ESTUDO COMPARATIVO DE CORRELAÇÕES E EQUAÇÕES EMPÍRICAS DE EFICÁCIA DE ESTADO PARA O FATOR DE COMPRESSIBILIDADE DE DETERMINAÇÃO DE GÁS NATURAL

COMPARATIVE STUDY OF EMPIRICAL CORRELATIONS AND EQUATIONS OF STATE EFFECTIVENESS FOR COMPRESSIBILITY FACTOR OF NATURAL GAS DETERMINATION

СРАВНИТЕЛЬНЫЙ АНАЛИЗ ЭФФЕКТИВНОСТИ ПРИМЕНЕНИЯ КОРРЕЛЯЦИОННЫХ ЗАВИСИМОСТЕЙ И УРАВНЕНИЙ СОСТОЯНИЯ ДЛЯ ОПРЕДЕЛЕНИЯ КОЭФФИЦИЕНТА СВЕРХСЖИМАЕМОСТИ ПРИРОДНОГО ГАЗА

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Received 08 May 2021; received in revised form 23 May 2021; accepted 14 December 2021

RESUMO

Introdução: Hoje, existem quatro grupos principais de métodos de cálculo do fator de compressibilidade do gás natural: medidas experimentais, equações de estado, correlações empíricas, métodos modernos baseados em algoritmos genéticos, redes neurais, modelagem atomística (método de Monte Carlo e dinâmica molecular). Um método escolhido corretamente pode melhorar a precisão do cálculo das reservas de gás e prever sua produção e processamento. **Objetivo:** Encontrar os métodos ideais para calcular o fator z seguindo as condições termodinâmicas características. **Métodos:** Para determinar o melhor método para calcular o fator de compressibilidade, a eficácia do uso de várias correlações empíricas e equações de estado para prever o fator de compressibilidade de sistemas de hidrocarbonetos (gases de reservatório e gases de separação) de várias composições foi avaliada pela comparação de resultados numéricos com experimentais dados. **Resultados e discussão:** Com base em 824 valores experimentais do fator de compressibilidade para 235 várias misturas de gases na faixa de pressão de 0,1 a 94 MPa e temperaturas de 273 a 437 K, a equação de estado ideal e dependência de correlação empírica para previsão precisa do fator z foi encontrado. É mostrado que para todas as misturas de gases a equação de estado de Peng-Robinson com o parâmetro de deslocamento e a equação de estado de Brusilovsky permitem obter melhores resultados. Para esses métodos, o erro relativo absoluto médio não excede 2%. Dentre as dependências de correlação, os melhores resultados são apresentados por Sanjari e Nemati Lay; Correlações de Heidaryan, Moghadasi e Rahimi com um erro não superior a 3%. **Conclusões:** Constatou-se que, para os métodos propostos, a redução da pressão tem um efeito mais significativo na precisão dos valores calculados do que a redução da temperatura. Foi demonstrado que ao estudar misturas de gases ácidos com um teor de dióxido de carbono superior a 10%, as equações de estado descrevem melhor o comportamento de fase do sistema em comparação com as correlações empíricas.

Palavras-chave: fator de compressibilidade, equação de estado, correlação empírica, gás natural, CO_2 .

ABSTRACT

Introduction: Today, there are four main groups of methods for calculating the compressibility factor of natural gas: experimental measurements, equations of state, empirical correlations, modern methods based on genetic algorithms, neural networks, atomistic modeling (Monte Carlo method and molecular dynamics). A correctly chosen method can improve the accuracy of calculating gas reserves and predicting its production and processing. **Aim:** To find the optimal methods for calculating the z -factor following the characteristic thermobaric conditions. **Methods:** To determine the best method for calculating the compressibility factor, the effectiveness of using various empirical correlations and equations of state to predict the compressibility factor of hydrocarbon

systems (reservoir gases and separation gases) of various compositions were evaluated by comparing numerical results with experimental data. **Results and Discussion:** Based on 824 experimental values of the compressibility factor for 235 various gas mixtures in the pressure range from 0.1 to 94 MPa and temperatures from 273 to 437 K, the optimal equation of state and empirical correlation dependence for accurate z-factor prediction was found. It is shown that for all gas mixtures the Peng-Robinson equation of state with the shift parameter and Brusilovsky equation of state allow achieving best results. For these methods, the average absolute relative error does not exceed 2%. Among the correlation dependences, the best results are shown by the Sanjari and Nemati Lay; Heidaryan, Moghadasi and Rahimi correlations with an error not exceeding 3%. **Conclusions:** It was found that for the proposed methods, the reduced pressure has a more significant effect on the accuracy of the calculated values than the reduced temperature. It is shown that when studying acid gas mixtures with a carbon dioxide content of more than 10%, the equations of state better describe the phase behavior of the system in comparison with empirical correlations.

Keywords: *compressibility factor, equation of state, empirical correlation, natural gas, CO₂.*

ABSTRACT

Введение: На сегодняшний день существует четыре основных группы методов для расчета коэффициента сжимаемости природного газа: экспериментальные измерения, уравнения состояния, эмпирические корреляции, а также современные методы, использующие генетические алгоритмы, нейронные сети, атомистическое моделирование (метод Монте-Карло и молекулярной динамики). Правильно выбранный метод может повысить точность подсчета запасов газа и прогнозирования его добычи и переработки. **Цель:** Найти оптимальные методики расчета z-фактора в соответствии с характерными термобарическими условиями. **Методы:** Для выбора оптимального метода расчета коэффициента сверхсжимаемости произведена оценка эффективности применения различных эмпирических корреляций и уравнений состояния для прогнозирования коэффициента сверхсжимаемости углеводородных систем (пластовые газы и газы сепарации) различного состава путем сравнения численных результатов с экспериментальными данными. **Результаты и обсуждение:** На основе 824 экспериментально полученных значений коэффициента сжимаемости для 235 составов различных газовых смесей в диапазоне давлений от 0,1 до 94 МПа и температур от 273 до 437 К произведена оценка поиска оптимального уравнения состояния и корреляционной зависимости для точного предсказания z-фактора. Показано, что для всех составов газов наилучшие результаты показывает уравнения состояния Пенга-Робинсона с шифт параметром и Брусиловского. Для этих моделей средний процент отклонения расчетных значений от экспериментальных данных не превосходит 2%. Среди корреляционных зависимостей лучшие результаты показывают зависимости Sanjari and Nemati Lay; Heidaryan, Moghadasi and Rahimi с ошибкой, не превосходящей 3%. **Заключение:** Установлено, что для большинства предложенных методов существенное влияние на точность расчетных значений в большей степени оказывает приведенное давление, чем приведенная температура. Показано, что при изучении кислых газовых составов с содержанием CO₂ свыше 10% уравнения состояния лучше описывают фазовое поведение системы в сравнении с эмпирическими корреляциями.

Keywords: *коэффициент сверхсжимаемости, уравнение состояния, эмпирическая корреляция, природный газ, диоксид углерода.*

1. INTRODUCTION:

Physical properties of natural gases, as well as their functional dependence on pressure, temperature, and molecular weight, are required for planning gas, oil, and gas condensate deposit development. The compressibility factor and viscosity of natural gas are two of the most important parameters in gas production and processing. Their importance cannot be overestimated in the context of maintaining fluid balance in the reservoir, estimating gas reserves, reservoir modeling, gas wells testing, analyzing the productivity, and predicting future gas production and processing (Heidaryan, Moghadasi, and Rahimi, 2010a; Heidaryan,

Salarabadi, Moghadasi, 2010b).

All methods for the compressibility factor determination can be divided into following groups: experimental measurements, equations of state, empirical correlations, as well as modern methods using genetic algorithms, neural networks, atomistic modeling (Monte Carlo method and molecular dynamics simulations).

The most accurate approach allowing determining the z-factor is experimental measurements, based on compression-expansion process. There are a lot of experimental data in scientific journals, books and articles. Thus, one of the first experimental data on the z-factor measurements was presented in (Buxton,

Campbell, 1967). The authors determined the compressibility factors for five mixtures of methane, carbon dioxide and ethane of propane at different temperatures and mixtures. In (Ababio, McElroy, Williamson, 2001) authors published the experimental results on methane-nitrogen mixtures of various compositions, in (McElroy, Fang, Williamson, 2001) one can find data for methane+ethane+carbon dioxide mixtures. More experimental values of the compressibility factor for different mixtures can be found in (Hall, 1973; Roe, 1972; Lapshin, Volkov, Shafiev, 2011; Obuba, Ikiesnkimama, Ubani, Ekeke, 2013; Fayazi, Arabloo, Mohammadi, 2014; Bian, Du, Tang, and Du, 2012). However, this method cannot be applied to every gas mixture because of its complexity, time consuming and cost. It also needs special equipment and human resources. The authors of (Drohm, 1988) discussed also the problem of quality of experimental PVT data obtained from the experiments performed on gas condensates.

