



# A New Relationship for the Prediction of the Formation of Gas Hydrate in Fluids Petroleum

Iulian Oprea <sup>a</sup>, Doru Stoianovici <sup>a</sup>, Timur Chis <sup>a\*</sup>  
and Doru Bârsan <sup>a</sup>

<sup>a</sup> Oil and Gas University, Ploiesti, Romania.

## **Authors' contributions**

*This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.*

## **Article Information**

DOI: 10.9734/JENRR/2023/v13i3264

## **Open Peer Review History:**

This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: <https://www.sdiarticle5.com/review-history/98459>

**Original Research Article**

**Received: 01/02/2023**

**Accepted: 02/04/2023**

**Published: 05/04/2023**

## **ABSTRACT**

The presence of gas hydrates in natural gas extraction, transport and storage facilities, creates problems related to the blocking of flow pores in the productive layer, the clogging of pipelines and especially the increase in the delivery and pumping pressure of natural gas. This aspect usually leads to damage to oil structures by damaging them and especially by stopping gas supplies. The present work presents the history of the identification of natural gas hydrates present in nature as well as their nucleation conditions.

Also, following the laboratory determinations, two new correlations could be made to indicate the pressure and temperature at the beginning of the nucleation of gas hydrates, starting from the determination of their specific gravity.

The new correlations were compared with the laboratory data and with the existing correlations in the specialized literature, the results being close.

Also, based on the observations of the formation of gas hydrates of some gases with a specific density between 0.6 and 1.0, it was possible to analyze the laboratory data with those obtained after running a new correlatio.

\*Corresponding author: E-mail: [timur-vasile@upg-ploiesti.ro](mailto:timur-vasile@upg-ploiesti.ro), [timur-vasile@upg-conpet.ro](mailto:timur-vasile@upg-conpet.ro);

*Keywords: Gas hydrates; nucleation pressure and temperature; hydrates correlation; natural gases.*

## 1. INTRODUCTION

Gas hydrates were first identified in 1810 by Humphrey Davy who described a hydrate consisting of mixtures of water and chlorine molecules [1].

Later Louis Paul Cailletet in 1878 identified a hydrate formed (upon a sudden drop in pressure) between acetylene and water.

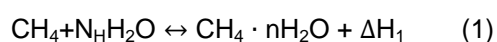
The first hydrate consisting of carbon disulfide combined with hydrogen sulfide molecules was identified in 1882 by Marcel Paul Schutzenberger [2].

Sully Thomas also identified hydrates, compounds of carbon tetrachloride and acetylene [3].

Hydrates (chelates- clathrate) have been defined as non-stoichiometric compounds consisting of mixtures of water molecules (or other liquid that can turn into a solid at a certain storage temperature and pressure) and mixtures of gases (or pure gases).

So hydrates are compounds (mixtures of gases and liquids) at pressures and temperatures suitable for the formation and maintenance of a stable structure (ice).

Yuri Makogon exemplified the hydrate formation reaction as [4]:



In the equation (1)  $N_H$  represents a hydration number, approximately equal to 6.1 for methane hydrates.

The hydrate formation reaction is usually exothermic and the dissociation reaction is endothermic.

The heat of formation  $\Delta H_1$  of methane hydrate and liquid water is 54.2 kJ/mol, and the heat of formation of methane hydrate and ice is 18.1 kJ/mol.

Gas hydrates, which are the subject of this work, are therefore defined as chemical structures of the clathrate type, in which water molecules (water crystals) form, at temperatures higher than its freezing point, host-type networks and which include in the structure (as a guest), gas molecules.

According to the above, gas hydrates (clathrates, cryohydrates) are crystalline solids formed on the basis of water (ice) and containing, included in the structure, gas molecules of small size (non-polar) or polar gas molecules with fragments large hydrophobic [5].

Gas hydrates are not chemical compounds because the molecules that form clathrates are not linked in the network [6].

The formation of gas hydrates can take place in the vapor phase or in the liquid phase, miscible or immiscible with water [7].

Molecules larger than  $nC_4$  can form cryohydrates only in the presence of a supporting gas [5].

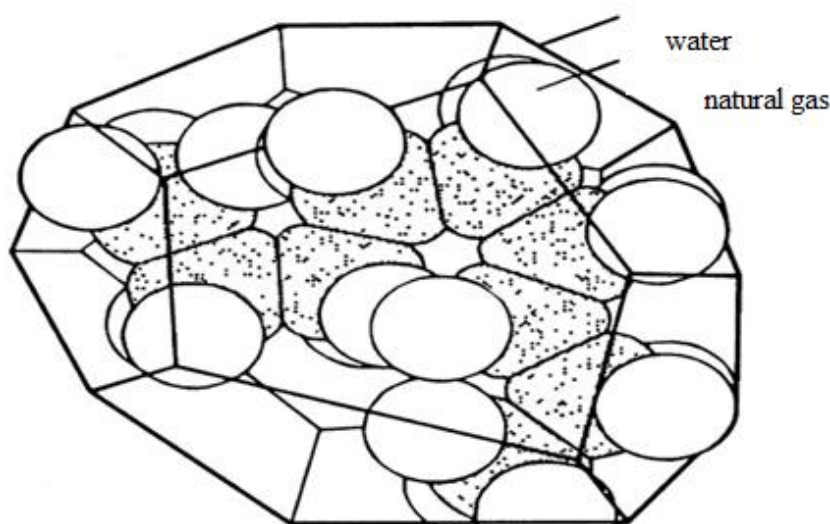
The structure and stability of cryohydrates are usually given by the Van der Waals bonds between the guest molecules and the water molecules that enclose them (Fig. 1) [8].

This connection being weak, it follows that gas hydrates are unstable combinations, they decompose relatively easily, only as a result of the decrease in pressure or the increase in temperature of the environment in which they were formed [9].

More than 100 molecules have been identified capable of forming hydrated gas when mixed with water at appropriate temperatures and pressures.

Most are components that are also found in the composition of natural gas, namely:  $N_2$ ,  $H_2S$ ,  $CO_2$ ,  $C_1$ ,  $C_2$ ,  $C_3$ ,  $iC_4$ . Methane hydrates have also been identified to be present on the bottom of the seas and oceans, in large quantities (it is estimated that the amount stored on the bottom of the seas and oceans is between 100 and 1000 billion metric cubic meters of methane gas embedded in gas hydrates). The largest gas hydrate deposits have been identified in the Norwegian continental shelf (Storegga area) and in the Black Sea [10].

Clathrates are considered an important energy resource and can also be used in natural gas and  $CO_2$  storage [11]. The chemical structures of Clathrate hydrates (gas hydrates, cryohydrates) are basically similar to those of ice crystals, only they contain gas molecules in the composition (molecules of methane, ethane, propane, etc., included in ice).



**Fig. 1. Gas hydrates formation**

The present work presents the history of the identification of natural gas hydrates present in nature as well as their nucleation conditions and following the laboratory determinations, two new correlations.

This new correlation is made to indicate the pressure and temperature at the beginning of the nucleation of gas hydrates, starting from the determination of their specific gravity.

Also, based on the observations of the formation of gas hydrates of some gases with a specific density between 0.6 and 1.0, it was possible to analyze the laboratory data with those obtained after running a new correlation.

## **2. THERMODYNAMICS OF GAS HYDRATES FORMATION**

The main conditions for the formation of gas hydrates are the modification (or variation) of the following properties of natural gas-water mixtures:

- a. Storage pressure of gases stored or transported on pipelines,
- b. Working or gas storage temperature,
- c. Humidity of associated gases,
- d. Possible existence of free water.

Also, the rate of formation of gas hydrates can be affected by the presence of hydrogen sulphide and mercaptan during the transportation of natural gas through pipelines, as well as by the high speed of gas flow through the pores of rocks

(possibility of transport and diffusion of stronger reservoir water in this case) [12].

At the same time, it was found that the existence of obstacles in the flow of wet natural gas can lead to the accumulation of separated water during transport in these areas and the propagation of hydro gas formation.

Each gas hydrate is formed under conditions of different temperature and pressure, there is a value of these properties (states of nature), above which the possibility of forming hydrates is very reduced [13].

The equilibrium temperature and the working pressure at which the nucleation of gas hydrates does not occur vary for different components of natural gas [14].

In site practice, it was found that the formation of methane gas hydrates takes place at the lowest equilibrium temperature and the highest corresponding formation pressure.

Also propane gas hydrates have the highest equilibrium temperature and the lowest corresponding formation pressure [15].

The nucleation of gas hydrates (the process of their formation) includes several stages of formation, namely:

- a. The existence of gas humidity and their saturation,
- b. Condensation of water when it reaches the dew point,

- c. Separation and deposition of water in accumulation areas,
- d. The absorption of some gas molecules in water (their inclusion) and the initiation (start) of the crystallization process due to the fulfillment of the nucleation conditions,
- e. Inclusion of some gas molecules in the crystal structure,
- f. Crystallization of the gas-water-ice mixture.

