Nafta-Gaz 2023, no. 2, pp. 84–95, DOI: 10.18668/NG.2023.02.02

Influence of the non-equilibrium state of real gases on their properties

Wpływ stanu nierównoważnego gazów rzeczywistych na ich właściwości

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ABSTRACT: This scientific work presents a study of areas of application and improvement for the Clapeyron–Mendeleev equation to determine the technological parameters of natural and associated petroleum gas under field conditions. As a result of scientific and practical research and laboratory work, the authors, based on the molecular kinetic theory of gases, developed and improved the Clapeyron–Mendeleev equations of state of real gases by adding some genuine parameters for natural and associated petroleum gases produced from oil and gas condensate fields. In this regard, two additional parameters are introduced in the Clapeyron–Mendeleev equation-relative density and relative velocity of gas: and this, as a new scientific result, helps determine any parameter from the seven included in the equation of state of natural and associated petroleum gases developed by the authors. Continuous technological process according to the system of "production, collection, preparation and transportation of products (oil + gas)", including, separately in non-equilibrium conditions of "collection, preparation and transportation of gas" due to internal energy, causes a natural change in a wide range of basic technological parameters that contribute to frequent changes in the physical and chemical state of the gas. Therefore, this work establishes that one of the main tasks is to show the composition of natural and associated petroleum gas as a result of irreversible transformations of hydrocarbon and acidic components of its internal energy, as a result of which the gas is characterised by a number of patterns in the composition and distribution of components of various hydrocarbon and heterogeneous compositions (i.e., physically and chemically heterogeneous). In these conditions, a practical calculation of gas facilities (gas treatment point, selection of gas separators, field gas pipelines, compressor stations) is carried out to determine process parameters using the Clapeyron–Mendeleev equation of state for real gases, and the results show large errors. This proves once again that many authors have developed equations of state for real gases based on the results of laboratory studies with single-atomic and laboratory gases (hydrogen, nitrogen, oxygen, carbon dioxide, etc.). However, the authors here carried out laboratory studies with products and associated petroleum gas. According to the results of laboratory studies, the authors recommend an improvement of the equation of state of natural and associated petroleum gases.

Key words: parameter, pressure, temperature, density, compressibility, viscosity, calorific value, movement speed.

STRESZCZENIE: W pracy przedstawiono studium obszarów zastosowania i doskonalenia równania Clapeyrona–Mendelejewa do wyznaczania parametrów technologicznych gazu ziemnego i towarzyszącego gazu ropopochodnego w warunkach złożowych. W wyniku badań naukowych i praktycznych oraz prac laboratoryjnych autorzy, w oparciu o molekularną teorię kinetyczną gazów, opracowali i udoskonalili równania stanu gazów rzeczywistych Clapeyrona–Mendeleeva poprzez dodanie niektórych parametrów rzeczywistych dla gazu ziemnego i towarzyszących gazów ropopochodnych wydobywanych ze złóż ropnych i kondensatowych. W związku z tym do równania Clapeyrona–Mendeleeva wprowadzono dwa dodatkowe parametry – gęstość względną i prędkość względną gazu, co, jako nowy wynik naukowy, pozwala na wyznaczenie dowolnego parametru z siedmiu parametrów zawartych w opracowanym przez autorów równaniu stanu gazu ziemnego i towarzyszącego gazu ropopochodnego. Ciągły proces technologiczny zgodnie z systemem „produkcji, odbioru, przygotowania i transportu produktów (ropa + gaz)", w tym osobno w warunkach nierównowagi „odbioru, przygotowania i transportu gazu", ze względu na energię wewnętrzną powoduje naturalną zmianę w szerokim zakresie podstawowych parametrów technologicznych, które przyczyniają się do częstych zmian stanu fizykochemicznego gazu. Dlatego też przedmiotowa praca jako jedno z głównych zadań stawia przedstawienie składu gazu ziemnego i towarzyszącego mu gazu ropopochodnego powstałego w wyniku nieodwracalnych przemian węglowodorowych i kwasowych składników jego energii wewnętrznej, w wyniku czego gaz ten charakteryzuje się szeregiem prawidłowości pod względem składu i rozprzestrzenienia poszczególnych składników węglowodorowych (o niejednorodnym składzie pod względem fizycznym i chemicznym). W tych warunkach przeprowadzono praktyczne obliczenia dla instalacji gazowych (punkt uzdatniania gazu, dobór separatorów gazu, gazociągi terenowe, tłocznie) w celu określenia parametrów technologicznych z wykorzystaniem równania stanu Clapeyrona–Mendelejewa dla gazów rzeczywistych. Wyniki wykazują duże błędy. Dowodzi to po raz kolejny, że wielu autorów opracowało równania stanu dla gazów rzeczywistych na podstawie wyników badań laboratoryjnych z gazami jednoatomowymi i laboratoryjnymi (wodór, azot, tlen, dwutlenek węgla itp.). Natomiast obecnie autorzy

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Article contributed to the Editor: 02.11.2022. Approved for publication: 08.02.2023.

przeprowadzili badania laboratoryjne z udziałem eksploatowanych węglowodorów i towarzyszącego im gazu ropopochodnego. Na podstawie wyników badań laboratoryjnych autorzy zalecili korektę równania stanu dla gazu ziemnego i towarzyszących mu gazów ropopochodnych.

Słowa kluczowe: parametr, ciśnienie, temperatura, gęstość, ściśliwość, lepkość, wartość opałowa, prędkość ruchu.

Introduction

In field conditions for the system of "production, collection, preparation and transportation" of natural or associated petroleum gas, the application of the Clapeyron–Mendeleev equation, when determining technological parameters, present errors. Despite, the numerous equations for the state of real gases derived by many authors, the use of these formulas to determine the state of natural or associated petroleum gas in field conditions is almost impossible.

It is known from field practice that, in the system of "production, collection, treatment and transportation" of natural or associated petroleum gas from oil and gas condensate fields, gas movement occurs constantly in an unsteady turbulent regime frequently changing with its basic physical and chemical technological states (Sternin, 2008).