Most of the modern methods used to determine the z-factor are based on the computational capabilities of modern computers. In (Chamkalani, Maesoumi, and Sameni, 2013) authors described the theoretical basis of Particle Swarm optimization and Genetic algorithm for optimal prediction of gas deviation factor. Authors of (Baniasadi, Mohebbi, and Baniasadi, 2012) developed a new correlation of natural gas compressibility factor using an artificial neural networks while authors of (Shateri, Ghorbani, Hemmati-Sarapardeh, and Mohammadi, 2015) predicted the compressibility factor of natural gas using the most powerful modeling approach, namely Wilcoxon generalized radial basis function network for analysis of a large data bank, covering a wide range of natural gases.

One of the “young” method for the z-factor determination is the atomistic modeling, including Monte Carlo (MC) method and molecular dynamics simulations. The authors of (Ungerer, Nieto-Draghi, Rousseau, Ahunbay, Lachet, 2007) determined the compressibility factor of pure methane using MC simulations, authors of (Lagache, Ungerer, Boutin, Fuchs, 2001, 2004) did also the same thing for other hydrocarbons. In (Neubauer, Tavitian, Boutin, Ungerer, 1999; Malyshev, Moiseeva, Kalinovskiy, 2018; Moiseeva, Malyshev, 2019) the applicability of the Molecular Dynamics Simulations to the z-factor determination is discussed and the computations for some natural gas components are presented.

The most reliable and time-tested methods for the compressibility factor determination are still empirical correlations and equations of state.

They allow one to accurately compute the z-factor of natural gas in a wide range of thermobaric parameters. These methods are used in the majority of the software, where physical properties of gas are need to be calculated. Therefore, the problem of choosing the best empirical correlation or the equation of state is always of high importance.

This study is aimed to compare the compressibility factor for natural gas mixtures calculated using empirical correlations and equations of state and to find the optimal methods for calculating the z-factor according to the reservoir and gas separator thermobaric conditions.

2. MATERIALS AND METHODS:

The basic formula for determining the compressibility factor of natural gas is described by Equation 1:

$$Z = \frac{PV}{nRT}, \quad (\text{Eq.1})$$

where P is the pressure, V is the volume, n is the number of moles of gas, R is the universal gas constant, T is the temperature.

Based on the theory of corresponding states, Z is also can be defined as a function of pseudo reduced pressure (P_{pr}) and pseudo reduced temperature (T_{pr}) as follows (Chamkalani et al, 2013):

$$P_{pr} = \frac{P}{P_{pc}}, \quad (\text{Eq.2})$$

$$T_{pr} = \frac{T}{T_{pc}}, \quad (\text{Eq.3})$$

where P_{pc} and T_{pc} stand for the pseudo critical pressure and temperature, respectively.

The physical meaning of this parameter is a correction factor, which describes the deviation of a real gas from ideal gas behavior. In this work, 13 empirical correlations and 6 equations of state used to calculate the compressibility factor were considered.

2.1. Empirical correlations

Experimental data for the compressibility factor of hydrocarbon mixtures obtained by different authors became the basis for creating convenient and easy-to-calculate correlation

dependences of the z-factor for the given pressure and temperature. To date, there are more than 20 empirical correlations (Heidaryan et al., 2010a). However, the existing applicability range imposes certain restrictions on their use in engineering calculations.

2.1.1 Azizi

In 2009, the study of Navid Azizi, Dr. R. Behbahani, Dr. M. A. Isazadeh, devoted to the z-factor of natural gas determination was published (Azizi, Behbahani, Isazadeh, 2010). The authors developed the correlation based on 3038 values of the Standing and Katz compressibility factor chart.

Equations 4-9 are suitable for calculating the compressibility factor of a dry gas for the pseudo reduced pressures and temperatures within the range of $0.2 \leq P_{pr} \leq 1$ and $1.1 \leq T_{pr} \leq 2$:

$$Z = A + \frac{B+C}{D+E}, \quad (\text{Eq.4})$$

$$A = a_0 T_{pr}^{2.16} + a_1 P_{pr}^{1.028} + a_2 P_{pr}^{1.58} T_{pr}^{-2.1} + a_3 \ln(T_{pr})^{-0.5}, \quad (\text{Eq.5})$$

$$B = a_4 + a_5 T_{pr}^{2.4} + a_6 P_{pr}^{1.56} + a_7 P_{pr}^{0.124} T_{pr}^{3.033}, \quad (\text{Eq.6})$$

$$C = a_8 \ln(T_{pr})^{-1.28} + a_9 \ln(T_{pr})^{1.37} + a_{10} \ln(P_{pr}) + a_{11} \ln(P_{pr})^2 + a_{12} \ln(P_{pr}) \ln(T_{pr}), \quad (\text{Eq.7})$$

$$D = 1 + a_{13} T_{pr}^{5.55} + a_{14} P_{pr}^{0.68} T_{pr}^{0.33}, \quad (\text{Eq.8})$$

$$E = a_{15} \ln(T_{pr})^{1.18} + a_{16} \ln(T_{pr})^{2.1} + a_{17} \ln(P_{pr}) + a_{18} \ln(P_{pr})^2 + a_{19} \ln(P_{pr}) \ln(T_{pr}). \quad (\text{Eq.9})$$

Coefficients a_i are presented in table 1.

The advantage of this correlation is that it is explicit and does not require an iterative solution.

2.1.2 Bahadori

In 2007, Alireza Bahadori, Saeid Mokhatab, Brian F. Towler presented an empirical equation for calculating the gas compressibility factor (Bahadori, Mokhatab, Towler, 2007). The equation is suitable for calculating the compressibility factor of gas when $0.2 \leq P_{pr} \leq 16$ and $1.05 \leq T_{pr} \leq 2.4$.

Correlation, developed based on the Standing-Katz chart, is an explicit function that does not require an iterative solution (Equations 10-14):

$$Z = a + bP_{pr} + cP_{pr}^2 + dP_{pr}^3, \quad (\text{Eq.10})$$

$$a = A_a + B_a T_{pr} + C_a T_{pr}^2 + D_a T_{pr}^3, \quad (\text{Eq.11})$$

$$b = A_b + B_b T_{pr} + C_b T_{pr}^2 + D_b T_{pr}^3, \quad (\text{Eq.12})$$

$$c = A_c + B_c T_{pr} + C_c T_{pr}^2 + D_c T_{pr}^3, \quad (\text{Eq.13})$$

$$d = A_d + B_d T_{pr} + C_d T_{pr}^2 + D_d T_{pr}^3. \quad (\text{Eq.14})$$

Constants A_i, B_i, C_i, D_i for the empirical dependence of Bahadory are presented in table 2.

The authors modified the correlation by introducing a correction ε for the given parameters to calculate the compressibility factor of gas mixtures with a high content of acid gas, in particular, carbon dioxide and hydrogen sulfide (Equation 15):

$$\varepsilon = \frac{a + by_{H_2S} + cy_{H_2S}^2 + dy_{H_2S}^3}{1.8}, \quad (\text{Eq.15})$$

where y_{H_2S}, y_{CO_2} are mole fractions of H_2S and CO_2 respectively, and the coefficients are calculated from Equations 16-19:

$$a = A_a + B_a y_{CO_2} + C_a y_{CO_2}^2 + D_a y_{CO_2}^3, \quad (\text{Eq.16})$$

$$b = A_b + B_b y_{CO_2} + C_b y_{CO_2}^2 + D_b y_{CO_2}^3, \quad (\text{Eq.17})$$

$$c = A_c + B_c y_{CO_2} + C_c y_{CO_2}^2 + D_c y_{CO_2}^3, \quad (\text{Eq.18})$$

$$d = A_d + B_d y_{CO_2} + C_d y_{CO_2}^2 + D_d y_{CO_2}^3. \quad (\text{Eq.19})$$

A_i, B_i, C_i, D_i are constants (table 3).

Then ε is used to determine the modified pseudo critical temperature (equation 20) and pressure (equation 21):

$$T_{pc}^{correct} = T_{pc} - \varepsilon, \quad (\text{Eq.20})$$

$$P_{pc}^{correct} = \frac{P_{pc}(T_{pc} - \varepsilon)}{T_{pc} + \varepsilon y_{H_2S}(1 - y_{H_2S})} \quad (\text{Eq.21})$$

The corrected pseudocritical parameters are substituted into Equations 9-12 to calculate the compressibility factor using Equation 8.