The presence of lower alkanes in the gases leads to the formation of a wet snow-like structure even at a temperature and working pressure lower than the conditions for solidification of water (Figs. 2 and 3).

The formation of gas hydrates is of a physical nature, the chemical bonds between hydrocarbons and water being weak.

Recent studies carried out with the help of the analysis of nuclear magnetic resonance spectra and dielectric adsorption spectra, have shown that hydrocarbon molecules rotate freely in the spaces of the crystal network of cryohydrates, which differ from the crystal network of ice [16].

The crystalline network of gas hydrates does not allow the inclusion of hydrocarbon molecules, with dimensions larger than the existing space in the interstices of the network [17].

The essential conditions for the formation of gas hydrates are the following [18]:

- a. the existence of liquid or solid water in the gas flow, or in the transfer area of the analyzed gases,
- b. certain pressure and temperature conditions,
- c. the presence of pulsations (movements, flows) of gas particles,
- d. the existence of obstacles that create turbulence in the gas flow.

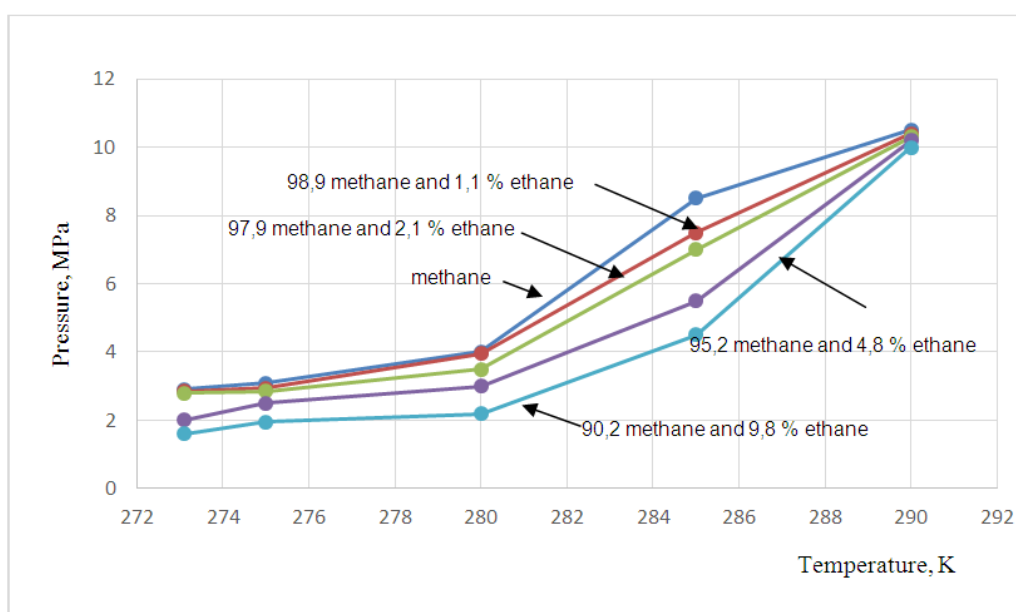
For the methane - water system, the gas hydrate formation diagram is shown in Fig. 4 [14].

The areas of existence of the state of the methane mixture mixed with water are delimited, depending on the storage pressure and the working temperature, as follows:

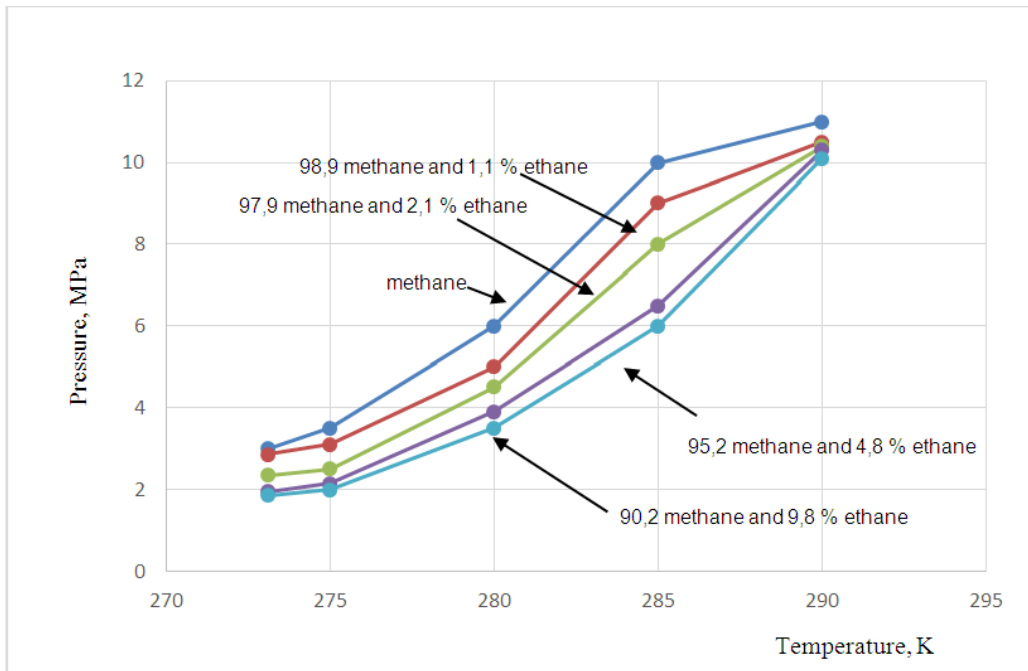
- a.  $L_1$  – area where water is in a liquid state,
- b.  $L_2$  – area where methane,  $CH_4$ , is in liquid phase,
- c.  $V_2$  – area where methane,  $CH_4$ , is in the vapor phase,
- d. H – area where the cryohydrate is formed,
- e. G – area where there is ice.

Likewise, gaseous hydrocarbon systems mixed with water have state diagrams similar to Fig. 4, differing only in the pressure and temperature of formation of the hydrate-ice, hydrate-water and methane-water states.

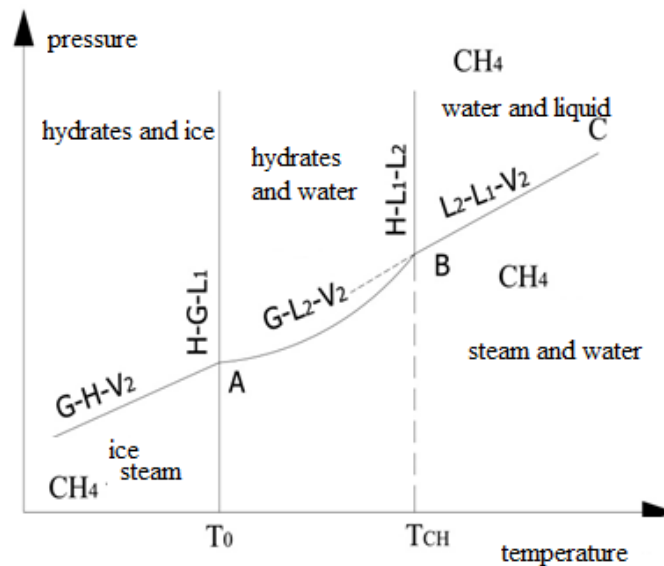
Points A and B are the equilibrium values (quadruple inflection points).



**Fig. 2. Variation of pressure-temperature equilibrium for methane and methane-ethane mixture in pure water (experimental data)**



**Fig. 3. Variation of pressure-temperature equilibrium for methane and methane-ethane mixture in salt water (experimental data)**



**Fig. 4. Diagram of state of methane in equilibrium with water**

At these points a state of equilibrium is defined for all four existing phases, namely at point A there is liquid water, ice, gaseous methane (saturated with water), and methane cryohydrate, and at point B there is liquid water (saturated with methane), liquid methane (saturated with water), gaseous methane (saturated with water) and methane cryohydrate.

Point C is the beginning of the zone where the methane-water system can no longer form cryohydrates (the properties of the phases being identical).

So we can determine the equilibrium points (*pressure, Temperature*) of liquid water  $L_1$  with gaseous methane  $V_2$  and cryohydrate H.

From the laboratory analyzes carried out during the doctoral internship, we found that cryohydrates are formed at temperatures higher than 0°C.

There is also a critical temperature  $T_{CH}$  above which, no matter how high the pressure, the cryohydrate is no longer formed.

This temperature is 21.5°C for methane and 25°C for the mixture of gaseous hydrocarbons.

The temperature range for the formation of gas hydrates decreases with the increase in the number of carbon atoms in the analyzed gas molecule, and the presence of some impurities (CO<sub>2</sub> and H<sub>2</sub>S) can lead to their higher stability.