Continuous technological process according to the system of "production, collection, preparation and transportation of products (oil + gas)", including, separately in non-equilibrium conditions of "gathering, preparation and transportation of gas" due to internal energy, causes a natural change in a wide range of basic technological parameters that contribute to frequent changes in the physical and chemical state of the gas. The thermal-physical-chemical property is the basis of the aggregation state of natural or associated petroleum gas, which is continuously in turbulent motion along the route from the reservoir to the consumer. The parameters of the physical and chemical state of natural or associated petroleum gas can be different: pressure, temperature, volume, density, compressibility, viscosity, speed. Therefore, a deep study of thermodynamic, gas-dynamic and non-equilibrium states of natural or associated petroleum gas is extremely relevant. Any solution for an extremely important and real problem, such as the conversion of the physical and chemical energy of natural or associated petroleum gas fuels into other energy, requires a deep study of the equations of state. In this direction, attempts made by many scientists to correct the classical Clapeyron–Mendeleev equation, taking into account technological real gases in an equilibrium state, turned out to be wide of the mark (Kudinov et al., 2022).

Therefore, this work establishes that one of the main tasks is to show the composition of natural and associated petroleum gas as a result of irreversible transformations of hydrocarbon and acidic components of its internal energy. Therefore, the gas is characterised by a number of patterns in the composition and distribution of components of various hydrocarbon and heterogeneous (heterogeneous physics and chemical) composition. In general, natural or associated petroleum, gas is considered as a natural object, reflecting the influence of the redistribution of the internal (kinetic) energy of the hydrocarbon molecule, as well as various external factors in the environment of the oil and gas condensate field. Hence it follows that natural or associated petroleum gas produced from an oil and gas condensate field does not completely obey the Clapeyron–Mendeleev equation of state for real gases.

Therefore, the authors carried out the laboratory research on natural or associated petroleum gas to study their physicochemical, thermochemical and thermodynamic (transformation of internal energy) properties, which makes it possible to improve the existing equations of state of real gases. It should be noted that, according to the molecular-kinetic theory of gases, practically transferred by the reservoir of a natural energy deposit to natural or associated petroleum gas, gas molecules are constantly in a non-equilibrium state. In this state, the average velocity of a gas molecule is proportional to the square root of the absolute temperature of the gas.

Therefore, a natural change in temperature leads to a change in the specific gravity of the gas, and a change in pressure significantly affects the speed of the gas flow.

Moreover, a change in gas pressure in the field and transport gas pipeline leads to a change in the speed of the gas flow, as a result of which the quality of gas preparation is greatly violated and the physicochemical, thermochemical properties of the gas deteriorate. In these conditions, when making practical calculations of gas facilities (gas treatment point, selection of gas separators, field gas pipelines, compressor stations) to determine process parameters using the Clapeyron–Mendeleev equation of state for real gases, the results show large errors. With the movement of gas in field or main gas pipelines, depending on the characteristics of the gas flow, according to the equation of state of real gases of Clapeyron–Mendeleev, only 5 technological flow parameters (P, V, Z, R, T) can be determined, which is extremely insufficient.

The improved version of the equation of state of real gases proposed by the authors can determine seven technological parameters (P, V, $\Delta_{rel.den}$, Z, R, T, $\overline{W}_{\Delta}$) of gas objects, which makes it possible to determine the calculated indicators much more accurately.

In this regard, the general characteristics of the work include the following scientific and practical areas:

Relevance of the work

The use of the equation of state of real gases of Clapeyron–Mendeleev for natural or associated petroleum gases in the process of calculating, designing gas facilities, and selecting equipment in practice leads to significant errors.

Therefore, in order to solve this urgent problem, the authors carried out laboratory research and theoretical work to improve the equation of state of real gases of Clapeyron–Mendeleev (Kazakov and Spevak, 2021).

Scientific novelty

The paper describes studies examining oil and gas companies based in Azerbaijan, where the study of the technological process of "extraction, collection, preparation and transportation of natural and associated petroleum gas" was carried out and frequent changes in the technological parameters of gas were determined. Such a change, as gas analyses have shown, greatly affects the physicochemical, thermodynamic properties of the gas and its energy state. Conducted laboratory analyses of gas and practical measurements of process parameters have shown that changes in process parameters have a very strong effect on the properties and state of the gas. Based on this, the authors made a correction to the Clapeyron–Mendeleev equation of state for 2 more parameters: relative density and relative gas flow rate (Kerimov, 2002).

After introducing 2 parameters into the equation of state and the resulting improved equation of state, it is possible to carry out a theoretical and practical calculation to determine the parameters of the equipment, and the results obtained turned out to be closer to the truth. At the same time, the error between the parameters determined by calculation and the measured parameters of natural and associated petroleum gas for operating equipment was 5–7%.

Theoretical studies

The work of many authors on the development of the equation of state of real gases shows that studies were carried out on monatomic gases only, the so-called laboratory gases, ammonia, nitrogen, oxygen, hydrogen, carbon dioxide, carbon dioxide. Therefore, the equations of state of gases developed by these authors are not practically applicable in the oil and gas industry.

Main objective and purpose of the work

In addition to the five parameters of real gases included in the equation of state of Clapeyron–Mendeleev, the characteristic features of natural or associated petroleum gases produced from gas condensate fields are also taken into account and, in addition to this equation, two more parameters are introduced, such as relative density and relative speed of gas flow movement. These two parameters significantly affect the physicochemical, thermochemical and thermodynamic properties, as well as the overall energy state of the gas.

It should be taken into account that frequent changes in the thermophysical, thermodynamic and physicochemical state of natural or associated petroleum gas moving in a turbulent regime also cause a constant change in the parameters and in its properties. With such a technological process, in order to apply the equation of state of real gases, Clapeyron–Mendeleev requires its improvement. This work is devoted to such an actual problem (Speight, 2006).

The derivation of a new improved version of the equation of state for real gases of the Clapeyron–Mendeleev requires a deeper approach. Therefore, the paper considers the possibility of using the Clapeyron–Mendeleev equation of state for real gases, consisting of five parameters for natural or associated petroleum gases with frequently changing technological parameters, by introducing an additional two new parameters: the relative density coefficient and the relative coefficient gas flow rate ($\bar{W}_{\Delta}$).

The technological process of product extraction, preparation and separation into oil, condensate, gas, water and mechanical impurities is carried out with different technological equipment according to the scheme in Figure 1. In point 5 (Figure 1), the product is divided into liquid (oil + water), high pressure natural and associated petroleum gas and low pressure associated petroleum gas. Natural and associated high-pressure petroleum gas is sent for additional treatment to field stations 8, 13, 14 and transported to point 15, then sent to the consumer (Table 3, Figure 1). Low pressure associated petroleum gas is then sent to the intake line of the gas lift or booster compressor station (GCS or BCS) 12.

Scientists conducted a research (practical measurement of data using appropriate calibrated downhole and wellhead instruments and equipment) in order to study changes in the technological parameters of the formation and bottomhole operation. After processing the data was obtained, a generalized table was compiled (Sokovnin et al., 2022).

