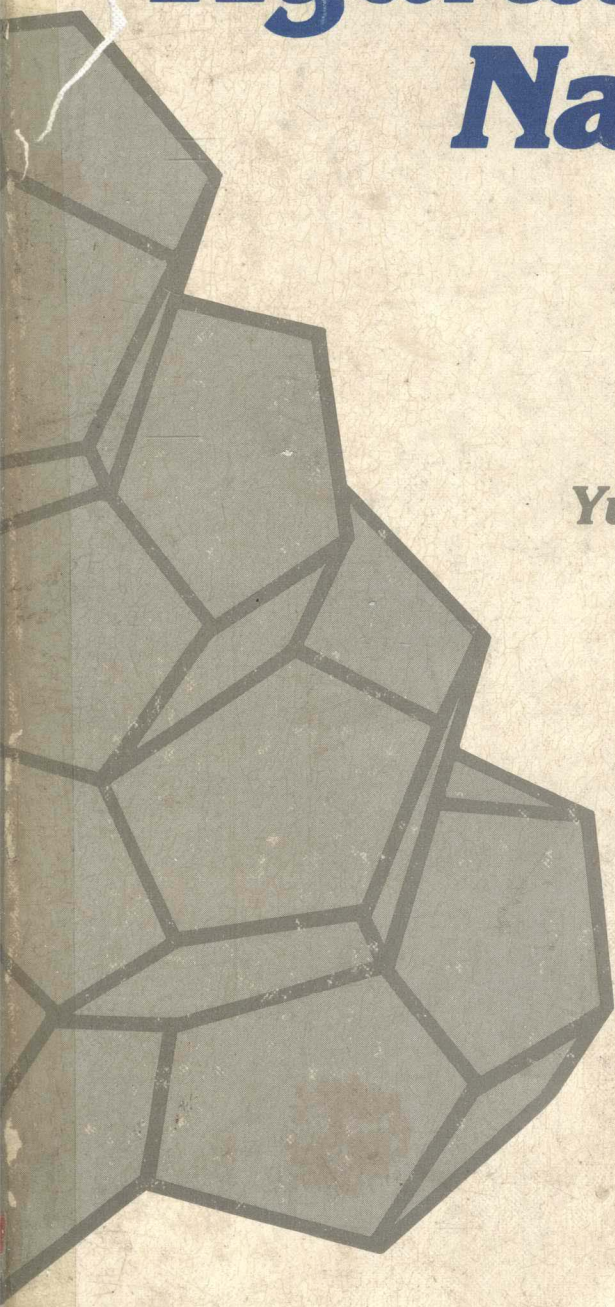


Hydrates of Natural Gas

by
Yuri F. Makogon



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TRANSLATOR'S NOTE

While exploring for oil and gas in Siberia, the Russians have discovered within the last 15 years large deposits of solid natural gas in reservoir rocks within different permafrost zones. Also, in operating their first pipelines laid in Arctic regions, the Russians have encountered many new problems associated with the formation of gas hydrates at low temperatures. In this connection, several years ago, Russian scientists conducted multifaceted and thorough research on hydrate gas, and in particular on conditions of its formation in permafrost strata as well as in pipelines operated under Arctic climatic regimes. The project's theoretical, experimental, and field studies were carried out by Russia's most prestigious petroleum research institute in cooperation with institutes of Arctic geology and permafrost. The results of this study were published in 1974 in Russian, and they point to a great potential for discovering deposits of solid natural gas not only in the permafrost zones but in some offshore areas as well, regardless of geographic latitude. The book in question is over 200 pages (about 50,000 words) and includes 115 diagrams, drawings, and photos, 30 tables, and 55 recent Russian references. To date, no comparable research work on this specific subject has ever been completed or published anywhere.