Also, isobutane mixed with water forms gas hydrates faster than normal butane, and the increase in the mineralization of the mixing water leads to a decrease in the hydrate formation temperature.

In order to obtain higher temperatures for the formation of methane hydrates, it is necessary to add gases to the mixture (ethane, propane, etc.).

Although the most reliable way to determine the conditions for the formation of gas hydrates is the laboratory experiment, however, calculation methods based on mathematical correlations are often used, which take into account the system pressure and/or relative density [12].

$$t_{ch} = t_{ch}(p; \delta_{rg}) \quad (2)$$

where:

$t_{ch}$  is the cryohydrate (gas hydrates) formation temperature, °C;

$p$  is system pressure, in bar;

$\delta_{rg}$  is the relative density of gases compared to air.

By analogy with the liquid-vapor equilibrium, Katz and his collaborators showed that the formation conditions of gas hydrates can also be calculated based on the empirically determined vapor-solid equilibrium constants and expressed by the ratio [12]:

$$k_i = \frac{y_i}{x_i} \quad (3)$$

where:

$k_i$  represents the equilibrium constant of hydrocarbons (is function to temperature and pressure);

$y_i$  is the molar fraction of hydrocarbon in gas phase;

$x_i$  is the molar fraction of hydrocarbons in solid phase (cryohydrate).

The conditions for the formation of gas hydrates are established by successive assumptions of the unknown parameter in the dew point equation until it is satisfied:

$$\sum_{i=1}^c \frac{y_i}{k_i^{T,P}} = 1 \quad (4)$$

Apart from high pressures and low temperatures, the formation of gas hydrates is also conditioned by the humidity of the gases.

The basic condition, for the beginning of the appearance of gas hydrates, is the presence at saturation of water vapor in the gases, because only in these conditions there is the possibility of condensation and deposition of free water, whose presence, according to certain authors, is mandatory for the formation of gas hydrates [7].

### 3. MATHEMATICAL CORRELATIONS USEFUL IN DETERMINING THE TEMPERATURE AND PRESSURE OF GAS HYDRATE FORMATION

The mathematical correlations for determining the formation conditions of gas hydrates by methods that take into account the relative density of gases are designed so that the results obtained match the results of experiments carried out in specialized laboratories and published in specialties literature, under different pressure conditions, temperature and composition.

Also, statistical analyzes of errors are used to evaluate the performance and accuracy of these correlations, to meet designers and operators who need to confidently use the best correlations in the applications and projects they work on.

Most correlations take into account the determination of the hydrate formation temperature or pressure.

The first mathematical relationship was written by John Paul Hammerschmidt [15], who proposes two relationships for the initial temperature of cryohydrate formation:

- the first proposed equation,

$$T_1 = 8,9 \cdot p^{0,285} \quad (5)$$

Expressing the pressure in equation (5) for a given temperature, the initial pressure of cryohydrate formation is:

$$p = (T/8,9)^{3,509} \quad (6)$$

where:

$T_1$  is the initial cryohydrate formation temperature, in F;

$p$  represents the system pressure, in psi.

or:

$$t = 10,6 \cdot p^{0,285} - 17,8 \quad (7)$$

where:

$t$  is the initial cryohydrate formation temperature, °C;

$p$  represents the system pressure, in bar.

The second equation proposed by Hammerschmidt [15] is:

$$t_2 = 20 \cdot \log(p) - 23 \quad (8)$$

where:

$t$  is the initial cryohydrate formation temperature, °C;

$p$  represents the system pressure, in bar.

Also a classic, very simple but useful method for determining the conditions for the formation of cryohydrates is the method designed by Katz diagrams, which is based on the relative density of gases compared to air (Fig. 5).

In this usual method in the extractive and gas processing industry, a series of mathematical regressions were used to approximate the shape of the Katz curves (according to GPAS) and in this way, empirical models were created to estimate the formation conditions of cryohydrates natural gas.

In the studies of Makogon [16], it was possible to write a correlation to estimate the formation pressure of cryohydrates, the relationships being:

$$\log(p) = \beta + 0,0497(T + KT^2) - 1 \quad (9)$$

Where:

$p$  is the pressure, expressed in MPa,  
 $T$  is the temperature expressed in °C,

$K$  and  $\beta$  are two correction coefficients, expressed in the equations below:

$$K = -0,006 + 0,011\delta_{rg} + 0,011\delta_{rg}^2 \quad (10)$$

$$\beta = 2,681 - 3,811\delta_{rg} + 0,011\delta_{rg}^2 \quad (11)$$

The cryohydrate formation temperature equation can be written in the form:

$$T = \sqrt{\frac{\log p + 1 - \beta}{0,0497 k} + \frac{0,25}{k^2}} - k \quad (12)$$

Motiee [17] obtained a relationship based on a regression polynomial necessary to determine the six coefficients that correlate temperature, pressure and relative gas density. The equations are of the form:

$$\log(p) = a_1 + a_2T + a_3T^2 + a_4\delta_{rg} + a_5\delta_{rg}^2 + a_6T\delta_{rg} \quad (13)$$

$$T = -253,24469 + 78,99667 \log p - 5,353544(\log p)^2 + 349,473877\gamma_g - 150,854675\delta_{rg}^2 + 27,604065\delta_{rg} \log p \quad (14)$$

Where temperature  $T$  is expressed in °C and system pressure  $p$  is in MPa.

Mokhatab and Towler [18] also proposed an equation where  $T$  is expressed in °Reamur and the system pressure  $p$  is in psi of the form

$$T = \frac{13,47 \ln p + 34,27 \ln \delta_{rg} - 1,675 \ln p \ln \delta_{rg} - 20,35}{20,35} \quad (15)$$

Ostergaard and Carroll [19] proposed a correlation to predict the hydrate formation temperature when the gases contain  $N_2$  and  $CO_2$  [20]

They created a factor [21]:

$$f_h = y_{C1} + y_{C2} + y_{C3} + y_{i-c4} + y_{n-c4} \quad (16)$$

This is a sum of the mole fractions of methane, ethane, propane and butane.

$$f_{nh} = y_{C5} + \dots \quad (17)$$

$$F_m = \frac{f_h}{f_{nh}} \quad (18)$$

Based on relations 17 and 18, the relations can be written:

$$\delta_{rg} = \frac{\sum_{i=C1}^{n-C4} y_i M_i}{28,96}$$

$$p_h = 0,1450377 \exp\left(\left(\frac{a_1}{\delta_{rg}+a_3} + a_3 Fm + a_4 Fm^2 + a_5\right) T + \frac{a_6}{\delta_{rg}+a_7} + a_8 Fm + a_9 Fm^2\right) \quad (19)$$

Where:

$p_h$  is the hydrate dissociation pressure, psi,  
 $T$  is temperature, °R,  
 $\delta_{rg}$  is the specific density of gases.

$$\begin{aligned} a_1 &= 2,50744 \cdot 10^3 \\ a_2 &= 0,46852 \\ a_3 &= 1,214644 \cdot 10^{-2} \\ a_4 &= -4,676111 \cdot 10^{-4} \\ a_5 &= -0,0720122 \end{aligned}$$

$$\begin{aligned} b_1 &= -2,0943 \cdot 10^{-4} \cdot \left(\frac{T}{1,8} - 273,15\right)^3 + 3,809 \cdot 10^{-3} \cdot \left(\frac{T}{1,8} - 273,15\right)^2 - \\ &2,42 \cdot 10^{-2} \cdot \left(\frac{T}{1,8} - 273,15\right) + 0,423 \\ b_2 &= 2,3498 \cdot 10^{-4} \cdot \left(\frac{T}{1,8} - 273,15\right)^3 - 2,086 \cdot 10^{-3} \cdot \left(\frac{T}{1,8} - 273,15\right)^2 + \\ &1,63 \cdot 10^{-2} \cdot \left(\frac{T}{1,8} - 273,15\right) + 0,65 \\ b_3 &= 1,1374 \cdot 10^{-4} \cdot \left(\frac{T}{1,8} - 273,15\right)^3 + 2,61 \cdot 10^{-3} \cdot \left(\frac{T}{1,8} - 273,15\right)^2 + \\ &1,26 \cdot 10^{-2} \cdot \left(\frac{T}{1,8} - 273,15\right) + 1,123 \\ b_4 &= 4,335 \cdot 10^{-4} \cdot \left(\frac{T}{1,8} - 273,15\right)^3 - 7,7 \cdot 10^{-3} \cdot \left(\frac{T}{1,8} - 273,15\right)^2 + \\ &4 \cdot 10^{-2} \cdot \left(\frac{T}{1,8} - 273,15\right) + 1,048 \end{aligned}$$

And the corrected pressure relation becomes

$$p_{cor} = p_h E_{CO2} E_{N2} \quad (22)$$

Sloan [19] uses a regression method to determine the 15 coefficients that correlate the temperature, pressure and relative density of gases to determine the conditions for the formation of gas hydrates.