Studying the data in Table 1, it becomes clear when natural or associated petroleum gas flow, a decrease in technological parameters is observed in the "formation-bottomhole" area (Figure 1).

As practical measurements show, with a change in temperature over the years, a decrease in gas pressure occurs, and at the same time, the gas velocity increases (Bautin and Ponkin, 2021).

Therefore, the state of natural or associated petroleum gas must be described by an equation that accounts for pressure, volume, temperature, density and speed. In practice, changing one of these parameters changes all the others. Therefore, the rate of movement of gas from the reservoir to delivery to the consumer is a means of moving the gas flow in the gas pipeline or in the structure, relative to the speed of sound in the gas, caused by internal thermodynamic properties. It must be admitted that the known equations of state of real gas, which we operate and apply, give inaccurate results when compared with the measured technological parameters of operating wells.

The technological process of the flow of natural or associated petroleum gas in field gas pipelines and facilities is accompanied by a change in technological parameters, in which the gas pressure decreases much more intensively than the temperature, and the movement speed and density change continuously in jumps. When liquid and gas pass from the bottom to the lifting pipes of the well, a pressure drop occurs, while the compression of the gas decreases and an expansion process is formed, as a result of which the rate of liquid rise and gas flow increases. Therefore, it is of particular importance to clarify the influence, in addition to P, V, T, of density, gas constant and gas velocity on the Clapeyron–Mendeleev equation of state for a real gas.

As a result of the analysis of the selected samples and the obtained laboratory data on the physical and chemical proper-

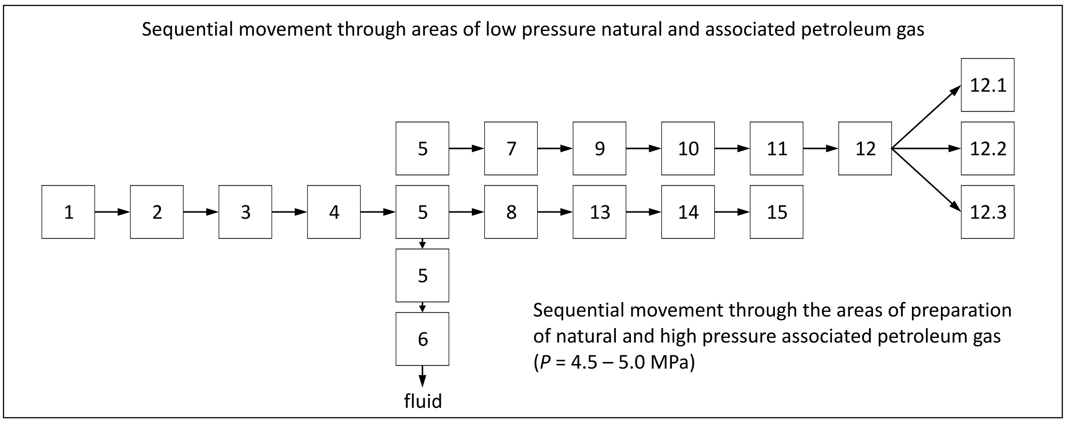

Figure 1. Schemes of the movement of produced products and collection points, preparation and transportation of oil and gas: 1 – layer; 2 – bottom hole; 3 – lifting pipes of the well; 4 – wellhead; 5 – primary field complex point for receiving, preparing and separating products into liquid and gas; 6 – point for receiving and preparing liquids (oil + water + mechanical impurities); 7 – primary point of field preparation of low-pressure associated petroleum gas; 8 – primary point of field preparation of high-pressure natural and associated petroleum gas; 9 – secondary point of field preparation of associated petroleum gas of low pressure; 10 – tertiary point of field preparation of associated petroleum gas of low pressure; 11 – head facilities for the final preparation and direction for the reception of compressor units; 12 – gas-lift (booster) compressor stations (GCS or DCS) for boosting low-pressure associated petroleum gas to the required pressure; 12.1 – point of transportation of high-pressure compressed associated petroleum gas to the system of gas-lift operation of gas-oil wells; 12.2 – point of injection of high-pressure compressed associated petroleum gas into the reservoir, to stabilise oil production; 12.3 – point of transportation to the consumer of compressed high-pressure associated petroleum gas; 13 – secondary point of field preparation of high-pressure natural and associated petroleum gas; 14 – tertiary complex facility for field preparation and purification of high pressure natural and associated petroleum gas; 15 – point of transportation of high pressure natural and associated petroleum gas to the consumer

Rysunek 1. Schematy transportu wydobywanych produktów oraz punktów odbioru, przygotowania i transportu ropy i gazu: 1 – warstwa; 2 – dolna część otworu; 3 – rury wydobywcze w otworze; 4 – głowica odwiertu; 5 – początkowy terenowy zbiorczy punkt odbioru, przygotowania i rozdzielenia produktów na ciecz i gaz; 6 – punkt odbioru i przygotowania cieczy (ropa + woda + zanieczyszczenia mechaniczne); 7 – początkowy punkt przygotowania w terenie towarzyszącego gazu ropopochodnego o niskim ciśnieniu; 8 – początkowy punkt przygotowania w terenie gazu ziemnego i towarzyszącego gazu ropopochodnego o niskim ciśnieniu; 9 – drugi punkt przygotowania terenowego towarzyszącego gazu ropopochodnego o niskim ciśnieniu; 10 – trzeci punkt przygotowania terenowego towarzyszącego gazu ropopochodnego o niskim ciśnieniu; 11 – urządzenia głowicowe służące do ostatecznego przygotowania i ukierunkowania do odbioru zespołów sprężarkowych; 12 – tłocznie (zwiększające ciśnienie) (GCS lub DCS) służące do zwiększania niskiego ciśnienia towarzyszącego gazu ropopochodnego do ciśnienia wymaganego; 12.1 – punkt transportu sprężonego towarzyszącego gazu ropopochodnego o wysokim ciśnieniu do systemu eksploatacji odwiertów gazowo-naftowych; 12.2 – punkt zatłaczania sprężonego towarzyszącego gazu ropopochodnego o wysokim ciśnieniu do złoża w celu stabilizacji wydobycia ropy naftowej; 12.3 – punkt transportu do odbiorcy sprężonego gazu ziemnego pod wysokim ciśnieniem; 13 – drugi punkt przygotowania złożowego gazu ziemnego i towarzyszącego gazu ropopochodnego o wysokim ciśnieniu; 14 – trzeci kompleksowy punkt przygotowania złożowego i oczyszczania gazu ziemnego i towarzyszącego gazu ropopochodnego o niskim ciśnieniu; 15 – punkt transportu gazu ziemnego i towarzyszącego gazu ropopochodnego o wysokim ciśnieniu do odbiorcy ties of natural or associated petroleum gas, summary Table 2 was compiled.