W. J. Cieslewicz

INTRODUCTION

The first published study on hydrates of gases goes back to 1811; it describes experiments carried out by English chemist H. Davy. Passing chlorine gas through water under atmospheric conditions at temperatures near 0°C. in a glass retort, Davy obtained a yellow precipitate. He identified it as chlorine hydrate; however, because of instability of the compound and the primitive instrumentation used in those days, Davy was unable to study thoroughly its properties. The first analyses of the hydrates of chlorine were carried out in 1823 by Faraday.

Between 1820 and 1880, virtually no studies of any kind were made on hydrates of gases, and it was only during the subsequent decades that the scientific interest in these compounds revived. During the following 50 years, the hydrates of the majority of individual gases and of several gas mixtures were obtained. In 1884, Rosebaum proposed the formula $8\text{H}_2\text{O}\cdot\text{Cl}_2$ for chlorine hydrate. Studies were carried out on the effect of pressure and temperature on the formation of hydrates of different gases; approximate composition of these hydrates was also determined and various phase diagrams were constructed. The new concepts of thermodynamics, first introduced during this period, were given proper consideration in analyzing the experimental data on hydrates.

Nevertheless, until the beginning of the 1930s, all research on gas hydrates carried out during the preceding 120 years was purely academic in character. The hydrates of gases did not have industrial application then, and neither did they interfere with the technological process of that time. During the 1930s, however, the rapid development of gas-producing industries called for serious applied research on gas hydrates, primarily to develop methods of preventing their formation and accumulation in wells drilled for gas and in pipelines.

During that period, Hammerschmidt in a published article showed that the problems often experienced by gas pipelines during the winter months

were caused not by the freezing of water in the pipeline, an assumption very common until then, but by formation of gas hydrates.

Thus began the third stage of gas hydrate studies. This period of applied research lasted for more than 20 years during which time practically all known methods of combating gas hydrate formation were developed.

Since the 1950s, investigations have been made on some properties of gas hydrates with employment of modern instrumental methods; serious theoretical research is also developing. At the present time this effort is beginning to yield a twofold result: (a) the methods of preventing hydrate formation are being perfected, and (b) gas hydrates are finding practical utilization in different industrial processes. Of special importance are the studies that led to the discovery of deposits of solid hydrates of natural gas in the sedimentary strata. This discovery was made by a group consisting of the following scientists: V.G. Vasil'ev, Yu. F. Makogon, F. A. Trebin, A. A. Trofimuk, and N. V. Cherskii.

Significant contributions to the study of gas hydrates were made also by the following scientists: B. A. Nikitin, I. N. Strizhev, I. E. Khodanovich, M. Kh. Shakhnazarov, G. A. Sarkis'iants, P. A. Tesner, Yu. P. Korotaev, F. K. Andriushchenko, V. A. Khoroshilov, S. Sh. Byk, V. I. Fomin, V. P. Tsarev, V. P. Vasil'chenko, V. I. Shagaidenko, A. M. Kuliev, R. M. Musaev, A. Dzhabadov, and A. Aliev.

Hundreds of articles have been published on the subject of hydrates, and a whole series of special laboratories have been established to study gas hydrates both in the earth's crust and surface and in the atmosphere. Still, a very great number of unsolved problems remain regarding the hydrates.

In this book the author gives both the results of earlier investigations already published and the results of studies of the last 10 years carried out by the author himself in cooperation with researchers working at a number of different scientific institutes and laboratories. The results of recent industrial research on gas hydrates are also included.

The author also acknowledges the assistance obtained from G. S. Lutoshkin, who reviewed this book, and also from the members of the faculty and staff of the laboratory in the Department of Development and Production of Gas and Gas Condensate Deposits of the Gubkin Petrochemical and Gas Industry Institute in Moscow, who participated in the discussion of the principal results of the author's research work described in this book.

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CHAPTER 1

PRESENT STATE OF THE PROBLEM OF NATURAL GAS HYDRATES

Problems must be solved nowadays related to the prevention of hydrate formation along the entire system of gas installations, starting with the producing wells, through transmission pipelines and finally, on occasion, in the local distribution networks supplying gas to the consumers.