With the mathematical correlation written by Sloan, good results are obtained in the temperature range between 1 and 15.55 °C, the pressure between 4.5 and 103.5 bar and the relative gas density  $\delta_{rg}$  between 0.552 and 0.9 [22].

The equation are the form:

$$T = 1 / \left[ \begin{aligned} &c_0 + c_1 \ln p + c_2 \ln \delta_{rg} + c_3 (\ln p)^2 + c_4 \cdot \ln p \cdot \ln \delta_{rg} + \\ &+ c_5 (\ln \delta_{rg})^2 + c_6 (\ln p)^3 + c_7 \ln \gamma (\ln p)^2 + c_8 (\ln \delta_{rg})^2 \ln p + c_9 (\ln \delta_{rg})^3 + \\ &+ c_{10} (\ln p)^4 + c_{11} \ln \delta_{rg} (\ln p)^3 + c_{12} (\ln \delta_{rg})^2 (\ln p)^2 + c_{13} (\ln \delta_{rg})^3 \ln p + c_{14} (\ln \delta_{rg})^4 \end{aligned} \right] \quad (23)$$

$$\begin{aligned} a_6 &= 3,6625 \cdot 10^{-4} \\ a_7 &= -0,485054 \\ a_8 &= -5,44367 \\ a_9 &= 3,89 \cdot 10^{-3} \\ a_{10} &= -29,9351 \end{aligned}$$

The existence of CO<sub>2</sub> and N<sub>2</sub> gases is given by a correction relation:

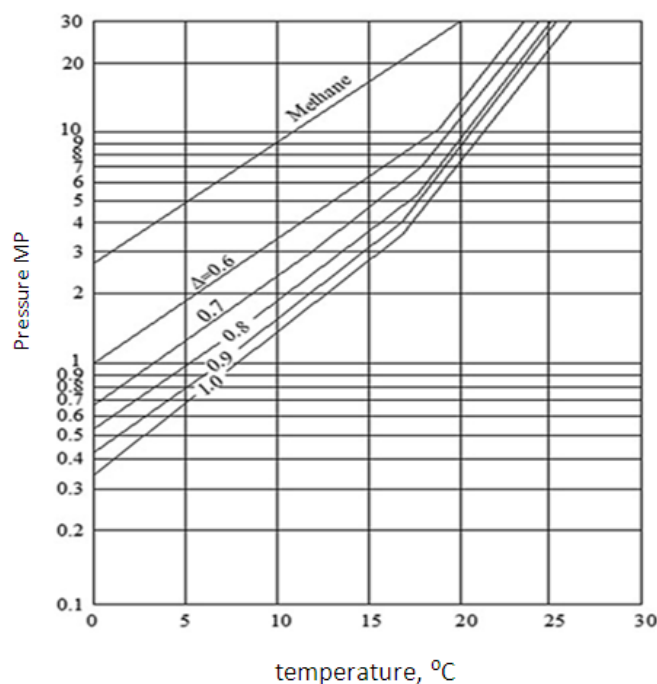
$$E_{CO2} = 1 + \frac{(b_1 Fm + b_2) \cdot y_{CO2}}{(1 - y_{N2})} \quad (20)$$

$$E_{N2} = 1 + \frac{(b_3 Fm + b_4) \cdot y_{N2}}{(1 - y_{CO2})} \quad (21)$$

Where:

$E_{CO2}$  is a correction factor for CO<sub>2</sub>,  
 $E_{N2}$  is a correction factor for N<sub>2</sub>,  
 $y_{CO2}$  represents the mole fraction of CO<sub>2</sub>,  
 $y_{N2}$  represents the mole fraction of N<sub>2</sub>,





**Fig. 5. The variation of hydrate formation pressure (psi) depending on the storage temperature and the value of the relative density of natural gas relative to air [14]**

Berge also presented a relationship that can predict the formation of cryohydrates [19], the equations used to evaluate the formation temperatures of gas hydrates being:

- for  $0,555 \leq \delta_{rg} < 0,58$

$$T = -96,03 + 25,37 \cdot \ln p - 0,64 \cdot (\ln p)^2 + (\delta_{rg} - 0,555) \cdot [80,61 \cdot p + 1,16 \cdot 10^4 / (p + 596,16) - (-96,03 + 25,37 \cdot \ln p - 0,64 \cdot (\ln p)^2)] / 0,025 \quad (24)$$

-and for  $0,58 \leq \delta_{rg} < 1,0$

$$T = \left\{ \left[ 1,23 \cdot 10^4 + 80,61 \cdot p - 2,1 \cdot 10^4 - 1,22 \cdot \frac{10^3}{\delta_{rg} - 0,535} - 1,71 \cdot 10^3 / (\delta_{rg} - 0,509) \right] \right\} / [p - (-260,42 - 15,18 / (\delta_{rg} - 0,535))] \quad (25)$$

In equations (24) and (25) the temperatures are calculated explicitly, for a known gas pressure and specific gravity.

The estimation of the pressure at which the formation of cryohydrates is possible can be evaluated by knowing the specific density  $\delta_{rg}$  and the temperature of the gas.

Kobayashi [23] achieved a very popular simulation model in the chemical industry, using a polynomial of the form:

$$T = 1 / (a_1 + a_2 \ln \delta_{rg} + a_3 \ln p + a_4 (\ln \delta_{rg})^2 + a_5 \ln p \ln \delta_{rg} + a_6 (\ln p)^2 + a_7 (\ln \delta_{rg})^3 + a_8 \ln p (\ln \delta_{rg})^2 + a_9 (\ln p)^2 \ln \delta_{rg} + a_{10} (\ln p)^2 + a_{11} (\ln \delta_{rg})^4 + a_{12} \ln p (\ln \delta_{rg})^3 + a_{13} (\ln p)^2 (\ln \delta_{rg})^2 + a_{14} (\ln p)^3 \ln \delta_{rg} + a_{15} (\ln p)^4) \quad (26)$$

The equation is useful for pressures of 65-1500 psi and temperatures between 34-62°F.

It also gives good results in the specific gravity range of gases:

$$0,552 \leq \delta_{r,g} \leq 0.9.$$

Ghiasi also developed a polynomial model based on Katz's graphs (Fig. 5), the algorithm being easy to apply:

$$T = a_0 + a_1 M_w + a_2 M_w^2 + a_3 \ln p + a_4 (\ln p)^2 + a_5 M_w \ln p \quad (27)$$

Where  $M_w$  represents the molecular mass of the gas.

And Riazi [24] proposed an equilibrium relationship of water-methane-hydrate temperature, based on 120 experimental data, the equation being of the form:

$$\begin{aligned} T = & a_1 \exp \left( \left( \frac{p - a_2}{a_3} \right)^2 \right) + a_4 \exp \left( \left( \frac{p - a_5}{a_6} \right)^2 \right) \\ & + a_7 \exp \left( \left( \frac{p - a_8}{a_9} \right)^2 \right) + a_{10} \exp \left( \left( \frac{p - a_{11}}{a_{12}} \right)^2 \right) \\ & + a_{13} \exp \left( \left( \frac{p - a_{14}}{a_{15}} \right)^2 \right) \end{aligned} \quad (28)$$

#### 4. NEW MATHEMATICAL CORRELATIONS USEFUL IN DETERMINING THE TEMPERATURE AND PRESSURE OF HYDRATE GAS FORMATION DETERMINED FROM EXPERIMENTAL DATA

Analyzing the experimental data of hydrate formation (over 1000 experiments) (Fig. 6) we managed to create mathematical equations (relation UPG1) that can lead to the determination of the temperature and pressure of their formation depending on the density of the analyzed gas (Tables 1, 2, 3 and 4) and Figs. 7-11.

Through the relationships obtained (UPG1), we plotted the graph of the hydrate formation pressure, as a function of the formation temperature and the relative density (Fig. 7) and compared it with the Katz graph (Fig. 5).

I also analyzed the relations obtained above with the relations from the fourth part of this article and with the relations proposed by the authors of this material, resulting from the realization of some laboratory experiments (relation UPG2).

In the UPG Ploiești (University of Oil and Gas Ploiesti) laboratory (Fig. 6), we created the possibility to perform an experiment based on the samples collected from a natural gas storage deposit, where for some pressure values we

determined the cryohydrate formation temperature (Fig. 11).

The gas mixture has various densities.

The installation, coupled to a gas chromatograph, consisted of a vessel that could detect the formation of cryohydrates.

The installation is also connected to a pressure boosting compressor.

Chamber pressure and temperature were measured at all times, and the onset of the cryohydrate formation point was photographed.