After practical measurement of gas parameters in the laboratory once a month for one year, the data were processed, and on the basis of this, another summary Table 3 was compiled. It shows the main technological parameters for three categories of gas by pressure (Grigoriev et al., 2021).

The results show that the energy non-equilibrium state of natural and associated petroleum gas of high, medium and low pressure often change. Under these conditions, to determine the velocity of the gas flow (w_g) starting at the lifting pipes of the well, as well as in all areas according to Figure 1, one can apply a more accessible formula, while taking pressure, gas volume and temperature for the current section (for an example, see Tables 1, 2 and 3), in the following form:

$$w_g = \frac{Z \cdot Q_0 \cdot T \cdot P_0}{P \cdot F \cdot T_0} \left[\frac{\text{m}}{\text{s}} \right] \tag{1}$$

where:

Q_0 – the volumetric flow rate of natural or associated petroleum gas under standard conditions (20°C and 1033 kg/cm^2), which is measured by the device [m^3/day],

T – the current gas temperature [°K],

T_0 – the atmospheric temperature under normal conditions [°K],

P – the current gas pressure [kg/cm^2],

F – the section of the pipe through which the gas moves, the value of which is determined taking into account the diameter of the pipe for the corresponding section [m^2],

P_0 – atmospheric pressure (usually taken equal to 1033 kg/cm^2),

Z – the compressibility factor.

In the absence of appropriate equipment for measuring the speed of the gas flow (w_g), it is determined taking into account the data in Tables 1, 2 and 3 by calculating according to formula (1).

To solve equation (1), using pre-measured technological indicators and knowing the technical dimensions of the gas pipeline, using equation (1), we first determine the gas velocity (w_{r_1}) in the field gas pipeline. At the end of the gas pipeline, where gas is supplied to the consumer, practical indicators are also measured, including the volume of supplied gas (Q), gas pressure (P_2) and, knowing the diameter of the gas pipeline, we determine the gas velocity (w_{g_2}) at the end of the gas pipeline using the equation we obtain (Kerimov, 2002; Speight, 2006):

at the beginning of the field gas pipeline, $w_{g_1} = Q_1/F$ (2)

at the end of the field gas pipeline, $w_{g_2} = Q_2/F$ (3)

where:

Q_1 –the measured volume of gas at the beginning of the field gas pipeline,

Q_2 –the measured volume of gas at the end of a field gas pipeline.

After determining the value of (w_{g_1}) and (w_{g_2}), it is possible to determine the value of the average gas velocity in the field gas pipeline using the formula:

$$w_{av} = \frac{w_{g_1} + w_{g_2}}{2} \tag{4}$$

From practice it is known that a change in pressure, density and temperature of the gas leads to changes in the volume and speed of the gas flow.

With extremely slow movement of gas along the field gas pipeline in an adiabatic process, the internal temperature of the gas is converted into kinetic energy, and it is related to the average speed of the gas flow, as can be seen from the indicators at the initial section of the gas pipeline. In this case, pressure and density, as a physical parameter, do not participate in the heat supply, technical work and change in potential energy, except for the effect of kinetic energy, since the technological parameters remain unchanged for a short time.

Problem solution method

Analysing the results of measuring technological parameters, we can conclude that practically natural or associated petroleum gas does not fully respond to the laws of gas dynamics, since the main technological parameters of moving gas from the reservoir to the consumer, passing a long way through numerous collection and preparation points, often change and the flow is turbulent.

Depending on the operating conditions of the system of "production, collection, preparation and transportation to the consumer" of natural or associated petroleum gas, the main determinants of the technological state are not only P, V, T but also the speed of gas movement in field facilities and gas pipelines ($\overline{w}_g$) and its density (ρ_g).

The total number of equations of state for real gases is currently large. All these equations can be divided into several classes depending on how they express all the technological parameters of the state of natural or associated petroleum gas produced from gas, gas condensate and gas-oil fields.

Further progress in science and technology required the development of a more advanced version of the equation of state for natural or associated petroleum gases, capable of correctly describing their behaviour at pressures up to 10 MPa and temperatures up to 320–315°K in the oil and gas production process.

Based on the foregoing, in the newly proposed improved version by the authors of the equation of state, the full energy and non-equilibrium state of natural and associated petro-

Table 1. Generalized results of a practical study of the operation of 6 operating gas condensate and 5 gas-oil wells to determine their main technological parameters of the BULLA-Sea and ALYATY-Sea fields

Tabela 1. Uogólnione wyniki praktycznego badania funkcjonowania 6 eksploatowanych odwiertów gazowo-kondensatowych i 5 odwiertów gazowo-ropnych w celu określenia ich głównych parametrów technologicznych w złożach BULLA-Sea i ALYATY-Sea

Approximate structure of the distribution of the main technological parameters of the "reservoir-bottomhole-wellhead" complex, produced products													
Years	Average reservoir pressure [MPa]	Average bottomhole pressure [MPa]	Average reservoir temperature [°C]	Average temperature at the bottom of wells [°C]	Average daily production			Average wellhead pressure [MPa]			Average wellhead temperature [°C]	Average well depth [m]	
					oil + condensate [ton/day]	water [ton/day]	natural gas + + associated oil [thousand m³/day]	hale annulus	central space	ring annulus		oil	gas condensate
1980	58.9	55.8	90	87	2715	8.5	1157	32	24	21	42	3850	5906
1981	56.8	53.7	90	87	2717	7.6	972	36	27	23	42	3850	5906
1982	53.9	49.9	88	86	2390	5.8	829	33	28	24	41	3850	5906
1983	51.4	46.8	87	84	2062	5.9	763	31	26	22	40	3850	5906
1984	49.3	44.6	86	83	1687	6.2	670	30	25	21	40	3850	5906
1985	46.7	41.8	87	83	1338	4.5	560	28	24	19	39	3790	5906
1986	44.3	39.4	85	81	1062	12.5	470	29	24	20	38	3790	5682
1987	42.6	36.2	83	80	880	27.5	390	28	25	19	38	3790	5682
1988	40.5	33.8	80	79	730	21.0	368	25	23	18	38	3790	5682
1989	38.3	30.4	78	77	670	15.0	345	23	21	18	37	3790	5682
1990	35.9	27.2	77	75	590	14.5	298	20	18	17	36	3750	5682
1991	33.7	33.7	76	74	463	13.4	276	19	18	16	36	3750	5682
1992	31.4	22.6	75	74	394	13.4	243	18	17	16	35	3750	5582
1993	28.6	20.2	73	73	332	14.6	229	16	15	14	35	3750	5582
1994	26.7	18.1	73	72	298	12.8	203	14	13	12	35	3750	5582
1995	24.5	16.6	71	69	237	13.8	187	13	12	12	34	3750	5582
1996	21.9	14.8	69	67	198	14.4	155	12	11	10	33	3750	5582
1997	18.7	13.1	69	64	167	15.2	142	11	10	9	33	3750	5582
1998	15.6	11.9	68	62	141	13.8	138	8	10	7	33	3750	5582
1999	13.2	9.2	67	60	129	13.9	127	7	6	5	32	3750	5582
2000	10.7	7.8	67	58	108	14.7	117	6	5	4	32	3750	5582