To combat the formation of hydrates, the gas-producing industry in Russia consumes every year over 60,000 tons of alcohol. In addition, it is necessary to solve problems of hydrate prevention in a number of technological processes involving treatment of natural gases.

On the other hand, the property of natural gases to form hydrate compounds with water could be profitably utilized in a number of ways, especially for: desalinization of water in relatively small quantities, storage and separation of gases, increasing of pressures, and elimination of high temperature fogs. Unfortunately, due to inadequate study of hydrate properties, their uses have not found application until now.

The data on conditions of formation and accumulation of monolithic hydrate crystals are especially scarce. Virtually no studies have been made of the electrical, optical, and mechanical properties of hydrates, and only very limited information is available on their thermodynamic properties.

HYDRATE STRUCTURE AND FACTORS THAT DETERMINE IT

Gas hydrates are crystalline inclusion-compounds (clathrates) characterized by strictly determined structures for different gases.

A fair number of publications have dealt with the structure of gas hydrates; the fundamental studies are those of B.A. Nikitin [51], who first advanced the idea that gas hydrates are nonstoichiometric inclusion compounds, "gas clathrates." Within the gas hydrate, the gas molecules are held by van der Waals forces in a metastable "host" crystal lattice made up of water molecules.

A gas hydrate is a solid solution. The solvent is water, whose molecules, on account of hydrogen bonding, form a three-dimensional shell into whose voids the volatile gas molecules penetrate.

The specific skeletal structure formed by the "host" water molecules strictly depends on the shape and size of the molecules of the gas which is

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in contact with the water. The degree in which the structure is filled with gas molecules depends on the external pressure and temperature.

Upon the formation of the hydrate and the building of the fine skeletal voids, water molecules are "forced apart" by the gas molecules entering these voids. In the hydrate state the specific volume of water increases to $1.26\text{--}1.32\text{ cm}^3/\text{g}$.

The hydrates of individual gases are characterized by structures I and II; the basis for each structure is a pentagonal dodecahedron (see Fig. 1).

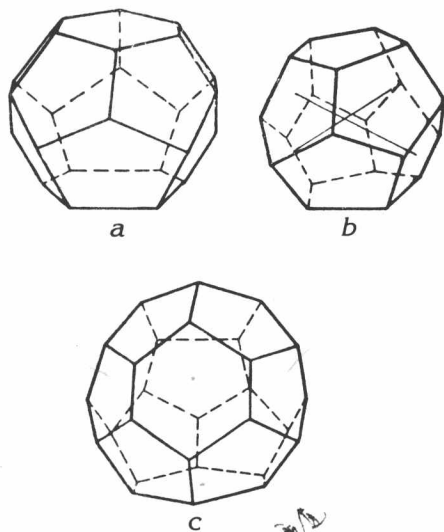


Fig. 1. Polyhedron

- a. form with 14 faces (structure I)
- b. pentagonal dodecahedron
- c. form with 16 faces (structure II)

This polyhedron consists of 20 water molecules held together by hydrogen bonds about 2.8 \AA in length. Because a dodecahedron has fivefold axes of symmetry perpendicular to the faces, not all of the space filled with hydrate can be closely packed with dodecahedra. Pentagonal dodecahedra are packed together with tetrahedra to form 12 pentagonal and 2 hexagonal faces in hydrates of structure I, and with hexahedra to form 12 pentagonal and 4 hexagonal faces in hydrates of structure II (see Fig. 2).

Structures I and II in Fig. 2 are cubic, with sides of about 12 \AA and 17.4 \AA , respectively.

Each unit cell of a hydrate of structure I consists of 46 water molecules, which form 2 small (dodecahedra) and 6 large (tetradecahedra) voids. The dodecahedron has a volume of about 169 \AA^3 , the tetradecahedron, one of about 216 \AA^3 .

