of the defects is the very thermodynamic stimulus for phase transformations and solid-phase reactions that can be purposefully controlled.

Under normal conditions, the relaxation energy of defects is dissipated upon return and recrystallization. Their temperature ranges, as a rule, do not coincide with the area of phase transformations, and the processes proceed independently, without influencing each other.

However, the range of return and recrystallization temperatures can be approximated to the phase transformation temperatures as follows:

$$T = T_0 + k\sqrt{T_0}, \quad (2)$$

where T_0 – recrystallization temperature under normal heating; k – the coefficient that depends on the rock nature in the gas hydrate.

The processes of relaxation of defects during return and recrystallization proceed rather slowly, from which it follows that the possibility of activating the phase transformations in the vast majority of cases is quite feasible. Thus, the results obtained indicate that the dissociation of gas hydrates requires the use of additional heat according to the refined Clausius-Clapeyron formula, which can be regulated by increasing the temperature according to the Formula (2).

Conclusions.

1. Currently, gas hydrates are an alternative source of energy, which can be considered as an additional energy. This requires the development of appropriate technical solutions, the study of the technological peculiarities of the existing methods for gas recovery from hydrates, as well as the determination of the dissociation process thermobaric parameters. In addition, it is important to study the possibility of using gas hydrate technologies for converting the hydrocarbon gases into a hydrate state for their storage.

2. As a result of the analysis of the conditions for hydrate formation, the peculiarities of the formation and stable occurrence of gas hydrates in natural conditions have been revealed. Possible variants of the existence of gas hydrate deposits in the sedimentary rock stratum have been identified. It has been revealed that gas hydrates usually occur not only in the form of pure hydrate reservoirs, but most often contain a certain share of rock intercalations, which makes the deposit structure heterogeneous.

3. It has been determined that the Clausius-Clapeyron equation $\frac{dT}{dP} = T \frac{\Delta V}{Q - \delta Q}$

in a modified form can be used to describe phase transitions both during the formation and dissociation of gas hydrates. One of the

possibilities of an increase in the internal energy in the gas hydrate initial state before the phase transformations is the accumulation of limiting concentrations of various defects and cavities in it. The relaxation energy of the defects is the very thermodynamic stimulus for phase transformations that can be purposefully controlled.

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ДОСЛІДЖЕННЯ ОСОБЛИВОСТЕЙ ФАЗОВИХ ПЕРЕХОДІВ ПРИ ДИСОЦІАЦІЇ ГАЗОВИХ ГІДРАТІВ

Мета. Аналітичні дослідження процесу дисоціації газових гідратів з урахуванням особливостей фазових переходів, що відбуваються при їх розкладанні та описуються рівнянням Клаузіуса-Клапейрона.

Методика. У роботі застосовано комплексний підхід, який включав аналіз та узагальнення літературних джерел, присвячених вивченню особливостей та термобаричних властивостей газових гідратів; процесів гідратоутворення й гідратонакопичення; методів розробки газогідратних покладів і технологій вилучення з них газу метану; проведення аналітичних розрахунків фазових переходів газогідратів.

Результати. Проаналізовані умови формування газогідратних покладів та встановлені особливості стабільного існування газогідратів. Узагальнено існуючі напрацювання провідних вчених у галузі розробки газогідратних технологій, науково-дослідних лабораторій світу, передових проектних інститутів і організацій. Розглянуто механізм гідратоутворення у гірських породах та приведено деякі існуючі класифікації газогідратних покладів у осадовій товщі порід. Встановлено, що газові гідрати у природних умовах, зазвичай, залягають не лише у вигляді чистих гідратних пластів, а, найчастіше містять певну частку породних включень, що робить структуру покладу неоднорідною. Виявлено механізми гідратоутворення та дисоціації гідратів газу. Встановлено, що рівняння Клаузіуса-Клапейрона у видозміненому вигляді може застосовуватися для описання фазових переходів як при утворенні, так і при дисоціації газогідратів з урахуванням неоднорідності покладу.

Наукова новизна. Уточнено рівняння Клаузіуса-Клапейрона для аналізу фазових перетворень у твердих фазах при гідратоутворенні й дисоціації газових гідратів, що враховує затрати додаткової кількості тепла від впливу властивостей породних включень.

Практичне значення. Результати досліджень є корисними для проектування раціональних термобаричних параметрів (тиску та температури) при розкладанні природних або техногенних газогідратів та оптимального керування кінетикою процесу.

Ключові слова: газогідрат, дисоціація, фазовий перехід, неоднорідність, термобаричні параметри

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