Table 2. Generalized data on the physicochemical properties of selected samples of natural and associated petroleum gases from 6 wells from gas condensate and from 6 wells from gas and oil fields, as well as from individual points (Figure 1) determined in a certified laboratory

Tabela 2. Uogólnione dane dotyczące właściwości fizykochemicznych wybranych próbek gazu ziemnego i towarzyszącego gazu ropopochodnego z 6 odwiertów gazowo-kondensatowych i z 6 odwiertów gazowo-ropnych oraz z poszczególnych punktów (rysunek 1) wyznaczonych w certyfikowanym laboratorium

Sample selection	Component composition and formula											Molecular weight	Density	Mechan. impurity	Conditions at the time of gas sampling		
	methane CH_4	ethane C_2H_6	propane C_2H_8	i-butane C_4H_{10}	p-butane C_4H_{10}	i-pentane C_6H_{12}	p-pentane C_5H_{10}	C_{6+}	CO_2	nitrogen Mg	O_2				pressure	temperature	temperature of atm. air
	[% vol.]											C_6H_{12}	p-pentane C_5H_{10}	[g/m³]	[MPa]	[°K]	[°K]
From Gas condensate well "Bulla-more" field	92.04	4.27	1.69	0.36	0.48	0.14	0.09	0.06	0.57	0.24	0.06	17.84	0.7419	0.001	1.85	285	278
From skn 1 azocondensate. Sangachali sea-Duvanny sea-Khara-Zyrya field	92.10	4.10	1.74	0.37	0.53	0.10	0.08	0.21	0.64	0.12	0.01	17.92	0.7456	0.001	3.50	300	283
From Gas condensate-nose, well "Bakhar" field	92.54	3.04	1.99	0.37	0.32	0.21	0.24	0.92	0.26	0.10	0.01	17.61	0.7265	0.001	2.30	287	285
From oil and gas well "Gunsshli" field (associated oil gas of medium pressure)	91.20	3.16	1.57	0.28	0.24	0.25	0.21	0.30	2.40	0.28	0.11	17.70	0.7365	0.001	2.85	293	284
From oil and gas well "Guneshli" field (associated oil and gas of high pressure)	90.83	3.66	1.30	0.29	0.31	0.12	0.08	0.08	3.04	0.20	0.09	18.77	0.7808	0.002	5.67	291	280
From oil and gas well "Sandy-Sea" field	91.03	3.56	1.19	0.25	0.24	0.23	0.20	0.29	2.63	0.27	0.11	18.39	0.7643	0.001	0.82	295	288
From gas-oil, well Hovsany field	92.16	3.52	1.49	0.27	0.23	0,26	0.22	0.29	1.18	0.27	0.11	18.28	0.7603	0.002	0.80	294	299
From oil and gas well "Zykh" field	92.50	2.85	1.96	0.28	0.24	0,23	0.20	0.27	1.08	0.28	0.11	18.22	0.7582	0.001	0.80	299	302
From oil and gas well "Neft Dashlary" field	91.73	3.32	0.71	0.27	0.19	0.18	0.07	0.23	3.04	0.17	0.09	18.10	0.7529	0.002	0.70	289	285
Primary point 7 for the preparation of low-pressure gas (Figure 1)	91.70	2.95	0.95	0.23	0.14	0.19	0.18	0.23	3.15	0.18	0.10	18.23	0.7518	0.001	0.80	283	284
Primary point 8 for gas treatment, high pressure (Figure 1)	92.18	2.17	0.93	0.22	0.31	0.20	0.19	0.30	3.13	0.22	0.10	17.94	0.7548	0.001	5.20	285	288
Point 15 of the final preparation and transfer to the consumer of nature, gas, high pressure (Figure 1)	92.17	2.17	1.17	0.23	0.20	0.20	0.18	0.22	3.14	0.22	0.10	17.93	0.7546	0.001	4.90	291	290
Clauses 12.1,12.2, 12.3 high-pressure compressed associated petroleum gas for transmission to the consumer (Figure 1)	91.52	2.38	1.53	0.26	0.20	0.20	0.18	0.22	3.14	0.27	0.10	17.47	0.7266	0.001	4.80	285	288

Table 3. Summary table of the main technological parameters of natural and associated petroleum gas in the system of production, collection, preparation and transportation to the consumer, from point 5 to points 12.1 and 12.3

Tabela 3. Zestawienie głównych parametrów technologicznych gazu ziemnego i towarzyszącego gazu ropopochodnego w systemie produkcji, odbioru, przygotowania i transportu do odbiorcy, od punktu 5 do punktów 12.1 i 12.3

No.	High pressure natural and associated petroleum gas				Medium pressure natural gas and low pressure associated petroleum gas			
	pressure	temperature	volume	density	pressure	temperature	volume	density
	[MPa]	[°C]	[thousand m³]	[kg/m³]	[MPa]	[°C]	[thousand m³]	[kg/m³]
5	4.8	17	4760	0.7488	0.95*	16	3985	0.7467
7	4.8	18	–	0.7486	0.84*	18	3982	0.7471
9	4.8	18	–	0.7485	0.75*	21	3978	0.7463
10	4.7	16	–	0.7459	0.68^	22	3976	0.7469
11	4.7	19	–	0.7448	0.55*	23	3973	0.7458
12	4.7	20	–	0.7448	0.50*	24	3971	0.7465
12.1	4.7	23	–	0.7445	6.50**	28	1345	0.7494
12.2	4.6	25	–	0.7445	6.50"	28	1488	0.7494
12.3	4.6	22	–	0.7445	4.50"	28	1738	0.7491
8	4.6	20	4757	07543			-	
13	4.6	19	4754	0.7524			-	
14	4.5	17	4753	0.7483			-	
15	4.5	15	4753	0.7481			-	

* Gas pressure at the BCS intake
** Gas pressure at the outlet of the booster compressor station (BCS)

leum gas is taken into account, linking pressure (P), volume (ϑ), temperature (T), and for accurate calculation, correction factors for the relative density (Δ) and two thirds of the relative average velocity of gas ($2/3\ \overline{w}_\Delta$) from the reservoir to the consumer.