2.1.3 Dranchuk and Abou-Kassem

In 1975, P. M. Dranchuk and J. H. Abou-Kassem proposed an empirical expression with eleven constants to calculate the gas compressibility factor (Dranchuk, Abou-Kassem, 1975):

$$Z = 1 - Z + \left(A_1 + \frac{A_2}{T_{pr}} + \frac{A_3}{T_{pr}^3} + \frac{A_4}{T_{pr}^4} + \frac{A_5}{T_{pr}^5} \right) \rho_r + \left(A_6 + \frac{A_7}{T_{pr}} + \frac{A_8}{T_{pr}^2} \right) \rho_r^2 - A_9 \left(\frac{A_7}{T_{pr}} + \frac{A_8}{T_{pr}^2} \right) \rho_r^5 + \frac{A_{10}(1 + A_{11} \rho_r^2) \rho_r^2}{T_{pr}^3} e^{-A_{11} \rho_r^2}, \quad (\text{Eq.22})$$

where $\rho_r = \frac{0.27P_{pr}}{ZT_{pr}}$.

The constants for the Equation 22 presented in Table 4 were found by analyzing 1500 points of the Standing-Katz chart for pressures and temperatures within the range of $0.2 \leq P_{pr} < 30$; $1 < T_{pr} < 3$ and $P_{pr} < 1$; $0.7 < T_{pr} < 1$.

Since the compressibility factor appears on both sides of the equation, it is necessary to use an iterative solution. It is recommended to use Equation 23 representing the Newton-Raphson method:

$$Z_{n+1} = Z_n - (f_z/f'_z), \quad (\text{Eq.23})$$

where n is the index number of iteration.

Table 4. Constants A_i for empirical dependence of Dranchuk and Abou-Kassem

i	A_i	i	A_i
1	0.326	7	0.736
2	-1	8	0.184
3	-0.533	9	0.105
4	0.0156	10	0.613
5	-0.0516	11	0.721
6	0.547		

2.1.4 Dranchuk-Purvis-Robinson

Equation 24 was developed by P. M. Dranchuk, R. A. Purvis, and D. B. Robinson in 1973 (Dranchuk, Purvis, Robinson, 1974). It is based on the Benedict-Webb-Rubbin equation of state.

$$Z = \frac{0.27P_{pr}}{yT_{pr}}, \quad (\text{Eq.24})$$

where pseudo-reduced density y is a solution of the Equation 25:

$$f(y) = 1 + R_1y - \frac{R_2}{y} + R_3y^2 - R_4y^5 + [R_5y^2(1 + A_{11}y^2)e^{-A_{11}y^2}], \quad (\text{Eq.25})$$

where A_i are constants from Table 4, R_i are calculated using Equations 26-30:

$$R_1 = A_1 + \frac{A_2}{T_{pr}} + \frac{A_3}{T_{pr}^3} + \frac{A_4}{T_{pr}^4} + \frac{A_5}{T_{pr}^5}, \quad (\text{Eq.26})$$

$$R_2 = \frac{0.27P_{pr}}{T_{pr}}, \quad (\text{Eq.27}) \quad Z =$$

$$R_3 = A_6 + \frac{A_7}{T_{pr}} + \frac{A_8}{T_{pr}^2}, \quad (\text{Eq.28})$$

$$R_4 = A_9 \left(\frac{A_7}{T_{pr}} + \frac{A_8}{T_{pr}^2} \right), \quad (\text{Eq.29})$$

$$R_5 = \frac{A_{10}}{T_{pr}^3}. \quad (\text{Eq.30})$$

2.1.5 Hall and Yarborough

In 1973, Kenneth R. Hall and Lyman Yarborough published an empirical correlation:

$$Z = 0.06125 \frac{P_{pr}te^{-1.2(1-t)^2}}{y}, \quad (\text{Eq.31})$$

where y is pseudo-reduced density, which can be calculated using Equation 23.

Equation 31 is developed using virial expansion and Carnahan-Starling equation of state (hard-sphere equation):

$$Z = \frac{pV}{Nk_B T} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}, \quad (\text{Eq.32})$$

where Z denotes the compressibility factor; p is the pressure; V is volume; k_B is Boltzmann constant;

T is temperature; η is packaging indicator.

An iterative solution is required to determine the compressibility factor using Equation 30. The reduced density can be found as a solution of Equation 33:

$$f(y) = -0.06125P_{pr}te^{-1.2(1-t)^2} + \frac{y+y^2+y^3-y^4}{(1-y)^3} - (14.76t - 9.76t^2 + 4.58t^3)y^2 + (90.7t - 242.2t^2 + 42.4t^3)y^{1.18+2.82t}, \quad (\text{Eq.33})$$

where $t = 1/T_{pr}$.

The authors mentioned that the method is not suitable for calculating when a reduced temperature is less than unity.

2.1.6 Heidaryan et al. (2010a)

The empirical expression 34 developed by Ehsan Heidaryan, Amir Salarabadi, Jamshid Moghadas is based on 1220 values of the Standing-Katz chart for the pressure and temperature in the range of $0.2 \leq P_{pr} \leq 15$ and $1.2 \leq T_{pr} \leq 3$ (Heidaryan, Salarabadi, Moghadas, 2010). It can be written as:

$Z =$

$$\frac{A_1 + A_2 \ln(P_{pr}) + A_3 (\ln P_{pr})^2 + A_4 (\ln P_{pr})^3 + \left(\frac{A_5}{T_{pr}}\right) + \left(\frac{A_6}{T_{pr}^2}\right)}{1 + A_7 \ln(P_{pr}) + A_8 (\ln P_{pr})^2 + \left(\frac{A_9}{T_{pr}}\right) + \left(\frac{A_{10}}{T_{pr}^2}\right)}, \text{ (Eq.34)}$$

where A_i are the constants presented in Table 5.

Table 5. Constants A_i for empirical expression of Heydaryan et al. (2010a)

i	A_i	i	A_i
1	1.115323727	6	1.157531187
2	-0.079039521	7	-0.053677807
3	0.01588138	8	0.0146557
4	0.008861345	9	-1.809973749
5	-2.161907926	10	0.954860388

2.1.7 Heidaryan et al. (2010b)

Later, in (Heidaryan, Moghadasi, Rahimi, 2010), the same authors proposed a modification of the empirical expression taking into account the presence of C7+ hydrocarbons and non-hydrocarbon components of natural gas (Equation 35):

$$Z = \ln \left(\frac{A_1 + A_3 \ln(P_{pr}) + \frac{A_5}{T_{pr}} + A_7 (\ln(P_{pr}))^2 + \frac{A_9}{T_{pr}^2} + \frac{A_{11}}{T_{pr}} \ln(P_{pr})}{1 + A_2 \ln(P_{pr}) + \frac{A_4}{T_{pr}} + A_6 (\ln(P_{pr}))^2 + \frac{A_8}{T_{pr}^2} + \frac{A_{10}}{T_{pr}} \ln(P_{pr})} \right) \quad \text{(Eq.35)}$$

Constants A_i are presented in table 6.

Table 6. Constants A_i for empirical expression of Heidaryan et al. (2010b)

A_i	$0.2 \leq P_{pr} \leq 3$	$3 < P_{pr} \leq 15$
A_1	2.827793	3.252838
A_2	-4.688191·10 ⁻¹	-1.306424·10 ⁻¹
A_3	-1.262288	-6.449194·10 ⁻¹
A_4	-1.536524	-1.518028
A_5	-4.535045	-5.391019
A_6	6.895104·10 ⁻²	-1.379588·10 ⁻²
A_7	1.903869·10 ⁻¹	6.600633·10 ⁻²
A_8	6.200089·10 ⁻¹	6.120783·10 ⁻¹
A_9	1.838479	2.317431
A_{10}	4.052367·10 ⁻¹	1.632223·10 ⁻¹
A_{11}	1.073574	5.660595·10 ⁻¹

2.1.8 Papay

In 1968 J. Papay proposed Equation 36 for calculating the compressibility factor (Papay,

1968):

$$Z = 1 - \frac{3.52 P_{pr}}{10^{0.9813 T_{pr}}} + \frac{0.274 P_{pr}^2}{10^{0.8157 T_{pr}}}. \quad \text{(Eq.36)}$$

2.1.9 Sanjari and Nemati Lay

In 2012 Ehsan Sanjari, Ebrahim Nemati Lay published an empirical expression (Equation 37) for the z-factor based on a virial equation (Sanjari, Nemati Lay, 2012). It was obtained by multiple regression analysis of 5844 experimental values of the compressibility factor for natural gas mixtures from 24 data sources in the range of $1.01 \leq T_{pr} \leq 3$ and $0.01 \leq P_{pr} \leq 15$:

$$Z = 1 + A_1 P_{pr} + A_2 P_{pr}^2 + \frac{A_3 P_{pr}^{A_4}}{T_{pr}^{A_5}} + \frac{A_6 P_{pr}^{(A_4+1)}}{T_{pr}^{A_7}} + \frac{A_8 P_{pr}^{(A_4+2)}}{T_{pr}^{(A_7+1)}}. \quad \text{(Eq.37)}$$

Constant values can be found in table 7.