Each experiment was performed 5 times, the measurement error being a maximum of 0.2%.

The experiment consisted in determining the cryohydrate formation temperature as a function of pressure for natural gas with a relative density of 0.6; 0.7; 0.8; 0.9 and methane.

The first analysis of the experimental data with the calculation relations was performed by analyzing the temperature and pressure of hydrate formation as a function of relative density.

The UPG 2 relationship is of the form ( $T$  is expressed in °C and  $p$  in MPa):

$$T = 6,9561 * \ln p - 0,875 * \ln \gamma + 1,543 / (B + \ln \gamma) + A \quad (29)$$

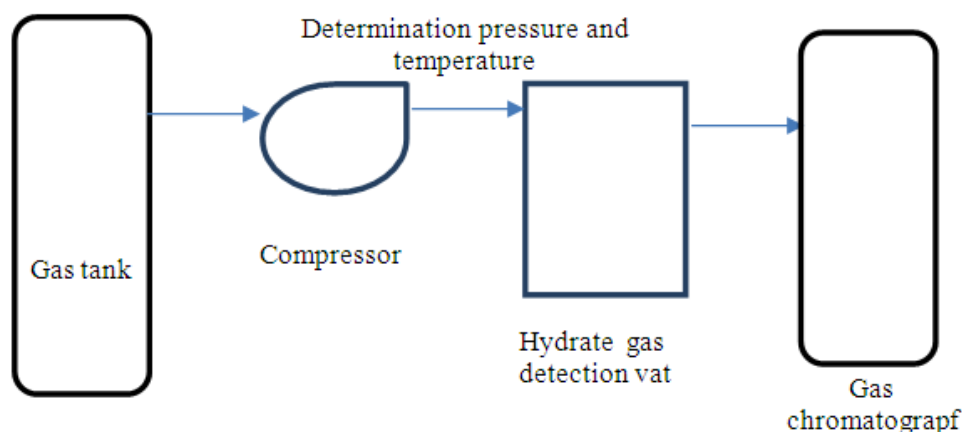


Fig. 6. The experiment necessary to determine the formation of gas hydrates

Table 1. Numerical correlations regarding the formation of cryohydrates in gases with different relative density - correlation 1 (pressure is expressed in MPa and temperature is expressed in °C) (relation UPG1)

The relative density of the analyzed gases	Correlations Pressure, Mpa function to temperature °C	The accuracy range of the relationship, temperature °C
0,6	$p = 1,0137 \cdot e^{0,1222 \cdot T}$	$T \leq 19,39$
0,7	$p = 1,0338 \cdot e^{0,1216 \cdot T}$	$T \leq 18,06$
0,8	$p = 0,5312 \cdot e^{0,1328 \cdot T}$	$T \leq 17,61$
0,9	$p = 0,4008 \cdot e^{0,1442 \cdot T}$	$T \leq 16,78$
1,0	$p = 0,3359 \cdot e^{0,1417 \cdot T}$	$T \leq 16,39$

Table 2. Numerical correlations regarding the formation of cryohydrates in gases with different relative density - correlation 2 (pressure is expressed in MPa and temperature is expressed in °C) (relation UPG1)

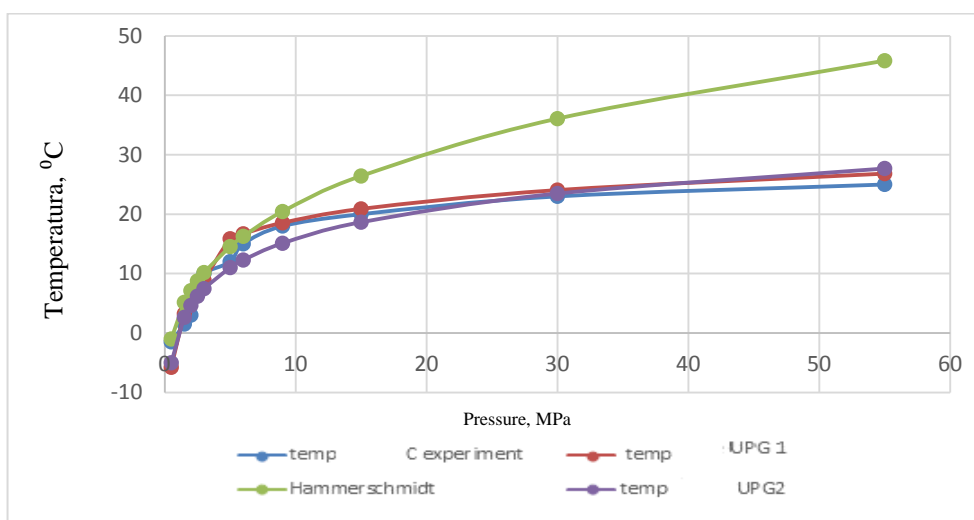
The relative density of the analyzed gases	Correlations Pressure, Mpa function to temperature °C	The accuracy range of the relationship, temperature °C
0,6	$p = 0,1528 \cdot e^{0,2198 \cdot T}$	$T > 19,39$
0,7	$p = 0,2083 \cdot e^{0,2074 \cdot T}$	$T > 18,06$
0,8	$p = 0,1258 \cdot e^{0,2146 \cdot T}$	$T > 17,61$
0,9	$p = 0,1200 \cdot e^{0,2106 \cdot T}$	$T > 16,78$
1,0	$p = 0,1068 \cdot e^{0,2115 \cdot T}$	$T > 16,39$

Table 3. Numerical correlations regarding the formation of cryohydrates in gases with different relative density - correlation 1 (pressure is expressed in MPa and temperature is expressed in °C) (relation UPG1)

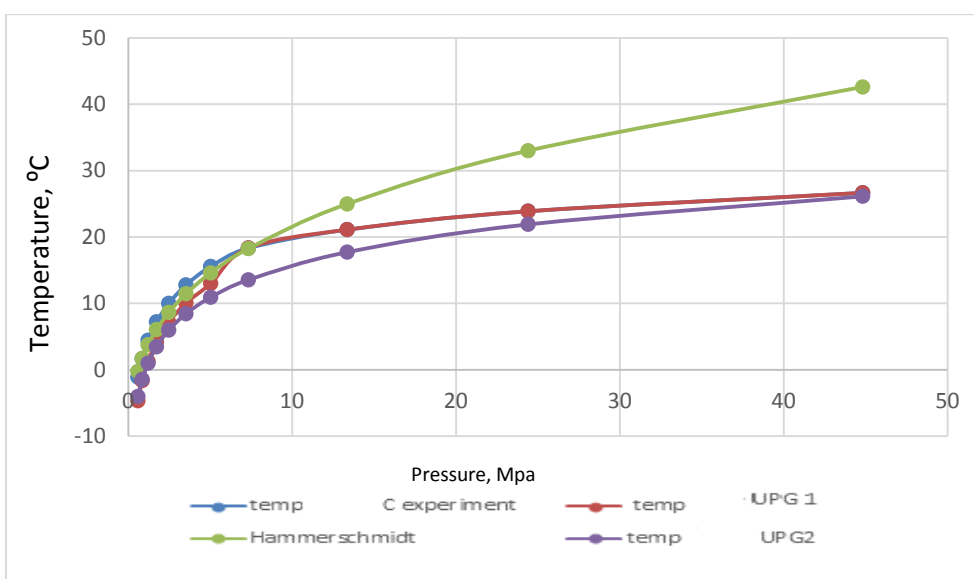
The relative density of the analyzed gases	Correlations Temperature °C function to Pressure, Mpa	The accuracy range of the relationship, Pressure, Mpa
0,6	$T = 8,1899 \cdot \ln x - 0,0992$	$p \leq 10,80$
0,7	$T = 8,2221 \cdot \ln x - 0,273$	$p \leq 6,91$
0,8	$T = 7,5218 \cdot \ln x + 4,7784$	$p \leq 5,51$
0,9	$T = 6,9343 \cdot \ln x + 6,3623$	$p \leq 4,49$
1,0	$T = 7,0822 \cdot \ln x + 7,6762$	$p \leq 3,43$

**Table 4. Numerical correlations regarding the formation of cryohydrates in gases with different relative density - correlation 2 (pressure is expressed in MPa and temperature is expressed in °C) (relation UPG1)**

The relative density of the analyzed gases	Correlations Temperature °C function to Pressure, Mpa	The accuracy range of the relationship, Pressure, Mpa
0,6	$T = 4,5723 \cdot \ln p + 8,4868$	$p > 10,8$
0,7	$T = 4,811 \cdot \ln p + 7,6022$	$p > 6,91$
0,8	$T = 4,6609 \cdot \ln p + 9,6522$	$p > 5,51$
0,9	$T = 4,7489 \cdot \ln p + 10,066$	$p > 4,49$
1,0	$T = 4,7278 \cdot \ln p + 10,577$	$p > 3,43$