Therefore, adding two additional technological parameters of the state of a moving flow of natural or associated petroleum gas into the equation of state of real gases of Clapeyron–Mendeleev under conditions of a non-equilibrium state of relative density and velocity is a crucial factor.

Taking into account the results of a practical study of a complex system "reservoir-consumer" according to Figure 1 and according to the results obtained in the study by measuring the main technological parameters, the authors propose the following equation, which differs from the previous equations of state of real gases:

$$P\partial\Delta = Z_{gp} RT \frac{2}{3} \overline{w}_\Delta \qquad (5)$$

where:

P – the pressure of natural or associated petroleum gas,

Z_{gp} – volume of produced gas,

Δ – the compressibility coefficient of a moving gas flow under conditions of a dynamically non-equilibrium state, a dimensionless quantity; relative density of gas, related to the density of dry air:

$$\Delta = \frac{\rho_g}{\rho_{da}} \qquad (6)$$

where:

ρ_{da} = 1.205 – dry air density under normal conditions [kg/m³],

ρ_g – gas density determined in the laboratory [kg/m³],

R – the universal gas constant – the same for all gases, whose dimension depends on type of gas and technical units in which the pressure and quantity of gas are measured. For example, if a universal gas constant is required expressed in kilomoles and knowing that at 0°C (273°K) and a pressure of 760 mm Hg (10 330 N/m²), the molar volume for all gases is almost the same and is 22.4 m³/kmol, the gas constant is determined as follows:

$$R = \frac{10330 \cdot 22.4}{273.15} = 848 \left[\mathrm{kg \cdot m / kmol \cdot deg}\right] \qquad (7)$$

If the gas constant for the amount of gas needs to be expressed in meters per degree Celsius, the value of the universal gas constant should be divided by the molecular weight (μ) of natural or associated petroleum gas, which is determined in a certified laboratory (in this case, Tables 2 and 3). Taking into account the molecular weight, the gas constant is determined by the formula:

$$R = \frac{848}{\mu} [\mathrm{m/°C}] \qquad (8)$$

For practical calculations in the process of production, collection, treatment and transportation of a gas stream and to determine how much the speed of natural or associated petroleum gas (w_g) is less or more than the speed of sound in gas (w_{da}), the concept of relative velocity ($\overline{w}_\Delta$), the gas flow is determined by the ratio:

$$w_\Delta = \frac{w_g}{w_{da}} \tag{9}$$

It is known that the speed of sound in a gas is called the propagation velocity in the gas of perturbations caused by a change in the pressure of the gas flow. In this case, the pressure amplitude is negligible compared to the total pressure of the gas flow in the field gas pipeline. Therefore, the speed of sound in a gas is related to the thermodynamic parameters of this gas. At the same time, sound vibrations caused by pressure changes propagate very quickly in the field gas pipeline, so there is no time for any noticeable heat exchange between the areas (Figure 1) of rarefaction and compression of the sound wave and the environment.

Field practice shows that a frequent change in the flow rate of gas supplied to the consumer leads to a change in gas pressure in the field gas pipeline, which propagates at speeds much greater than the speed of sound.

In this case, the total heat content of the gas is completely converted into kinetic energy, (i.e., internal energy), which is formed as a result of an internal chemical reaction of a gas. From this it turns out that the maximum value of the speed of sound in a gas, derived under the assumption of a constant heat capacity approximately ($C \approx 0.24$), will have the following form:

$$w_{\max.da} \approx 44.8\sqrt{T_0}$$

where: T_0 – atmospheric air temperature and is taken close to normal $T_0 \approx 273$°K. Then the maximum possible speed of the outflow of sound in the gas will be, $w_{\max.da} \approx 739$ m/s. Here, it is necessary to note another example of the method for determining the speed of sound in a gas.

With such a technological process, the molecules of nitrogen, carbon dioxide, etc., practically present in the composition of the gas, which worsen the quality of the gas, are lighter than the molecules of natural or associated petroleum gas, and the speed of the gas molecule can reach 660–680 m/s. According to Landau and Kitaigorodsky, the speed of sound in gas is approximately equal to the average speed of molecules in gas and is taken to be about $w_{\max.da} \approx 739$ m/s (Sokovnin et al., 2022).

Based on this, the obtained value of the relative velocity according to the formula (9) finally takes the form:

$$w_\Delta = \frac{w_g}{w_{da}} = \frac{w_r}{335} \tag{10}$$

where:
335 – the speed of sound in gas [m/s],
w_g – the flow rate of natural or associated petroleum gas is either determined practically with the help of appropriate apparatus or determined by formula (1).

In field practice, the operating personnel carries current technological process of the compressibility coefficient of a moving gas flow under non-equilibrium state conditions of natural or associated petroleum gas (Z_{gp}) included in formula (9) using practically measured data in the following sequence:

1. in a certified laboratory, the density of the gas is determined from the selected sample ρ_g, and by parametric instruments, pressure and temperature of natural or associated petroleum gas (Table 3);
2. after which, for convenience and more accurate calculation, the pseudo critical pressure is determined P_{nkp} and pseudo critical temperature according to the acceptable formulas of Istomina:

$$\left.\begin{aligned} P_{par} &= 4.937 - 0.464\Delta \\ T_{par} &= 171.5\Delta + 97 \end{aligned}\right\} \tag{11}$$

Using the data obtained in the laboratory for ρ_g, the value for Δ, is found, after which R_{pcr} and T_{pcr} are determined. Using the data (P, T) according to the Table 3, and the value of P_{pcr}, T_{pcr}, the reduced parameters of pressure P_{pr} and temperature T_{pr} are determined by the formulas:

$$\left.\begin{aligned} P_{par} &= \frac{P}{P_{par}} \\ T_{par} &= \frac{T}{T_{par}} \end{aligned}\right\} \tag{12}$$

where P, T are the current values of pressure and temperature of the gas, measured by instruments directly in the area (Figure 1) and the parameters were measured to calculate the compressibility coefficient. With known values of P_{pr} and T_{pr}, according to the most widely known empirical nomogram of Brown and Katz (Kudinov et al., 2022), the value of Z_{gp} for natural or associated petroleum gas is determined with sufficient accuracy. For practical calculations in the fields, measurements show that changes in the pressure of natural or associated petroleum gas in the range of 3.5–7.5 MPa and, according to the Brown–Katz nomogram, the compressibility factor Z_{gp} fluctuates within Z_{gp} = 0.8–0.9.