Table 7. Constants A_i for empirical expression of Sanjari and Nemati Lay

A_i	$0.01 < P_{pr} < 3$	$3 < P_{pr} < 15$
A_1	0.007698	0.015642
A_2	0.003839	0.000701
A_3	-0.467212	2.341511
A_4	1.018801	-0.657903
A_5	3.805723	8.902112
A_6	-0.087361	-1.136
A_7	7.138305	3.543614
A_8	0.08344	0.134041

2.1.10 Sohrab Towfighi

In 2019, Sohrab Towfighi published an empirical equation developed by regression analysis of the Standing-Katz chart using machine learning and parameter optimization based on the Levenberg-Marquardt algorithm (Towfighi, 2019). They obtained Equation 38 with 6 constants allowing the calculation of the compressibility factor. Constants are presented in Table 8:

$$Z = A_1 \left(\left(\frac{T_{pr}}{P_{pr}} \right)^{A_2} \right) + A_3 \left(\left(\left(\frac{A_4}{\left(\frac{T_{pr}}{P_{pr}} \right)^{A_5}} \right) \right)^{\left(\frac{T_{pr}-A_5}{\left(\frac{T_{pr}}{P_{pr}} \right)^{A_6}} + A_6 \right)} \right). \quad \text{(Eq.38)}$$

Table 8. Constants A_i for the empirical dependence of Sohrab Towfighi

i	A_i
1	0.2962187
2	1.285777
3	0.9946115
4	0.04115234
5	3.364051
6	0.5728996

2.1.11. Latonov-Gurevitch

In 1969 an approximation of the Standing and Katz compressibility factor chart was presented in (Latonov, Gurevich, 1969) by Russian researchers V.V. Latonov, G.R. Gurevich (Equation 39):

$$Z = (0.4 \lg T_{pr} + 0.73)^{P_{pr}} + 0.1 P_{pr}. \quad (\text{Eq.39})$$

In the literature, one can also find Equation 40 written in the following form:

$$Z = (0.173761 \ln T_{pr} + 0.73)^{P_{pr}} + 0.1 P_{pr}. \quad (\text{Eq.40})$$

These methods are recommended for dry gas over a wide range of pressure and temperature values. However, in the presence of condensate in the gas mixture, the calculation error turns out to be very high.

2.2. Equations of state

Cubic equations of state (EOS) are widely used in the oil and gas industry due to their simplicity and ability to describe the thermodynamic properties of liquids and gases with a high degree of accuracy. There are two-, three-, four- and five-parameter cubic equations of state.

2.2.1 Redlich-Kwong EOS

In 1949, O. Redlich and J. Kwong proposed a two-parameter EOS for gases (Equation 41) (Redlich, Kwong, 1949):

$$p = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)}, \quad (\text{Eq.41})$$

where a and b are constants corresponding to the

considered fluid and are calculated using Equations 42-43:

$$a = \frac{0.42748R^2T_{pc}^{2.5}}{P_{pc}}, \quad (\text{Eq.42})$$

$$b = \frac{0.08664RT_{pc}}{P_{pc}}, \quad (\text{Eq.43})$$

where T_c, P_c are the critical temperature and pressure.

Cubic Redlich-Kwong EOS for z-factor computation is described by:

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0. \quad (\text{Eq.44})$$

The range of its applicability is derived from the expression $\frac{P}{P_c} < 0.5 \frac{T}{T_c}$.

To calculate the properties of multicomponent systems, the coefficients a_m and b_m are used, which are calculated using equations 45-46.

$$a_m = \left(\sum_{i=1}^N y_i a_i^{0.5} \right)^2, \quad (\text{Eq.45})$$

$$b_m = \sum_{i=1}^N y_i b_i, \quad (\text{Eq.46})$$

where a_i, b_i are coefficients of i -th component; y_i is the mole fraction of i -th component; N is several components in the mixture.

The Redlich-Kwong equation is a successful empirical modification of the Van der Waals equation of state; the introduction of the temperature dependence $T^{0.5}$ in the denominator has no theoretical justification.

2.2.2 Soave-Redlich-Kwong EOS

The Italian scientist J. Soave proposed a modification of the Redlich-Kwong equation in 1972 (Soave, 1972). The coefficient b remained unchanged since the Equation 43, the coefficient a was presented as a function of temperature and acentric factor.

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)}, \quad (\text{Eq.47})$$

where $a = \alpha \cdot 0.42747R^2 \frac{T_{pc}^2}{P_{pc}}$; $b = 0.08664R \frac{T_{pc}}{P_{pc}}$; $\alpha = [1 + (0.48508 + 1.55171\omega - 0.15613\omega^2)(1 - T_r^{0.5})]^2$.

Cubic Soave-Redlich-Kwong equation for the z-factor determination has the same form as Equation 44 with $A = a\alpha \frac{p}{R^2T^2}$, $B = b \frac{p}{RT}$.

For multicomponent systems coefficients a_m and b_m are calculated using the additivity rule (Equations 48-49):

$$a_m = \sum_{i=1}^N \sum_{j=1}^N (1 - C_{ij}) y_i y_j (a_i a_j)^{0.5}, \quad (\text{Eq.48})$$

$$b_m = \sum_{j=1}^N y_j b_j, \quad (\text{Eq.49})$$

where N is several components in the mixture; C_{ij} is pair interaction correction factor; y_i – mole fraction of the i -th component; a_i – coefficient a for pure i -th component; b_i – coefficient b for a pure i -th component.

2.2.3 Peng-Robinson EOS

Peng-Robinson equation of state has become the most used equation of state in the oil and gas industry. In 1974 D.Robinson and his graduate student Peng proposed the equation 50 (Peng, Robinson, 1976):

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)+b(V-b)}. \quad (\text{Eq.50})$$

Cubic Peng-Robinson equation of state for z -factor computation is

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0. \quad (\text{Eq.51})$$

The compressibility factor for the gas phase is determined as the smallest positive root of equation 51. Coefficients are calculated from the following expressions (Equations 52-57):

$$A = a\alpha \frac{P}{R^2 T^2}, \quad (\text{Eq.52})$$

$$B = b \frac{P}{RT}, \quad (\text{Eq.53})$$

$$a_c = 0.457235 R^2 \frac{T_{pc}^2}{P_{pc}}, \quad (\text{Eq.54})$$

$$b = 0.077796 R \frac{T_{pc}}{P_{pc}}, \quad (\text{Eq.55})$$

$$\alpha(T_{pr}, \omega) = [1 + m(1 - T_{pr}^{0.5})]^2, \quad (\text{Eq.56})$$

$$m = \begin{cases} 0.37464 + 1.542261\omega - 0.26992\omega^2, & \omega \leq 0.49, \\ 0.37464 + 1.48503\omega - 0.16442\omega^2 + \\ 0.01666\omega^3, & \omega > 0.49 \end{cases} \quad (\text{Eq.57})$$

For multicomponent systems coefficients a_m and b_m are determined using Equations 48-49.

2.2.4 Peng-Robinson EOS with the shift parameter

Comparing the experimental data with the

calculated values of molar volumes revealed an error that remained practically unchanged in a wide pressure range.

In 1988, Yavery and Yungren proposed introducing a linear correction c for the molar volume V of the phase calculated from the equation of state (Jhavery, Youngren, 1988). Thus, the “correct” volume of the phase $\tilde{V}$ was calculated by the formula: $\tilde{V} = V - c$. The introduction of the correction increased the accuracy of liquid density calculating and had a minimal effect on the vapor density at low and medium pressures, since its molar volume was an order of magnitude larger than the correction.

For multicomponent systems, the parameter c is determined by the mixing rule (Equation 58):

$$c = \sum_{i=1}^N c_i x_i, \quad (\text{Eq.58})$$

where N is several components in the mixture; x_i is the mole fraction of the i -th component; c_i is the correction constant for the pure i -th component, which is determined by the formula $c_i = s_i b_i$. Multiplier s for some natural gas components is presented in work (Jhavery, Youngren, 1988).