The small voids of structure I can hold gas molecules with dimensions

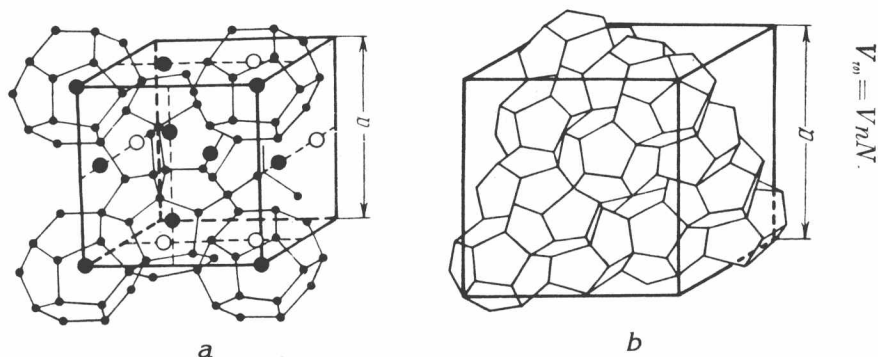


Fig. 2. Packing of dodecahedrons in the hydrate unit cell of structure I (a) and II (b).

not exceeding 5.2 \AA ; the large voids, those with dimensions not exceeding 5.9 \AA .

When gases such as Ar, CH_4 , and H_2S (and others whose molecular dimensions do not exceed 5.2 \AA) form hydrates, both small and large voids can be completely filled. The composition of such a hydrate can be determined from the expression $8\text{G}\cdot 46\text{H}_2\text{O}$ or $\text{G}_1\cdot 5.75\text{H}_2\text{O}$, where G_1 can be a molecule of Ar, CH_4 , H_2S , and so on. If the molecular diameter of a gas (C_2H_6 , Cl_2 , SO_2 , etc.) exceeds 5.2 \AA , then only the large voids of the hydrate are filled.

Gases with dimensions in the range of $5.9\text{--}6.9 \text{ \AA}$ (C_3H_8 , $i\text{-C}_4\text{H}_{10}$, CH_2Cl_2 , CHCl_3 , etc.) form hydrates of structure II. The unit cell of a hydrate of structure II consists of 16 small and 8 large voids formed by 136 molecules of water. The maximum diameter of the small voids is 4.8 \AA and of the large ones, 6.9 \AA . When an individual component of a hydrate former is present that gives rise to hydrate structure II, then only large voids become filled with the molecules of this gas G. In this case, the composition of the hydrate corresponds to the formula $8\text{G}_1\cdot 136\text{H}_2\text{O}$ or $\text{G}_1\cdot 17\text{H}_2\text{O}$.

However, in the presence of gas mixtures, double hydrates form whose small voids can fill with gases having suitable molecular size. (As a rule, the gases forming the hydrate structure I are: CH_4 , H_2S , CO_2 , and others.) The composition of such double hydrates is expressed by the formula $8\text{G}_1\cdot 16\text{G}_2\cdot 136\text{H}_2\text{O}$ or $\text{G}_1\cdot 2\text{G}_2\cdot 17\text{H}_2\text{O}$.

At the present time, several compounds are known which form gas hydrates with a crystal lattice that is different from structure I and II. For example, diethylamine hydrate $(\text{C}_2\text{H}_5)_2\text{NH}\cdot 8.67\text{H}_2\text{O}$ has an orthorhombic symmetry and two types of unit cells, one of which consists of 12 pentagons and 6 hexagons, while the other consists of 4 tetragons, 8 pentagons, and 6 hexagons. The hydrate of the tertiary butyl amine

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$(\text{CH}_3)_3\text{CNH}_2 \cdot 9.75\text{H}_2\text{O}$ possesses a cubic symmetry with crystal lattice parameters of 19 \AA , that is somewhat larger than for structure II (17.4 \AA). One unit cell of this hydrate consists of 4 tetragons and 4 pentagons and another consists of 3 heptagons, 2 hexagons, 9 pentagons, and 3 tetragons.