**Fig. 7. Hydrate formation conditions, function of temperature, pressure and relative gas density (0,6) (relation Hammerschmidt, UPG1, UPG2 and experimental data)**



**Fig. 8. Hydrate formation conditions, function of temperature, pressure and relative gas density (0,7) (relation Hammerschmidt, UPG1, UPG2 and experimental data)**

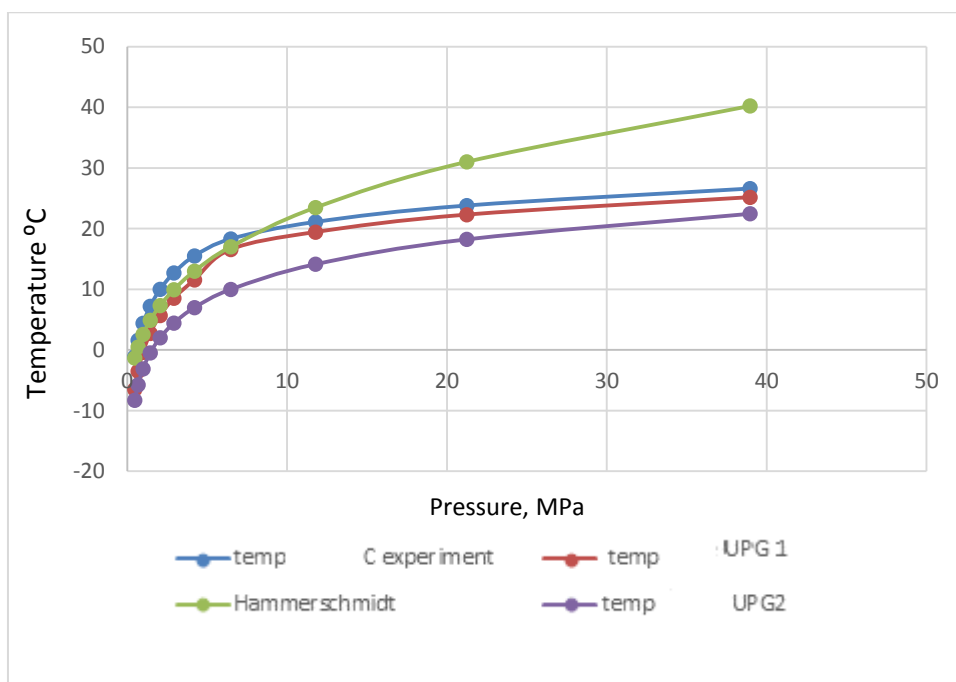


Fig. 9. Hydrate formation conditions, function of temperature, pressure and relative gas density (0,8) (relation Hammerschmidt, UPG1, UPG2 and experimetal data)

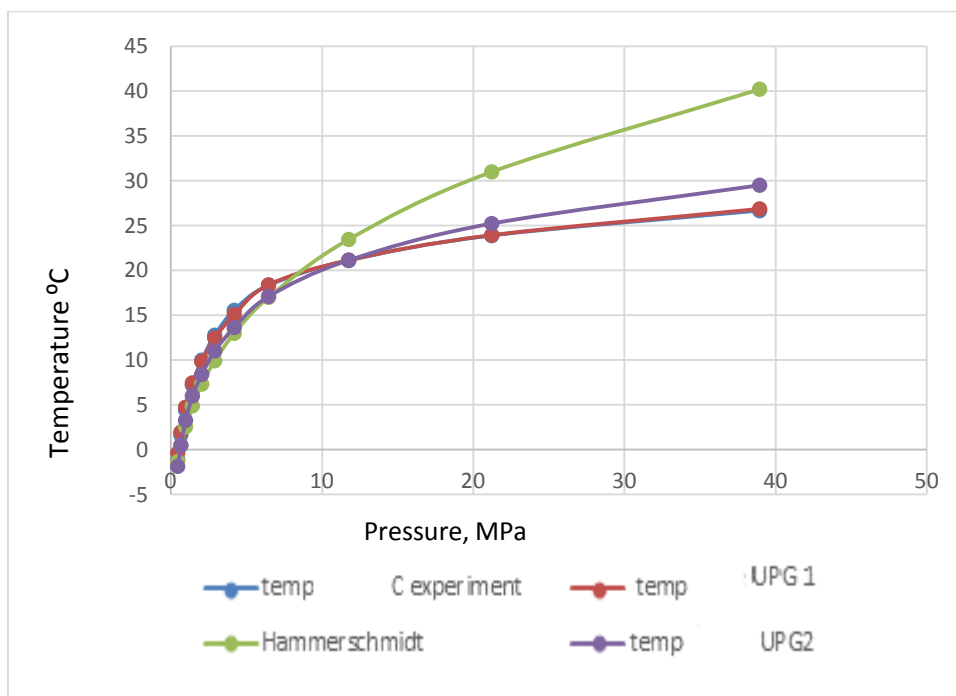
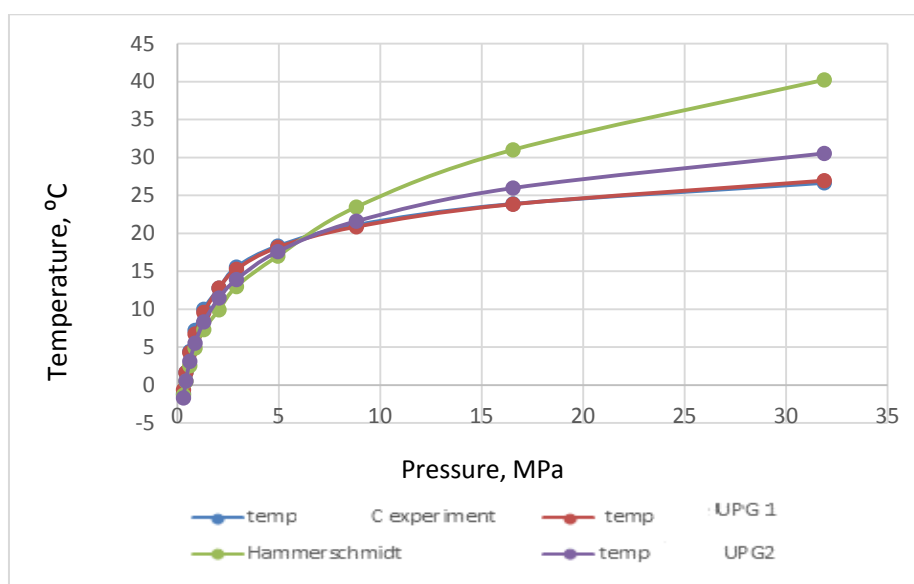
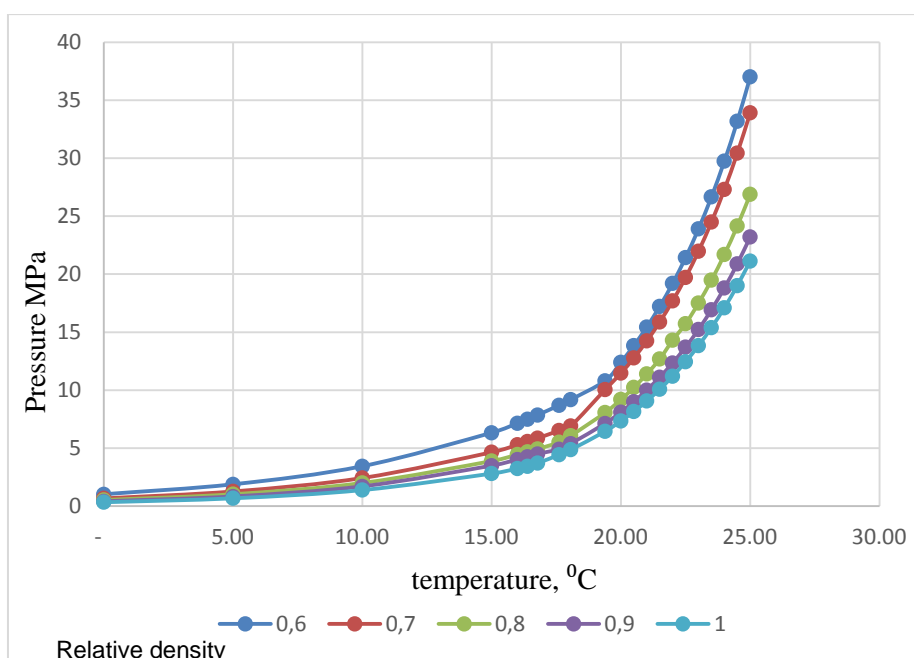


Fig. 10. Hydrate formation conditions, function of temperature, pressure and relative gas density (0,9) (relation Hammerschmidt, UPG1, UPG2 and experimetal data)



**Fig. 11. Hydrate formation conditions, function of temperature, pressure and relative gas density (1,0) (relation Hammerschmidt, UPG1, UPG2 and experimental data)**



**Fig. 12. Hydrate formation conditions, function of temperature, pressure and relative gas density (calculated data) (relation UPG1)**

- Where A is a numerical coefficient equal to:
- a. 3.7 for relative densities between 0.4 and 0.6;
  - b. 5.556 for relative densities between 0.6 and 0.65;
  - c. 9.75 for relative densities between 0.65 and 0.75;
  - d. 18.31 for relative densities between 0.75 and 0.85;
  - e. 23.22 for relative densities between 0.85 and 0.95;
  - f. -148.5 31 for densities greater than 1
- B is a coefficient equal to 0.01

To investigate the accuracy of the calculated relationships against the determined data, we used the following common statistical criteria, namely the coefficient ( $R^2$ ), the root mean square deviation (RMSD) and the percent absolute mean relative deviation (AARD%).