Thus, the cubic Peng-Robinson equation of state with a shifting parameter is written as Equation 59:

$$P = \frac{RT}{V+c-b} - \frac{a}{(V+c)(V+c+b)+b(V+c-b)}. \quad (\text{Eq.59})$$

The compressibility factor can be found from Equation 60:

$$Z^3 + (B + 3C - 1)Z^2 + (A - 3B^2 - 2B + 2BC + 3C^2 - 2C)Z + (AC - 2BC - C^2 + C^2B + C^3 - 3CB^2 - AB + B^2 + B^3) = 0, \quad (\text{Eq.60})$$

Where A, B, C are derived from Equations 61-63.

$$A = \frac{aP}{R^2 T^2}, \quad (\text{Eq.61})$$

$$B = \frac{bP}{RT}, \quad (\text{Eq.62})$$

$$C = \frac{cP}{RT}. \quad (\text{Eq.63})$$

2.2.5 Harmens-Knapp EOS

The three-parameter equation of state, proposed by the authors A. Harmens and H. Knapp in 1980, was aimed to improve the expression of the temperature function describing

phase behavior of the superheated steam (Harmens, 1980).

$$p = \frac{RT}{V-b} - \frac{a}{V^2+bcV-b^2(c-1)}. \quad (\text{Eq.64})$$

The cubic Harmens-Knapp Equation 64 for z-factor determination is written as Equations 65-76:

$$Z^3 + (Bc - B - 1)Z^2 + [A + B^2(1 - 2c) - Bc]Z + [B^3(c - 1) + B^2(c - 1) - AB] = 0, \quad (\text{Eq.65})$$

$$A = a \frac{P}{R^2 T^2}, \quad (\text{Eq.66})$$

$$B = b \frac{P}{RT}, \quad (\text{Eq.67})$$

$$\text{where } a = \alpha(T_{pr}) \Omega_a R^2 \frac{T_{pc}^2}{P_{pc}}, \quad (\text{Eq.68})$$

$$b = \Omega_b R \frac{T_{pc}}{P_{pc}}, \quad (\text{Eq.69})$$

$$c = 1 + \frac{1-3\zeta}{\beta\zeta}, \quad (\text{Eq.70})$$

$$\Omega_a = 1 - 3\zeta + 3\zeta^2 + \beta\zeta(3 - 6\zeta + \beta\zeta), \quad (\text{Eq.71})$$

$$\Omega_b = \zeta\beta, \quad (\text{Eq.72})$$

$$\begin{cases} \alpha(T_r) = [1 + E(1 - T_{pr}^{0.5}) - F(1 - T_{pr}^{-1})]^2, & T_{pr} \leq 1; \\ \alpha(T_{pr}) = 1 - (0.6258 + 1.5227\omega) \ln T_{pr} + \\ (0.1533 + 0.41\omega)(\ln T_{pr})^2, & T_{pr} > 1; \end{cases} \quad (\text{Eq.73})$$

$$\begin{cases} E = 0.50 + 0.27767\omega + 2.17225\omega^2, \\ F = -0.022 + 0.338\omega - 0.845\omega^2, & \text{when } \omega \leq 0.2; \\ E = 0.41311 + 1.14657\omega, \\ F = 0.0118, & \text{when } \omega > 0.2 \end{cases} \quad (\text{Eq.74})$$

$$\beta = 0.10770 + 0.76405\zeta - 1.24282\zeta^2 + 0.96210\zeta^3, \quad (\text{Eq.75})$$

$$\zeta = 0.3211 - 0.080\omega + 0.0384\omega^2. \quad (\text{Eq.76})$$

2.2.6 Patel-Teja EOS

In 1982 Patel and Teja developed the modified equation of state (Equation 77). The key modification became the introduction of the third parameter c and Ω_c (Patel, Teja, 1982).

$$p = \frac{RT}{V-b} - \frac{a[T]}{V(V+b)+c(V-b)}. \quad (\text{Eq.77})$$

Patel and Teja found that using the adjusted critical compressibility factor would improve the accuracy of the calculations. The cubic equation of Patel-Teja is Equation 78 with Equations 79-94.

$$Z^3 - (C - 1)Z^2 + (A - 2BC - B^2 - B - C)Z +$$

$$(B^2C + BC - AB) = 0. \quad (\text{Eq.78})$$

$$\text{where } A = a \frac{P}{R^2 T^2}, \quad (\text{Eq.79})$$

$$B = b \frac{P}{RT}, \quad (\text{Eq.80})$$

$$C = c \frac{P}{RT}, \quad (\text{Eq.81})$$

$$a[T] = \Omega_a R^2 \frac{T_{pc}^2}{P_{pc}} \alpha[T_{pr}], \quad (\text{Eq.82})$$

$$b = \Omega_b R \frac{T_{pc}}{P_{pc}}, \quad (\text{Eq.83})$$

$$c = \Omega_c R \frac{T_{pc}}{P_{pc}}, \quad (\text{Eq.84})$$

$$\alpha = \left[1 + F \left(1 - T_{pr}^2 \right) \right]^2, \quad (\text{Eq.85})$$

$$\Omega_a = 3\zeta_c^2 + 3(1 - 2\zeta_c)\Omega_b + \Omega_b^2 + 1 - 3\zeta_c, \quad (\text{Eq.86})$$

$$\Omega_b^3 + (2 - 3\zeta_c)\Omega_b^2 + 3\zeta_c^2\Omega_b - \zeta_c^3 = 0, \quad (\text{Eq.87})$$

$$\Omega_c = 1 - 3\zeta_c, \quad (\text{Eq.88})$$

ζ_c is corrected critical compressibility factor given by the following formula

$$\zeta_c = 0.329032 - 0.076799\omega + 0.0211947\omega^2, \quad (\text{Eq.89})$$

$$F = 0.452413 + 1.30982\omega - 0.295937\omega^2, \quad (\text{Eq.90})$$

$$a_{ij} = \xi_{ij}(a_{ii}a_{jj})^{1/2}, \quad (\text{Eq.91})$$

$$a_m = \sum_i \sum_j x_i x_j a_{ij}, \quad (\text{Eq.92})$$

$$b_m = \sum_i x_i b_i, \quad (\text{Eq.93})$$

$$c_m = \sum_i x_i c_i. \quad (\text{Eq.94})$$

In particular cases, it is possible to take ζ_c equal to the critical compressibility factor, but this negatively affects the accuracy of calculations.

2.2.7 Brusilovsky EOS

Brusilovsky, A. I. in 1990 presented the four-parameter equation 95 (Brusilovsky, 1992):

$$P = \frac{RT}{V-b} - \frac{a(T,V)}{(V+c)(V+d)}, \quad (\text{Eq.95})$$

where b, c, d are the constants for the considered fluid; φ is the temperature function equal to unity at a critical temperature.

In cubic form it is written as Equation 96:

$$Z^3 + (C + D - B - 1)Z^2 + (A - BC + CD - BD - D - C)Z - (BCD + CD + AB) = 0. \quad (\text{Eq.96})$$

Coefficients A, B, C, D are derived from Equations 97-100:

$$A = a \frac{P}{R^2 T^2}, \quad (\text{Eq.97})$$

$$B = b \frac{P}{RT}, \quad (\text{Eq.98})$$

$$C = c \frac{P}{RT}, \quad (\text{Eq.99})$$

$$D = d \frac{P}{RT}, \quad (\text{Eq.100})$$

The structure of the coefficients can be understood from Equations 101-110:

$$a = a_c \cdot \varphi(T_{pr}, \omega), \quad (\text{Eq.101})$$

$$\varphi(T_{pr}, \omega) = [1 + \psi(1 - T_{pr}^{0.5})]^2, \quad (\text{Eq.102})$$

$$a_c = \frac{\alpha R^2 T_{pc}^2}{P_{pc}}, \quad (\text{Eq.103})$$

$$b = \frac{\beta R T_{pc}}{P_{pc}}, \quad (\text{Eq.104})$$

$$c = \frac{\sigma R T_c}{P_{pc}}, \quad (\text{Eq.105})$$

$$d = \frac{\delta R T_{pc}}{P_{pc}}, \quad (\text{Eq.106})$$

$$\alpha = \Omega_c^3, \quad (\text{Eq.107})$$

$$\beta = Z_c^* + \Omega_c - 1, \quad (\text{Eq.108})$$

$$\sigma = -Z_c^* + \Omega_c [0.5 + (\Omega_c - 0.75)^{1/2}], \quad (\text{Eq.109})$$

$$\delta = -Z_c^* + \Omega_c [0.5 - (\Omega_c - 0.75)^{1/2}]. \quad (\text{Eq.110})$$

Here Z_c^*, Ω_c are independent parameters of the equation of state. Their values, along with the function $\varphi = \varphi(T)$, completely determine the equation of state of a pure substance.

It is noted that Z_c^* is not the value of the coefficient at the critical point, but for two-coefficient equations of state Z_c^* is determined by the given form of the equation, and for three- and four-coefficient equations it is to be found.

The values of the parameters ψ, Ω_c, Z_c^* for pure components are given in (Brusilovsky, 1992).