Hydrates formed by trimethylene oxide and cyclopropane (trimethylene) and the deuterohydrate of cyclopropane can, depending on the temperature, produce hydrate structure I or II.

Under conditions existing during the production and transportation of natural gases, mixed hydrates are formed. They can contain double hydrates of structure II whose large voids are occupied by propane and isobutane while the small ones, by such gases as methane, H_2S , or CO_2 . These mixed hydrates, however, can also contain simple hydrates of structure I consisting of such gases as methane, ethane, H_2S , and CO_2 when these gases are present in excess.

The maximum ratio between the number of water molecules and the molecules of the hydrate-forming gas (value n)—with complete filling of all voids of the hydrate lattice by gas molecules—is 5.75 for structure I and 17 for structure II. However, under actual conditions, n can substantially increase because of incomplete filling of the hydrate-lattice voids by the molecules of the hydrate-forming gas. The value n depends on pressure and temperature of hydrate formation (see "Formation and Decomposition of Hydrates," Chapter 1).

CONDITIONS OF GAS HYDRATE FORMATION

The beginning of the process of gas hydrate formation depends on gas composition, on the state of the water, and on ambient pressure and temperature. The pressure-temperature relationship of hydrate formation processes is usually represented by a phase diagram for heterogenous systems, with coordinates p and T . The first diagram of heterogenous equilibrium was constructed by Rosenbaum for hydrate of chlorine. Since then many researchers used this diagram to depict the equilibrium conditions of gas hydrate formation within the moderate pressure region.

We have obtained complete diagrams for the heterogenous state of the gas-water system for gases whose critical temperature exceeds the hydrate-formation temperature at $t > 0^\circ\text{C}$. (Fig. 3) and for gases whose critical temperature is less than the freezing point of water (Fig. 4).

Curve *OFGH* represents the relationship between the crystallization temperature of pure water and pressure. Curve *AC* (Fig. 3) shows the relationship between the vapor pressure of the pure hydrate-forming gas (C_2H_6) and the temperature. The equilibrium curve showing the dependency of hydrate formation temperature on pressure consists of characteristic curve

will form from water and from the hydrate-forming gas, both in the vapor state. For curve BC the derivative is $dt/dp > 0$. Curve C_dD determines the formation conditions of a hydrate from water and the hydrate-forming gas, both in the liquid state. The slope of C_d curve depends on the nature of change in the specific volume of the hydrate-forming gas as it converts from gas to hydrate state. This slope is characterized by the value $dt/dp = T\Delta V/\lambda$, where: T is the temperature; ΔV —change of molar volume with conversion of the hydrate-forming gas into the hydrate state; λ —heat of hydrate formation at a given temperature t ; $\Delta V = V - V_H$ (where V —molar volume of the hydrate-forming gas at equilibrium pressure and temperature; and V_H —molar volume of the hydrate-forming gas in the hydrate state). With $\Delta V > 0$, the curve C_dD has a slope to the right (clockwise); with $\Delta V < 0$; to the left (counterclockwise).

For gases whose critical temperature is higher than the hydrate formation temperature, we know the relationship that exists between the compressibility of these gases and the pressure required to keep them in liquid state. Knowing the hydrate composition and its density at a given pressure and temperature, it is easy to determine the specific volume of the hydrate-forming gas in its hydrate state and to find ΔV .

Calculations show that at relatively low pressures, the curve C_d is directed to the right for hydrate-forming gases: CO_2 , C_2H_6 , H_2S , and Cl . But to the left for C_3H_8 and CHCl_3 . Experimental data for H_2S , CO_2 , and chloroform confirm the expressed assumptions.

Curve E_d defines the conditions of p and t at which $dt/dp = 0$; that is, during hydrate formation at a pressure determined by point d . Molar volumes of gas in the free state and in hydrate state are at that point equal. With $p < p_d$, $dt/dp > 0$ while with $p > p_d$, $dt/dp < 0$. Thus, the temperature corresponding to point d is critical for hydrate of the given composition.