Low values of RMSD and AARD% and values close to 1 for  $R^2$  are preferred [23,24].

R-squared ( $R^2$ ) is a statistical measure that represents the proportion of variance for a

dependent variable explained by an independent variable or variables in a regression model.

The statistical equations are as follows:

$$R^2 = 1 - \frac{\sum_{i=1}^n (pred_i - exp_i)^2}{\sum_{i=1}^n (pred_i - average(exp_i))^2} \quad (30)$$

$$\%AARD = \frac{100}{n} \sum_{i=1}^n \frac{|pred_i - exp_i|}{exp_i} \quad (31)$$

$$MPE = \frac{100}{n} \sum_{i=1}^n \frac{(pred_i - exp_i)}{exp_i} \quad (32)$$

**Table 5. The statistical criteria for determining the temperature of formation of cryohydrates as a function of the measured pressure for the relative gas density of 0.7**

The relationship	$R^2$	RMSD	AARD
Regression UPG 1	0,9996	-5,132	192,45
Hammerschmidt (5)	0,9975	-1,995	220,00
Regression UPG 2 (29)	0,9992	-19,17	336,18

**Table 6. The statistical criteria for determining the temperature of formation of cryohydrates as a function of the measured pressure for the relative gas density of 0.8**

The relationship	$R^2$	RMSD	AARD
Regression UPG 1	0,9991	-11,775	350,64
Hammerschmidt (5)	0,9984	-9,305	77,09
Regression UPG 2 (29)	0,9970	-36,425	722,73

**Table 7. The statistical criteria for determining the temperature of formation of cryohydrates as a function of the measured pressure for the relative gas density of 0.9**

The relationship	$R^2$	RMSD	AARD
Regression UPG 1	0,9999	-4,05	9,64
Hammerschmidt (5)	0,9984	-9,75	72,91
Regression UPG 2 (29)	0,9998	-7,19	59,55

**Table 8. The statistical criteria for determining the temperature of formation of cryohydrates as a function of the measured pressure for the relative gas density of 1,0**

The relationship	$R^2$	RMSD	AARD
Regression UPG 1	0,9999	-5,68	9,09
Hammerschmidt (5)	0,9984	-9,75	72,91
Regression UPG 2 (29)	0,9998	-7,62	32,09

**Table 9. Error correlation relations of cryohydrate formation pressure as a function of temperature (experimental data, equations from part 4 of this paper)**

Experiment pressure	Temperature, F - relative gas density =0,555					Relative error			
	Exp	Sloan	Berger	Motiee	Hamm	Sloan	Berger	Motiee	Hamm
485.0	35.0	35.4	35.4	40.8	51.0	1.1	1.1	16.5	45.8
600.0	40.0	40.2	40.1	44.8	55.1	0.4	0.2	12.1	37.8
800.0	45.0	45.2	45.0	49.0	59.8	0.5	-0.1	8.9	32.9

**Table 10. Error correlation relations of cryohydrate formation pressure as a function of temperature (experimental data, equations from part 4 of the paper and UPG correlation 2), relative gas density equal to 0.6**

Experiment Pressure psi	Temperature, F - relative gas density =0,6						Relative error				
	Exp	Sloan	Berger	Motiee	Hamm	UPG2	Sloan	Berger	Motiee	Hamm	UPG2
250.0	40.0	39.3	30.7	36.1	42.9	40,65	-1.7	-23.2	-9.8	7.3	1,6
480.0	50.0	49.4	51.5	46.1	51.7	46,5	-1.1	3.0	-7.9	3.4	3,5
980.0	60.0	59.4	65.3	56.0	63.4	55,5	-1.0	8.9	-6.7	5.6	4,5
2625.0	70.0	65.1	74.7	68.0	83.9	67,9	-7.1	6.7	-2.8	19.9	2,1

**Table 11. Error correlation relations of cryohydrate formation pressure as a function of temperature (experimental data, equations from part 4 of the paper and UPG correlation 2), relative gas density equal to 0.65**

Experiment Pressure psi	Temperature, F - relative gas density =0,65						Relative error				
	Exp	Sloan	Berger	Motiee	Hamm	UPG2	Sloan	Berger	Motiee	Hamm	UPG2
110.0	30.0	34.5	4.4	27.5	34.0	29,55	14.9	-85.2	-8.3	13.3	0,45
390.0	50.0	53.5	52.2	47.4	48.7	45,40	7.1	4.3	-5.1	-2.5	4,6
2050.0	70.0	66.3	74.6	68.7	78.2	66,18	-5.3	6.5	-1.9	11.7	3,82

**Table 12. Error correlation relations of cryohydrate formation pressure as a function of temperature (experimental data, equations from part 4 of the paper and UPG correlation 2), relative gas density equal to 0.7**

Experiment Pressure psi	Temperature, F - relative gas density =0,7						Relative error				
	Exp	Sloan	Berger	Motiee	Hamm	UPG2	Sloan	Berger	Motiee	Hamm	UPG2
120.0	35.0	39.5	14.4	33.4	34.8	35,28	12.8	-58.7	-4.6	-0.5	-0,28
340.0	50.0	54.8	51.7	49.2	46.9	48,32	9.6	3.3	-1.5	-6.3	1,68
690.0	60.0	63.4	65.3	58.7	57.3	55,19	5.6	8.9	-2.1	-4.4	4,81
3400.0	75.0	56.2	77.3	76.5	90.3	77,15	-25.1	3.1	1.9	-20.4	-2,5



**Table 13. Error correlation relations of cryohydrate formation pressure as a function of temperature (experimental data, equations from part 4 of the paper and UPG correlation 2), relative gas density equal to 0.8**

Experiment Pressure psi	Temperature, F - relative gas density =0,8						Relative error				
	Exp	Sloan	Berger	Motiee	Hamm	UPG2	Sloan	Berger	Motiee	Hamm	UPG2
72.0	30.0	33.6	-4.6	32.0	30.1	30,17	12.1	-115.4	6.8	0.4	-0,17
280.0	50.0	54.4	49.7	52.0	44.3	47,18	8.7	-0.5	4.0	-11.3	2,82
1700.0	70.0	64.2	74.8	72.8	74.1	69,76	-8.2	6.9	4.0	5.9	0,24

**Table 14. Error correlation relations of cryohydrate formation pressure as a function of temperature (experimental data, equations from part 4 of the paper and UPG correlation 2), relative gas density equal to 0,9**

Experiment Pressure psi	Temperature, F - relative gas density =0,9						Relative error				
	Exp	Sloan	Berger	Motiee	Hamm	UPG2	Sloan	Berger	Motiee	Hamm	UPG2
110.0	40.0	41.3	19.0	42.3	34.0	41,04	3.2	-52.6	5.8	-15.1	-1,04
230.0	50.0	51.9	46.0	52.1	41.9	50,28	3.9	-8.0	4.3	-16.1	-0,28
2600.0	75.0	49.6	77.0	76.6	83.7	80,64	-33.9	2.7	2.1	11.6	-5,64

**Table 15. Error correlation relations of cryohydrate formation pressure as a function of temperature (experimental data, equations from part 4 of the paper and UPG correlation 2), relative gas density equal to 1,0**

Experiment Pressure psi	Temperature, F - relative gas density =1,0						Relative error				
	Exp	Sloan	Berger	Motiee	Hamm	UPG2	Sloan	Berger	Motiee	Hamm	UPG2
110.0	40.0	41.3	19.0	42.3	34.0	40,36	3.2	-52.6	5.8	-15.1	-0,36
230.0	50.0	51.9	46.0	52.1	41.9	49,59	3.9	-8.0	4.3	-16.1	0,41
2600.0	75.0	49.6	77.0	76.6	83.7	79,96	-33.9	2.7	2.1	11.6	-4,96

## 5. CONCLUSION

The common parameters that are the basis of the correlations for determining the formation of cryohydrates are the temperature and the pressure of the system.