Coefficients of the Brusilovsky equation of state for a multicomponent gas mixture are calculated using Equations 111-114.

$$a = \sum_{i=1}^N \sum_{j=1}^N (1 - C_{ij}) y_i y_j (a_i a_j)^{0.5}, \quad (\text{Eq.111})$$

$$b = \sum_{j=1}^N y_j b_j, \quad (\text{Eq.112})$$

$$c = \sum_{j=1}^N y_j c_j, \quad (\text{Eq.113})$$

$$d = \sum_{j=1}^N y_j d_j, \quad (\text{Eq.114})$$

Pair interaction coefficients depend on the temperature, as shown by Equation 115:

$$C_{ij} = e_{ij} + q_{ij}(T - 273.15) \cdot 10^{-3} + h_{ij}(T - 273.15)^2 \cdot 10^{-5}, \quad (\text{Eq.115})$$

where e_{ij}, q_{ij}, h_{ij} are constant values represented in (Drohm, 1988).

2.3. Pseudocritical parameters

It has been experimentally proven that the method of calculating the reduced parameters for the mixture using experimentally found or calculated critical parameters gives insufficient accuracy for the compressibility factor determination using the EOS (Bretschneider, 1966) (Equations 116-117).

$$P_{pr} = \frac{P}{P_c} \quad (\text{Eq.116})$$

$$T_{pr} = \frac{T}{T_c} \quad (\text{Eq.117})$$

For multicomponent mixtures, there is no single rule to calculate P_c, T_c

The calculated reduced values for the mixture (Equations 118-119) should satisfy the dependencies obtained from the EOS and be suitable for a pure substance.

$$T_{pr} = T/T_{pc} \quad (\text{Eq.118})$$

$$P_{pr} = P/P_{pc}. \quad (\text{Eq.119})$$

Assuming that the critical parameters for mixtures can be calculated as a sum of mole fraction of each component multiplied by the corresponding critical parameter, Kay proposed a method for calculating the pseudocritical parameters T_{pcr} and P_{pcr} (Equations 120-121) (Kay, 1936).

$$T_{pc} = \sum x_i T_{ci}, \quad (\text{Eq.120})$$

$$P_{pc} = \sum x_i P_{ci}. \quad (\text{Eq.121})$$

Joffe, analyzing the van der Waals equation, proposed formulae for calculating pseudocritical parameters (Equations 122-123) (Joffe, Zudkevitch, 1966):

$$T_{pc} = \frac{\left[\sum_{i=1}^N x_i \frac{T_{ci}^{1.25}}{P_{ci}^2} \right]^{\frac{4}{3}}}{\left[\sum_{i=1}^N x_i \frac{T_{ci}}{P_{ci}} \right]^{\frac{2}{3}}}, \quad (\text{Eq. 122})$$

$$P_{pc} = \frac{\left[\sum_{i=1}^N x_i \frac{T_{ci}^{1,25}}{P_{ci}^2} \right]^{\frac{4}{3}}}{\left[\sum_{i=1}^N x_i \frac{T_{ci}}{P_{ci}} \right]^{\frac{5}{3}}} \quad (\text{Eq.123})$$

Prausnitz and Gunn modified pseudocritical pressure calculation (Prausnitz, 1958):

$$P_{pc} = \frac{RT_{pc}}{\sum_{i=1}^N x_i V_{M_{ci}}} \sum_{i=1}^N x_i Z_{ci}, \quad (\text{Eq.124})$$

where $V_{M_{ci}}$ – critical mole volume of the component in the mixture.

Pseudocritical parameters calculated using Kay's rule differ from other rules by less than 2% if $0,5 < \frac{T_{ci}}{T_{ci+1}} < 2$ and $0,5 < \frac{P_{ci}}{P_{ci+1}} < 2$.

For P_{cm} Kay's rule shows the same results as other rules when $P_{ci} \approx P_{ci+1}$ or $V_{ci} \approx V_{ci+1}$. The calculation results can differ up to 10% when $0,5 < P_{ci}/P_{ci+1} < 2$ and $T_{ci}/T_{ci+1} \approx 1$. For other conditions the difference would be greater.

To determine pseudocritical parameters, Kay's rule is most often used. If high accuracy is required, the Joffe or Prausnitz and Gunn formulae are used.

For a more accurate determination of the pseudocritical parameters P_{pc} , T_{pc} of gas mixtures of gas condensate fields, it is recommended to use the equations 125-128 (Stewart, Burkhard, and Voo, 1959):

$$P_{pc} = \frac{K}{J^2}, \quad (\text{Eq.125})$$

$$T_{pc} = \frac{K}{J}, \quad (\text{Eq.126})$$

$$K = \left[\frac{\sum x_i T_{ci}}{P_{ci}^{0,5}} \right]^2, \quad (\text{Eq.127})$$

$$J = \frac{1}{3} \sum \frac{x_i T_{ci}}{P_{ci}} + \frac{2}{3} \left[\sum x_i \left(\frac{T_{ci}}{P_{ci}} \right)^{0,5} \right]^2, \quad (\text{Eq.128})$$

For acid gases, if the concentration of CO_2 and H_2S is less than 25% for each and is less than 50% for both, it is recommended to use the following formulae:

$$P_{pc}^* = \frac{P_{pc} T_{pc}^*}{[T_{pc} + x_{\text{H}_2\text{S}}(1 - x_{\text{H}_2\text{S}})\varepsilon]}, \quad (\text{Eq.129})$$

$$T_{pc}^* = T_{pc} - \varepsilon, \quad (\text{Eq.130})$$

$$\varepsilon = 14x_{\text{H}_2\text{S}}^{-0,36} x_{\text{CO}_2}^{0,8} + 0,8x_{\text{H}_2\text{S}}^{0,7}, \quad (\text{Eq.131})$$

where $x_{\text{H}_2\text{S}}$, x_{CO_2} – mole fractions of H_2S and CO_2 respectively; P_{pc} , T_{pc} – pseudocritical pressure and temperature.

3. RESULTS AND DISCUSSION:

3.1. Comparison of the compressibility factors calculated by different methods

In this work, the collection and aggregation of experimental studies of various gas mixtures from the integrated field research laboratory of the Integrated Well and Reservoir Survey Department of the Branch office of Gazprom VNIIGAS LLC in Ukhta, as well as sources (Buxton, Campbell, 1967; Ababio *et al.*, 2001; Drohm, 1988; McElroy *et al.*, 2001; Hall, 1973; Roe, 1972; Brusilovsky, 2002; Lapshin *et al.*, 2011; Obuba *et al.*, 2013; Fayazi *et al.*, 2014; Bian *et al.*, 2012) were carried out. There were considered 824 experimentally obtained values of the compressibility factor for 235 gas mixtures (natural gas and gas of separation) in the pressure range from 0.1 to 94 MPa and temperatures from 273 to 437 K. All the considered studies are presented in Table 9.

Samples of natural and associated petroleum gas, consisting of methane and heavier hydrocarbons (including C5 + fractions) were considered. Hydrocarbon gas mixtures with non-combustible components such as carbon dioxide, hydrogen sulfide, nitrogen, helium were also considered.

Table 9. Experimental studies of various gas mixtures

Number of measurements	Temperature, °C	Pressure, MPa	Compound of CH ₄ , %	Citation
315	11-111	0.1-34	71-92	Branch office of Gazprom VNIIGAS LLC in Ukhta
165	37-71	7-48	58-89	(Buxton and Campbell, 1967)
83	35-60	0.6-12	20-50	(Ababio, McElroy, Williamson, 2001)
61	104-164	1.4-47	55-86	(Drohm, 1988)
61	10-60	0.7-8.6	30-40	(McElroy, Fang, Williamson, 2001)
58	78-153	14-94	30-91	(Hall, 1973)
27	0-21	0.2-10.2	92-93	(Roe, 1972)
19	40	8-64	59	(Brusilovsky, 2002)
17	20	29-31	80	(Lapshin <i>et al.</i> , 2011)
12	75	2.9-31.4	89-91	(Obuba, 2013)
6	32	3.7-18.8	91	(Fayazi, 2014)

For all experimental data, the compressibility factor was calculated by the 19 methods described above. Pseudocritical parameters were calculated according to Kay's rule. The accuracy of the calculated values was assessed using mathematical statistics (Tables 10,11; Figure 1).

Types of errors are represented in Equations 132-136.

Average Absolute Relative Error (AARE),

$$AARE\% = \frac{100}{N} \sum_{i=1}^N \left| \frac{z_i^{pred} - z_i^{exp}}{z_i^{exp}} \right|, \quad (\text{Eq. 132})$$

where z_i^{pred} – the calculated value of compressibility factor, z_i^{exp} – experimental value of compressibility factor.