Pressure characteristic for point d of different gases varies within broad limits: from several atmospheres to several thousand. With pressure increase above point d , hydrate-formation temperature drops.

The heterogenous state diagrams of gas-water systems in the region corresponding to the existence of hydrates is characterized by the presence of several quadrupolar points. For gases whose critical temperature is higher than the hydrate-formation temperature at $t > 0^\circ\text{C}$. (ethane, propane, butane, hydrogen sulfide, carbon dioxide, etc.), there are four quadrupolar points— A , B , C , and D (see Fig. 3). Point A is determined by the intersection of the vapor pressure curve (AC) of the hydrate-forming gas, with the equilibrium curve of hydrate formation at $t < 0^\circ\text{C}$. At point A , gas G , liquefied gas G_1 , hydrate H , and ice are all in equilibrium. Knowing the

analytical dependence of the vapor pressure of the hydrate-forming gas and of the equilibrium pressure of hydrate formation on t (with t being $< 0^\circ\text{C}$. in each case), one can determine the parameters of point A. The accuracy of determining the position of point A depends on the accuracy of the equations representing the dependence between the vapor pressure and hydrate-formation pressure at $t < 0^\circ\text{C}$. The experimental determination of point A parameters is complicated.

Point B is the second quadrupolar point and is found at the intersection of hydrate-formation equilibrium curve ABC with the curve of the freezing point of water, OF. At point B, gas, water, ice, and hydrate are in equilibrium. The position of point B can be readily determined, experimentally or analytically. It is done by jointly solving the equations of dependence of the water-freezing temperature and of hydrate-formation temperature on pressure.

The third quadrupolar point is C. Its position is determined by the intersection of the vapor pressure curve of the hydrate-forming gas with the hydrate-formation equilibrium curve at $t = 0^\circ\text{C}$. At point C, gas, water, hydrate, and condensed gas are in equilibrium. A number of researchers regard the temperature at C as critical, that is, as a temperature above which the hydrate cannot form at any pressure. These researchers have indicated the critical temperature of methane to be $+21.5^\circ\text{C}$.; ethane, $+14.5^\circ\text{C}$.; propane, $+8.5^\circ\text{C}$.; and carbon dioxide, $+10^\circ\text{C}$. These data, however, cannot be correct inasmuch as the temperature at point C can represent the critical point only for gases whose derivative, at pressures above point C, will be $dt/dp < 0$; for example, for propane and chloroform. On the other hand, the majority of gases, at pressures above C, are characterized by the relationship $dt/dp > 0$, for instance, ethane, carbon dioxide, hydrogen sulfide, etc.

Conditions of hydrate formation ($p > p_c$) from liquefied carbon dioxide and hydrogen sulfide were studied experimentally. The results led to the conclusion that the temperature corresponding to point C is not critical. It was also possible to construct a complete heterogenous state diagram for the gas-water systems under conditions of hydrate formation. The temperature of point C is in general not critical, and it only determines the pressure above which hydrate forms from the condensed, rather than from gaseous, hydrate-forming gas.

On the heterogenous diagram, the critical temperature of hydrate formation is determined by the point at which the ambient pressure corresponds to that value at which the specific volumes of the hydrate-forming gas in the free and in the hydrate state are equal. A further increase in pressure leads to an increase in the specific volume of the gas during its conversion into a hydrate

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state, that is, where $dt/dp < 0$.

D is the fourth quadrupolar point. It represents the intersection of the hydrate-formation equilibrium curve CdD with the curve for the freezing point of water (GH) under high pressures. At this point, ice, water, gas, and hydrate are in equilibrium.

The heterogenous diagram of the gas-water system for gases whose critical temperature is less than the temperature of freezing point of water (curve OF in Fig. 4) is characterized by only three quadrupolar points.