These parameters are the most important in the extraction, transport and processing processes of natural gas.

In Tables 10-15, the experimental data were compared with the results obtained by using the mathematical correlations of the foreign researchers Sloan, Berge, Motiee Hammerschmidt, as well as the one made in the framework of this thesis and which has as its field of applicability the relative densities included.

In Table 9. it is found that the formation temperatures of the cryohydrates determined with the help of Sloan and Berge's correlations were the closest to the experimental data, and at the same time it is observed that Hammerschmidt's correlation leads to unsatisfactory results.

In Tables 10-15 it is observed that the formation temperature of the cryohydrates determined with the help of Sloan's correlations was the closest to the experimental data.

In terms of accuracy, the UPG2 correlation was second and the Hammerschmidt correlation third, falling within the range of temperatures below 15.5 °C (600 F) and pressures below 138 bar (2000 psi). However, at temperatures above 15.5 °C (600F) and at higher pressures, the UPG and Motiee correlations turn out to be the best of all.

Berge's correlation turns out to be erroneous at pressures below 20.7 bar (300 psi).

Tables 10-15 show that the cryohydrate formation temperatures calculated with Motiee's correlation are consistent with experimental data, and the Sloan and Hammerschmidt correlations give significant errors at temperatures higher than 15.5°C (600bF) and at higher pressures of 138 bar (2000 psi).

It is also observed that the Berge and UPG2 correlations give large errors at pressures lower than 20.7 bar (300 psi) and at temperatures lower than 50 °C (1200 F).

In this material we quantitatively compared the experimental data with four correlations widely used in the oil and gas industry to evaluate the formation conditions of cryohydrates, namely the Hammerschmidt, Berge, Motiee Sloan and UPG2 correlations.

From this comparative study, it can be concluded that:

- 1- Motiee's correlation obtains results appropriate to the experimental data when the relative density of the gas is included in the interval .
- 2- Berge's correlation obtains good results when the relative gas density is equal to 0.555. However, the errors increase greatly as the relative density of the gas increases and when the temperature is lower than 10 °C (6500F) and the pressure is lower than 14 bar (200 psi).
- 3- Sloan's correlation leads to good results, when the relative density of the gas is equal to 0.555 but, large errors appear with the increase of the relative density of the gas, as well as when the pressure increases above 103.5 bar (1500 psi).
- 4- Hammerschmidt's correlation leads to erroneous results when the relative gas density is equal to 0.555. Hammerschmidt's correlations are the simplest and can be used as usual correlations for determining the conditions of appearance of cryohydrates. This correlation gives good results in the range of low pressures and temperatures.
- 5- The UPG 2 correlation leads to very good results, when the relative density of the gas is equal to 0.6 or 0.7, but also at relative densities greater than 0.9 to 1.0, for the high pressure range of above 67.5 bar (980 psi). Large errors occur with increasing relative gas density at low pressures below 8.5 bar (120 psi) and low temperatures below 43.5 °C (1100F). Based on this classification regarding the establishment of the fields of applicability of the correlations depending on their accuracy, the establishment of the cryohydrate formation temperature was pursued.

In the continuation of the work, the correlations were used in order to determine the place of formation of the cryohydrate plugs both in the deep equipment and in the surface equipment of the probes located on the underground gas storage deposit at Urziceni.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

## REFERENCES

1. Qadir MI, Asrar M. Gas hydrates: A fuel for future but wrapped in drilling challenges. In: SPE/PAPG Annual Technical Conference. Islamabad, Pakistan: Society of Petroleum Engineers; 2011.
2. Sloan ED, Koh C. Clathrate hydrates of natural gases. 3rd ed. Taylor & Francis; 2007.
3. Ameripour S, Barrufet M. Improved correlations predict hydrate formation pressures or temperatures for systems with or without inhibitors. *J Can Petrol Technol.* 2009;48(5):45-50.
4. Englezos P. Clathrate hydrates. *Ind Eng Chem Res.* 1993;32(7):1251-74. DOI: 10.1021/ie00019a001.
5. Hassanpouryouzband A, Joonaki E, Vasheghani FM, Takeya S, Ruppel C, Yang J et al. Gas hydrates in sustainable chemistry. *Chem Soc Rev.* 2020;49(15):5225-309. DOI: 10.1039/C8CS00989A
6. Bialas J, Haeckel M. Gas hydrate accumulations in the Black Sea. In: Mienert J, Berndt C, Tréhu AM, Camerlenghi A, Liu CS, editors. *World atlas of submarine gas hydrates in continental margins.* Cham: Springer; 2022. DOI: 10.1007/978-3-030-81186-0\_38.
7. Available: [https://en.wikipedia.org/wiki/Clathrate\\_hydrate](https://en.wikipedia.org/wiki/Clathrate_hydrate).
8. Mokwenye PO. Evaluation of gas hydrate in gas pipeline transportation theses and dissertations; 2020. Available: <https://commons.und.edu/theses/3383>
9. Campbell JM. Gas conditioning and Processing. Vol I- Campbell Petroleum services, USA; 1993.
10. Maekawa T. Equilibrium conditions for gas hydrates of methane and ethane mixtures in pure water and sodium chloride solution. *Geochemical Journal.* 2001;35:59-66.
11. Janicki G, Schlüter S, Hennig T, Lyko H, Deerberg G. Simulation of methane recovery from gas hydrates combined with storing carbon dioxide as hydrates. *J Geol Res.* 2011;2011:Article ID 462156. DOI: 10.1155/2011/462156
12. Lee JY, Byung BJ, Yun TS, Lee J, Cho GC. Review on the gas hydrate development and production as a new energy resource. *KSCE J Civ Eng.* 2011;15(4):689-96. DOI: 10.1007/s12205-011-0009-3 – www
13. Stratula C. *Purificarea Gazelor, Ecl. București: Stiintifica si Enciclopedica; 1984.*
14. Shimekit, B., Mukhtar, H., 2012, *Natural Gas Purification Technologies - Major Advances for CO<sub>2</sub> Separation and Future Directions, Advances in Natural Gas Technology; 2012.* Available: <http://www.intechopen.com/>.
15. Hammerschmidt EG. *Assoc. Monthly. Am. Gas.* 1936;18:278.
16. Loh J, Maddox R, Erbar J. New hydrate formation data reveal differences, *OGJ.* 1983;96-8.
17. Songhe W, Jilin Q, Zhenyu Y, Jianming Z, Ma W. A simple rheological element based creep model for frozen soils. *Cold Reg Sci Technol.* 2014;10/01(106). DOI: 10.1016/j.coldregions.2014.06.007
18. Chen Q, Wu N, Liu C, Zou C, Liu Y, Sun J et al. Research progress on global marine gas hydrate resistivity logging and electrical property experiments. *J Mar Sci Eng.* 2022;10(5):645. DOI: 10.3390/jmse10050645
19. Hou G, Liang D, Li X. Experimental study on hydrate anti-agglomeration in the presence of rhamnolipid. *RSC Adv.* 2018;8(69):39511-9. DOI: 10.1039/c8ra07215a. PMID35558046
20. Toki T, Uehara Y, Kinjo K, Ijiri A, Tsunogai U, Tomaru H et al. Methane production and accumulation in the Nankai accretionary prism: Results from IODP Expeditions 315 and 316. *Geochem J.* 2012;46(2):89-106. DOI: 10.2343/geochemj.1.0155
21. Atig D, Broseta D, Pereira JM, Brown R. Contactless probing of polycrystalline methane hydrate at pore scale suggests weaker tensile properties than thought. *Nat Commun.* 2020;11(1):3379. DOI: 10.1038/s41467-020-16628-4
22. Hammerschmidt EG. Formation of gas hydrates in natural gas transmission lines. *Ind Eng Chem.* 1934;26(8):851-5. DOI: 10.1021/ie50296a010
23. Chiș T. Determination of the optimal mixtures of Romanian crudes oil for processing, 12 th International Scientific

- Conference. SGEM International Multidisciplinary Scientific Geo Conference EXPO Proceedings. Proceedings of the conference ISSN-2704 (Conferinta Inclusă în ISI Conference). 2012;2: 441-8.  
DOI: 10.5593/sgem2012/s05.v2002
24. Chiş T. The Romanian oil classification. Proceedings of the conference ISSN, 11th International Scientific Conference, SGEM, Varna, Bulgaria, Jun 20-24 2011. 1314-2704 (Conferinta Inclusă În ISI Conference). 2011;1:715-8.  
DOI: 10.5593/sgem2011/s05.109

© 2023 Oprea et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

*Peer-review history:*

*The peer review history for this paper can be accessed here:  
<https://www.sdiarticle5.com/review-history/98459>*