Mean Squared Error (MSE)

$$MSE = \frac{\sum_{i=1}^N (z_i^{pred} - z_i^{exp})^2}{N}. \quad (\text{Eq.133})$$

Root Mean Squared Error (RMSE)

$$RMSE = \sqrt{\frac{\sum_{i=1}^N (z_i^{pred} - z_i^{exp})^2}{N}}. \quad (\text{Eq.134})$$

Standard deviation (SD)

$$SD = \sqrt{\frac{1}{N-1} \sum_{i=1}^N \left(z_i^{pred} - \text{average}(z_i^{exp}) \right)^2}, \quad (\text{Eq.135})$$

where $\text{average}(z_i^{exp})$ is the mean value of the observation.

Coefficient of determination (R^2)

$$R^2 = 1 - \frac{\sum_{i=1}^N (z_i^{pred} - z_i^{exp})^2}{\sum_{i=1}^N (z_i^{pred} - \text{average}(z_i^{exp}))^2}. \quad (\text{Eq.136})$$

Calculations of the compressibility factor using empirical dependencies were carried out, taking into account the boundary conditions for reduced pressure and reduced temperature (Table 12). Calculations using the equations of state were performed for all experimental values without introducing boundary conditions.

Results presented in Tables 10-11 show that the empirical dependencies of Sanjari and Nemati Lay; Heidaryan, Moghadas, and Rahimi; Dranchuk and Abou-Kassem, as well as the Peng-Robinson equation of state with the shift parameter and Brusilovsky equation allow achieving the most accurate results for most gas compositions. The graphs of the average absolute relative error in the coordinates $T_{pr} - P_{pr} - AARE$ (Figures 2-3) clearly shows that the accuracy of the calculated values is more influenced by the reduced pressure than the reduced temperature. For Bahadori, Papay, Heidaryan, Sohrab Towfighi, Latonov-Gurevich, Peng-Robinson, Harmens-Knapp methods, the error increases with reduced pressure (Figures 2, 3). Modification of the Peng-Robinson equation of state allows to solve this problem and significantly increases the accuracy

of compressibility factor predicting (Figure 3(a,d)).

Table 12. The range of thermobaric conditions in which the empirical dependencies are valid

Method	P_{pr}	T_{pr}
Azizi	$0.2 \leq P_{pr} \leq 11$	$1.1 \leq T_{pr} \leq 2$
Bahadori	$0.2 < P_{pr} < 16$	$1.05 < T_{pr} < 2.4$
Bahadori for gases with CO ₂ and H ₂ S	$0.2 < P_{pr} < 16$	$1.05 < T_{pr} < 2.4$
Dranchuk and Abou-Kassem	$0.2 \leq P_{pr} \leq 30$ $P_{pr} \leq 1$	$1 < T_{pr} \leq 3$ $0.7 < T_{pr} \leq 1$
Dranchuk Purvis Robinson	$0.2 \leq P_{pr} \leq 30$	$1 \leq T_{pr} \leq 3$
Hall and Yarborough	$0.8 \leq P_{pr}$	$1.2 \leq T_{pr}$
Heidaryan	$0.2 < P_{pr} < 17$	$1.2 < T_{pr}$
Heidaryan, Moghadas and Rahimi	$0.2 < P_{pr} < 17$	$1.2 < T_{pr}$
Papay	$P_{pr} \leq 8$	$T_{pr} \leq 2$
Sanjari and Nemati Lay	$0.01 \leq P_{pr} \leq 15$	$1.01 \leq T_{pr} \leq 3$
Sohrab Towfighi	$0.2 \leq P_{pr} \leq 16$	$1.05 \leq T_{pr} \leq 3$
Latonov-Gurevitch	$0.2 \leq P_{pr} \leq 16$	$1 \leq T_{pr} \leq 3$

The point-by-point analysis of the results does not identify the best method in the entire range of the studied pressures and temperatures (Figure 4). However, in considering the temperature and pressure ranges corresponding to separation processes and reservoir conditions in the oil and gas industry, several conclusions can be made. In the range of temperatures and pressures not exceeding 20 °C and 2 MPa, respectively, the Sanjari and Nemati Lay correlation among the empirical dependences turns out to be the best method, and the best equation of state is Soave-Redlich-Kwong. For temperatures and pressures characteristic for field conditions (temperature 20-100 °C, pressure 2-40 MPa), it is recommended to choose the optimal model for predicting the compressibility factor according to Table 12.

3.2 Mixtures with high fraction of CO₂

The development of most oil and gas

condensate fields with a high methane content is now entering its final stage. In recent years, more and more natural gas deposits with high CO₂ content have been found worldwide (Gachuz-Muro, Sanchez-Bujanos, Castro-Herrera, Rodriguez-Pimentel, 2011; Jokhio, Tiab Escobar, 2001). Modeling the development and operation of such facilities requires special knowledge due to the aggressiveness of carbon dioxide under conditions characteristic for processes occurring under high pressure and temperature (Koriakin, 2018; Nešić, 2011), as well as in plumes and equipment of surface facilities (Ponomarev Yusupov, 2020). The presence of CO₂ in such objects can significantly affect the value of the compressibility factor. Therefore, 212 points were analyzed for mixtures with CO₂ content above 10% among the above experimental results. The accuracy of both correlation dependences and equations of state is presented in Figures 5, 6. According to Figure 5, it is possible to distinguish the pressure range in which there are certain preferences for choosing the correlation dependence.

However, the results show that for acid gases, the equations of state are more preferable. In this case, in the range of pressures not exceeding 8 MPa, the Soave-Redlich-Kwong equation of state shows good results, and for higher pressures, it's better to use the Brusilovsky and Peng-Robinson equation of state with the shift parameter.

3.3 Influence of pseudocritical parameters on the value of the z-factor

The analysis of the influence of the method for calculating pseudocritical parameters on the accuracy of the compressibility factor determination is carried out in this subsection.

The Bahadori method for calculating the compressibility factor of gas mixtures with a high content of acid components is not considered in this subsection due to the fact that it already provides the correction of the pseudocritical parameters.

The compressibility factor determined for the pseudocritical conditions calculated according to different rules are shown in Figures 7-9.

For the methods of Latonov-Gurevich with natural logarithm; Latonov-Gurevich; Sanjari and Nemati Lay; Dranchuk and Abou-Kassem; Dranchuk-Purvis-Robinson; Papay; Sohrab Towfighi, an increase in the calculation accuracy

by 0.02-0.1% is observed when using Equations 122-123. For Hall and Yarborough; Heidaryan, Moghadasi and Rahimi; Heidaryan; Bahadori methods, equations 122-123 are not recommended. When determining the z-factor of gas mixtures using the Latonov-Gurevich correlation, in order to increase the accuracy (by 0.1%), it is recommended to use equations (122-123) (Figures 7).

Figure 8 represents the pseudocritical parameters for mixtures with acid content in the range of 10-47% for pseudocritical parameters calculated using Equations 129-130 and Kay's rule (Equations 120-121). The accuracy of the z-factor determination using the empirical correlations significantly increase when the equations 129-130 are used to calculate the pseudocritical parameters. The increase in the accuracy is in the range of 0.5-1.6%.

The z-factor for P_{pc} and T_{pc} calculated using Prausnitz-Gunn rule is presented in Figure 9. It is shown that an increase in the calculation accuracy for all the empirical correlations is in the range of 0.03-0.23% when using the Prausnitz-Gunn rule. For the Sohrab Towfighi method, the calculation accuracy is increased by 0.23%. For Bahadori and Heidaryan methods, it is not recommended to apply the Prausnitz-Gunn rule.

3.3 Discussion

The results of the study shows that there is no universal method for compressibility factor calculation as natural gas is a complex mixture containing hydrocarbon and non-hydrocarbon components and its physical properties strongly depend on thermobaric conditions. That's why the development of the methods for the z-factor computation still going on and new methods and approaches appear.

It is shown that the accuracy of each method strongly depends on the gas composition. Thus, the equations of state which show good results for hydrocarbons and other simple substances are poor for substances with high content of CO₂. In this case the current study helps to establish the criteria of applicability of each method.