Thus, equation (6) describes the full energy in a non-equilibrium state of a moving natural or associated petroleum gas, connecting all the main frequently changing technological parameters and obeying it and this helps determine each parameter separately in field conditions.

The equation (5) proposed by the authors is highly accurate. The main parameters of natural and associated petroleum gas are determined practically during the operation of the gas production, collection, treatment and transportation system to the consumer, and do not exclude the possibility of other methods for refining the Clapeyron–Mendeleev equation of state for real gas in the future.

The speed of gas movement is calculated according to formula (1) for example, as shown in Table 1 and we accept the following data: Q = 1 157 000 m^3/day; P_0 – gas pressure, equal to atmospheric (barometric) pressure, is usually taken equal to 10 330 kg/m^2 or 10 330 kg/sm^2; T – is the temperature at the wellhead, taken equal to 315°K; T_0 – is the atmospheric temperature at the wellhead under normal conditions, taken equal to T_0 = 273°K; P is the gas pressure at the wellhead, is taken equal to P = 240 kg/sm^2; F – is the section of the riser pipe [m^2], knowing that the inner diameter of the lifting pipe, D = 16 mm = 0.076 m.

Then: $F = 0.785 \cdot D^2 = 0.785 \cdot 0.005776 = 0.0045$ [m^2]

Comparing all the data in formula (1) and collating it within a single measurement system, we find for the first option the speed of movement of natural or associated petroleum gas in the lifting pipes of the well:

$$w_g = \frac{1157000 \cdot 1 \cdot 315 \cdot 10000}{240 \cdot 0.0045 \cdot 273 \cdot 10000 \cdot 86400} = 14.3\,[\mathrm{m/s}]$$

Knowing the speed of sound in gas, 335 m/s, using formula (9), the relative flow rate of natural or associated petroleum gas through field facilities and gas pipelines, is found:

$$w_\Delta = \frac{w_g}{w_{dg}} = \frac{14.3}{335} = 0.043$$

Next, to solve formula (5), the compressibility coefficient of a moving gas flow under conditions of a non-equilibrium state of natural or associated petroleum gas (Z_{gp}) is found and using the data in Tables 2 and 3, on the part of the operating personnel, the calculation is carried out as follows. At the time of calculation, the density (specific gravity) of natural or associated petroleum gas is determined in the laboratory, and the pressure and temperature of the gas are determined using parametric instruments (Table 3).

First, the pseudo critical pressure and temperature of natural or associated petroleum gas are found using formula (11).

Taking the arithmetic mean value of the density according to Table 2 for natural or associated petroleum gas, determined in the laboratory, ρ_g = 0.7488, the relative density (Δ) is found under standard conditions according to the formula (6):

$$\Delta = \frac{\rho_g}{\rho_{dg}} = \frac{0.7488}{1.205} = 0.62$$

Using the relative gas density data, the pseudo critical parameters of pressure and temperature is determined using formula (11):

$$\left.\begin{aligned} P_{par} &= 4.937 - 0.464 \cdot 0.62 = 4.65 \\ T_{par} &= 171.5 \cdot 0.62 + 97 = 203.3°K \end{aligned}\right\}$$

Using the data R_{par} and T_{par} and according to the Table 2, taking the arithmetic mean value P, T, the reduced parameters of pressure and temperature are determined according to formula (12)

$$P_{par} = \frac{P}{P_{par}} = \frac{4.8}{4.65} = 1.03$$

$$T_{par} = \frac{T}{T_{pat}} = \frac{290}{203.3} = 1.43$$

Subsequently, once P_{pr} and T_{pr} are known according to the experimental nomogram of Brown and Katz, we find Z_{gp} = 0.89.

Now, knowing the value of Z_{gp}, as the second option, we can determine the speed of movement of natural or associated petroleum gas through the lifting pipes of the well according to the formula (Grigoriev et al., 2021):

$$w_g = 0.01247 \frac{Q \cdot Z_{gp} \cdot T_{av}}{D^2 \cdot P_{av}} [\mathrm{m/s}] \tag{13}$$

where:

Q – the volume of produced gas measured at the wellhead [m^3/h],

T_{av} – the average gas temperature [°K],

D – the diameter of the lifting pipe [sm],

P_{av} – the average gas pressure in the central space at the wellhead (Table 1) [kgf/sm^2].

To determine the speed of movement of natural or associated petroleum gas through the lifting pipes of the well, the following data from Table 1 is accepted:

Q = 48 208 m^3/h; Z = 0.89; T_{sp} = 315°K is the temperature at the wellhead; D = 7.6 is the inner diameter of the butting pipe, cm; P_{av} = 240 kgf/sm^2 – gas pressure in the central space of the wellhead.

Comparing the data in formula (13), the following is obtained:

$$w_g = 0.01247 \frac{48208 \cdot 0.89 \cdot 315}{7.6^2 \cdot 240} = 12.16\,[\mathrm{m/s}]$$

To determine the relative velocity of natural or associated petroleum gas, taking into account the value w_g = 12.16 m/s, we accept the speed of sound in the gas, as in the first variant, of sound w_g = 335 m/s and obtain:

$$\bar{w}_\Delta = \frac{w_g}{w_{gs}} = \frac{12.16}{335} = 0.036$$

Therefore, the value of the relative flow rate of natural or associated petroleum gas in two variants using formula (10) 0.043 and 0.036, determined in field conditions by calculation, makes it possible to establish the difference between them (0.007), which is extremely insignificant.

Therefore, equation (5) allows calculations to be performed during the operation of oil, gas and gas condensate wells, in field conditions for the gas production, collection, treatment and transportation system to determine the physicochemical properties of gases and each parameter separately. Moreover, the technological parameters (P, V, T) included in equation (5) are found by practical measurement during gas production, collection, treatment and transportation, and other pmeters Z_{gp}, w_Δ and Δ are determined by calculating in the presence of measured data and taking into account the results of laboratory defining of gas density.