Fig. 4 shows such a diagram for methane. Curve AbC expresses the dependence of methane vapor pressure on temperature. Point a corresponds to the pressure and temperature of crystallization for pure methane on a curve of saturation. At point b is the critical temperature and pressure for methane. Curve bC is thermal rise of methane pressure at V -constant; $OFGH$ is dependence of the freezing point of water on pressure; and AB determines the relationship of hydrate-formation pressure on temperature at $t < 0^\circ\text{C}$. Points A and B , as in Fig. 3, are quadrupolar.

The principal feature of the heterogenous diagram for gases whose critical temperatures are below the temperature of the freezing point of water is the absence of a sharp bend at point C (at the point of intersection of curves AbC and Bd) and the absence of a sharp change in the derivative dt/dp and of its sign at point C . The change of sign of the derivative of curve BdD occurs at point d because with hydrate formation, where $p < p_d$, the molar volume diminishes as the gas converts from the free to the hydrate state. Where $p > p_d$, the molar volume of the gas increases as it converts from the free to hydrate state. Curve Ed corresponds to the value of ambient pressure, at which the free-gas specific volume is equal to that of gas in the hydrate state at corresponding pressure and temperature of hydrate formation (curve Bd). Thus, with $p > p_d$, we have $dt/dp < 0$; that is, the hydrate formation temperature corresponding to point d is the critical temperature, above which the hydrate cannot exist at any pressure. The third quadrupolar point is point D , the temperature of which is less than the critical t_d .

In constructing the complete heterogenous diagrams of a gas-water system under conditions of existence of hydrates, the following liberties were allowed:

1. The effect of the solubility of gas in water on the freezing point of the water was disregarded;
2. The possibility of the occurrence of new crystal modifications of the hydrate at extremely low temperatures, or at very high pressures, was disregarded (there are no theoretical or experimental data indicating the presence of such modifications).

Of greatest interest to the gas extracting industry is the zone defined by conditions of hydrate formation from liquid water at moderate pressure. This zone lies to the right of the freezing curve, since under these conditions intensive formation and accumulation of hydrates take place as a result of an excess of liquid water.

Complete heterogenous diagrams of gas-water systems, under conditions in which hydrates can exist, present not only theoretical but also practical interest. Specifically, by knowing the composition of the hydrate that forms and its density, one can determine the critical temperature above which the hydrate will not form under any pressure. The specific volumes of gas in the free and in hydrate states, at the critical point, are equal.

By knowing the critical temperature of hydrate formation for individual gases, we can determine the range of existence of their hydrates, both with free contact and in dispersed media; we can also determine maximum pressures during the hydrate decomposition in a closed volume and the distribution of zones of gas and rock outbursts in mining of coal beds.

METHODS FOR DETERMINING CONDITIONS OF GAS-HYDRATE FORMATION

It is necessary to know the conditions of gas-hydrate formation in order to plan properly the technological installations and processes of gas production, transport, processing, and distribution to consumers.

At present, several methods exist for determining the pressure and temperature at which hydrates begin to form: (a) graphic, (b) analytical, (c) graphic-analytical, and (d) experimental. Rough data for determining the start of hydrate formation is obtained by the graphic method. With this method, for gas mixtures not containing H_2S , the curves shown in Fig. 5 are appropriate. Equilibrium curves are shown in Fig. 6 for some of the most common individual components.

Analogous curves are constructed on the basis of results of direct measurements for natural gases of different composition. Shown in Fig. 7 are equilibrium curves of hydrate formation obtained by different authors for gases from several gas fields.

① To solve technological design problems, it is simpler to use an analytical method to express the relationship between pressure and temperature of hydrate formation. Usually [16, 17], equations of such dependence are given in the form of: $\lg p = at + b$, that is, when the dependence of p on T has a linear character in semilogarithmic coordinates. However, as actual experimental investigations show, such dependence frequently does not have