4. CONCLUSIONS:

In the presented work, based on 824 experimentally obtained values of the compressibility factor for 235, various gas mixtures in the pressure range from 0.1 to 94 MPa

and temperatures from 273 to 437 K, the search for the optimal equation of state and correlation dependence for accurate prediction of the z-factor was evaluated. Analysis of the results allows us to make the following conclusions:

1. In the entire range of investigated pressures and temperatures for all gas mixtures, the best results are shown by the Peng-Robinson equations of state with the shift parameter and the Brusilovsky equation of state. The Average Absolute Relative Error of the calculated values compared to experimental data does not exceed 2% for these models. Among the correlation dependences, the best results are shown by Sanjari and Nemati Lay; Heidaryan, Moghadasi and Rahimi correlations with an error not exceeding 3%.
2. A point-by-point analysis of the compressibility factor shows that for most of the proposed methods, the reduced pressure has more significant effect on the accuracy of the calculated values than the reduced temperature. For the Bahadori, Papay, Heidaryan, Sohrab Towfighi, Latonov-Gurevich, Peng-Robinson, Harmens-Knapp methods, the error increases significantly with increasing reduced pressure.
3. When studying acid gas mixtures with a CO₂ content of more than 10%, preference should be given to equations of state. In the entire range of temperatures and pressures up to 8 MPa, the Soave-Redlich-Kwong equation of state has a clear advantage for such compositions. At higher pressures, preference should be given to the Peng-Robinson equation of state with the shift parameter and Brusilovsky equation.

5. ACKNOWLEDGMENTS:

The work was supported by the Grant of the President of Russian Federation (grant MK-1102.2020.8)

The authors thank Volkov A. N. and Kiian P.V. from Branch office of Gazprom VNIIGAS LLC in Ukhta for providing experimental measurements for comparison.

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Table 1. Constants a_i for Azizi empirical dependence

i	a_i	i	a_i
1	0,037314	11	-24449114791,153100
2	-0,014081	12	19357955749,327400
3	0,016326	13	-126354717916,607000
4	-0,030778	14	623705678,385784
5	13843575480,943800	15	17997651104,333000
6	-16799138540,763700	16	151211393445,064000
7	1624178942,649760	17	139474437997,172000
8	13702270281,086900	18	-24233012984,095000
9	-41645509,896475	19	18938047327,520500
10	237249967625,013000	20	-141401620722,689000

Table 2. Constants A_i, B_i, C_i, D_i for the empirical dependence of Bahadory

i	A_i	B_i	C_i	D_i
a	0,969469	-1,349238	1,443959	-0,368600
b	-0,107783	-0,127013	0,100828	-0,012319
c	0,018481	0,052341	-0,050688	0,010870
d	-0,000584	-0,002146	0,002096	-0,000459

Table 3. Constants A_i, B_i, C_i, D_i for the empirical dependence of Bahadory for gases with acidic components

i	A_i	B_i	C_i	D_i
a	4,094086	$1,15680575 \cdot 10^2$	$-1,6991417 \cdot 10^2$	$5,62209803 \cdot 10$
b	$1,45517461 \cdot 10^2$	$-3,9672762 \cdot 10^2$	$3,93741592 \cdot 10^2$	$-2,17915813 \cdot 10^2$
c	$-1,95766763 \cdot 10^2$	$3,835331543 \cdot 10^2$	$-6,08818159 \cdot 10^2$	$3,704173461 \cdot 10^2$
d	$5,24425341 \cdot 10$	$-2,0133960 \cdot 10^2$	$3,51359351 \cdot 10^2$	$-2,20884255 \cdot 10^2$

Table 10. Statistical data for the case of not taking into account the methods applicability range

Method	AARE	MSE	RMSE	SD	R2
* Peng-Robinson EOS	1,870609	0,000645	0,02539	0,143565	0,970192
* Brusilovsky EOS	1,945247	0,000695	0,026358	0,146829	0,968043
* Patel-Teja EOS	1,98631	0,000814	0,028524	0,14263	0,962882
* Harmens-Knapp EOS	2,146308	0,001013	0,031831	0,134876	0,957147
Sanjari and Nemati Lay	2,887442	0,007913	0,088954	0,112872	0,646208
* Soave-Redlich-Kwong EOS	2,535057	0,00111	0,033315	0,148475	0,964145
Heidaryan, Moghadasi and Rahimi	2,916752	0,001157	0,034017	0,149505	0,961519
Dranchuk and Abou-Kassem	2,89765	0,001159	0,034049	0,148782	0,960681
Dranchuk-Purvis-Robinson	2,897658	0,001159	0,034049	0,148782	0,960681
Hall and Yarborough	2,916752	0,001157	0,034017	0,149505	0,961519
Papay	6,044089	0,050963	0,225749	0,35271	0,85031
Azizi	3,037741	0,001245	0,035284	0,154106	0,96068
* Peng-Robinson EOS with shift-parameter	3,219377	0,001616	0,040197	0,136433	0,957737
Sohrab Towfighi	3,783834	0,006905	0,083099	0,105103	0,736031
Latonov-Gurevitch (formula with $\ln$)	3,553486	0,00261	0,051085	0,15244	0,888272
Latonov-Gurevitch	3,554237	0,00261	0,051089	0,152443	0,888263
Heidaryan	5,373959	0,008287	0,091031	0,166027	0,741604
Bahadori for gases containing CO ₂ and H ₂ S	4,570042	0,003594	0,05995	0,152738	0,855099
Bahadori	5,86146	0,004977	0,070546	0,159061	0,839022

Table 11. Statistical data for the case of taking into account the methods applicability range

Method	AARE	MSE	RMSE	SD	R2	C
* Peng-Robinson EOS	1,906302	0,000652	0,025528	0,1159	0,952893	28
* Brusilovsky EOS	1,985446	0,000706	0,026569	0,119445	0,950558	28
* Patel-Teja EOS	2,010508	0,000805	0,028372	0,116145	0,942481	28
* Harmens-Knapp EOS	2,14359	0,000942	0,030685	0,109613	0,933218	28
Sanjari and Nemati Lay	2,272306	0,001024	0,032005	0,11211	0,922934	14
* Soave-Redlich-Kwong EOS	2,59733	0,001136	0,033702	0,120254	0,944163	28
Heidaryan, Moghadasi and Rahimi	2,853375	0,001075	0,032781	0,121569	0,944274	91
Dranchuk and Abou-Kassem	2,998977	0,001205	0,034706	0,150798	0,960601	32
Dranchuk-Purvis-Robinson	2,998978	0,001205	0,034706	0,150798	0,960601	32
Hall and Yarborough	3,183188	0,001246	0,035292	0,157492	0,963785	187
Papay	2,924742	0,00156	0,039493	0,088955	0,812701	114
Azizi	3,157948	0,001294	0,035977	0,106037	0,912075	106
* Peng-Robinson EOS with shift-parameter	3,214932	0,001433	0,037856	0,112618	0,937865	28
Sohrab Towfighi	3,502897	0,003257	0,05707	0,099716	0,796591	44
Latonov-Gurevitch (formula with $\ln$)	3,539731	0,001948	0,044138	0,100205	0,870776	44
Latonov-Gurevitch	3,540538	0,001949	0,044144	0,100209	0,870753	44
Heidaryan	4,177206	0,001965	0,044324	0,132446	0,925592	91
Bahadori for gases containing CO ₂ and H ₂ S	4,302181	0,002872	0,053596	0,134157	0,846081	44
Bahadori	5,605219	0,004128	0,064252	0,139824	0,824332	44

Reference: Column 'C' is the number of values not taken into statistics because thermobaric conditions did not satisfy the applicability range of the method.

Figure 1. AARE for different methods of compressibility factor calculation

a) Azizi

b) Bahadori

c) Bahadori with high content of CO_2 and H_2S

d) Dranc k Purvis Robinson

e) Dranc k and Abou-Kassem

f) Hall and Yarbrough

g) Heidary

h) Heidaryan Moghadasi and Rahimi

i) Papay

j) Sohrab Towfighi

k) Latonov-Gurevitch with $\ln$

l) Latonov-Gurevitch

Figure 2. AARE for the empirical correlations

a) Brusilovsky EOS

b) Patel-Teja EOS

c) Peng-Robinson EOS

d) Peng-Robinson EOS with shift-parameter

e) Soave-Redlich-Kwong EOS

f) Harmens-Knapp EOS

Figure 3. AARE for the equations of state

Figure 4. Best methods (by AARE) among the empirical dependencies

Figure 5. Best methods (by AARE) among the empirical dependencies for mixtures with high fraction of CO₂

Figure 6. Best methods (by AARE) among the equations of state for mixtures with high fraction of CO_2

Figure 7. AARE of the compressibility factor with pseudocritical consitions calculated: AARE-1 using Kay's rule (Equations 120-121), AARE-2 – using Equations 122-123

Figure 8. AARE of the compressibility factor of acid gas with pseudocritical conditions calculated: AARE-1 using Kay's rule (Equations 120-121), AARE-3 – using Equations 129-131

Figure 9. AARE of the compressibility factor with pseudocritical conditions calculated: AARE-1 using Kay's rule (Equations 120-121), AARE-4 – using Prausnitz and Gunn rule (Equations 122,124)