It should be emphasised that the equation of the full energy and non-equilibrium state of a moving natural or associated petroleum gas flow (5) proposed by the authors is acceptable and convenient for evaluation calculations.

In order to practically verify compliance in a real system for the collection, preparation and transportation of natural or associated petroleum gas, the Clapeyron–Mendeleev equation $PV = ZRT$ was used for a calculation to determine the volume of gas. The technological parameters of gas measured in one gas condensate well are accepted at the site of the primary field complex receiving and processing station (Figure 1), i.e., at the end of the gas collection, treatment and transportation system, after which the gas is sent to the general system. At the same time, it should be taken into account that all other gas condensate wells also work in a common system for final preparation. Thus, for the calculation, the following operating technological parameters were taken from the gas condensate well, the Sangachal Sea-Duvanny Sea-Khara-Zyrya field, which is in the middle stage of development and taken at the time of gas measurement and sampling (Table 2): gas pressure $P = 35$ kgf/cm^2; average gas temperature $T = (273 + 27)$°K; average compressibility factor $Z_{gp} = 0.89$; relative density $\Delta = 0.62$, average relative gas velocity $\overline{w}_\Delta = 0.043$ and gas constant R in m/deg. determined for produced natural gas. Knowing the molecular weight of the gas determined in the laboratory, $\mu = 17.92$, we find:

$$R = \frac{848}{17.92} = 47.3\,[\text{m/deg}]$$

In field conditions, a well operation engineer first determines the volume of gas produced from one gas condensate well, using the Clapeyron–Mendeleev equation, and, at the same time, comparing the received data and leading to a unified measurement system, according to the equation $PV = ZRT$ obtains:

$$V = \frac{ZRT}{P} = \frac{0.89 \cdot 47.3 \cdot (273 + 27) \cdot 10000}{35} = \\ = 3.608314\,[\text{m}^3/\text{kg}]$$

Multiplying by the weight of 1 m^3 of gas determined in the laboratory and equal to 0.7346 kg, the estimated volume of natural gas produced from one gas condensate well is obtained:

$$V = 3\,608\,314 \cdot 0.7346 = 2\,650\,668\ [\text{m}^3]$$

Now, using the same data, according to the equation of the authors, the engineer determines the volume of produced gas for one well and, having reduced it to a single measurement system, obtains:

$$V = \frac{Z_{gp} \cdot R \cdot T \cdot \frac{2}{3} \cdot \overline{w}_\Delta}{P \cdot \Delta} = \\ = \frac{0.89 \cdot 47.3(273 + 27) \cdot \frac{2}{3} \cdot 0.043 \cdot 10000}{35 \cdot 0.62} = \\ = 166285\,[\text{m}^3/\text{kg}]$$

Taking into account the weight of 1 m^3 of gas and the volume of gas obtained according to the authors' equation a calculation is performed to determine the volume of natural gas produced from one gas condensate well:

$$V = 166\,285 \cdot 0.7346 = 122\,152\ [\text{m}^3]$$

However, in the field, a preliminary practical measurement of the volume of gas produced from one well by the corresponding measuring devices at the outlet from the site of the primary field complex for receiving and treating gas (Figure 1) shows 182 543 m^3. Now let us' compare the calculated indicators of the gas volume with the practically measured volume:

- according to the Clapeyron–Mendeleev equation:
  2 650 663 m^3 – 182 543 m^3 = 2 468 125 m^3;
- according to the authors' equation:
  182 543 m^3 – 122 152 m^3 = 60 391 m^3.

Therefore, according to the first option, the calculated gas volume is 2 468 125 m^3 or more than 13.8 times more than the practically measured gas volume. This is unacceptable in field practice, since the gas condensate field is at the middle stage of development, the discrepancy with the measured volume for one gas condensate well is very large. Comparison of the calculated indicators leads to the conclusion that the Clapeyron–Mendeleev equations of state for a real gas, developed on the basis of an experiment conducted in laboratory conditions with a small amount of ammonia, nitrogen, hydrogen, carbon dioxide, carbon monoxide, in their states are completely different from the physical and chemical state of natural or associated petroleum gas, which give large errors (Mamontov and Serov, 2021).

Unlike other equations, the authors' equation of state was developed for the non-equilibrium state of a real gas that exists in the system of "production, treatment and transportation of natural or associated petroleum gas", much closer to the measured indicators.

This is clearly seen from the second option, where the calculated gas volume is 60 391 m^3 or 1.56 times less compared to the measured gas volume. Therefore, according to the second option, the calculated volume is extremely close to the practically measured gas volume, and infield practice this option can be considered quite acceptable.

Conclusions

In the scientific and practical methodology "The influence of the non-equilibrium state of real gases on their properties" developed by the authors of this paper, the following main areas are considered:

1. Analysis of the current state in the system of "production, collection, preparation and transportation to the consumer" (Figure 1) of natural or associated petroleum gas produced from gas, gas condensate and gas-oil fields showed frequent changes in the technological parameters of gases. Extensive field material is considered in terms of technological parameters that affect the frequent changes in technological parameters directly influencing the internal physical and chemical state of natural or associated petroleum gas. The possibility of using the existing equations of state of real gases for produced natural or associated petroleum gas moving through field gas pipelines under conditions of a non-equilibrium state and frequently changing technological parameters was studied according to simple and absolutely rigorous physical reasoning.
2. Analysis of the existing equations of state of real gases and each physical parameter included in these equations separately, as well as the correspondence of these real gas parameters to be used for the system of "production, collection, preparation and transportation to the consumer" of natural or associated petroleum gas. Clarification of the reasons for the incomplete correspondence of the existing equations of state of real gases, which makes it possible to apply for natural or associated petroleum gases moving along field gas pipelines with frequently changing physical parameters and chemical properties in a non-equilibrium state.
3. The issue of a detailed study of the existing equations of state of real gases, including the Clapeyron–Mendeleev equations and the search for ways to apply these equations in the fields in order for carrying out calculations to determine all the physical parameters of natural or associated petroleum gas in the system of "production, collection, preparation and transportation to the consumer". It was found that the use of the Clapeyron–Mendeleev equation in its current form leads to large errors due to some physical technological parameters of the gas that are not taken into account in the equation.

In other words, the physical and chemical properties of natural or associated petroleum gas, as well as its volume supplied to the consumer, are significantly affected by changes in the following technological parameters (P, V, T, Δ, w_Δ, Z_{gp}, R). Therefore, it was necessary to take these parameters into account in an improved version of the real gas equation of state (5), as proposed by the authors.

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