Calculating the Vapor–Liquid Phase Equilibrium for Multicomponent Systems Using the Soave–Redlich–Kwong Equation

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Abstract—An algorithm for calculating the vapor–liquid phase equilibrium for multicomponent gases is presented. A six-component gas mixture is considered. The algorithm for calculating phase equilibrium is based on the solution to the Soave–Redlich–Kwong equation of state for real gases. An iteration algorithm for updating phase equilibrium constants is used. The total vapor fraction is determined using the solution to the Rachford–Rice equation. The difficulties of developing such algorithms are considered in full detail. The derived solution is compared with results obtained in the commercial package HYSYS (version 3.2) when the Soave–Redlich–Kwong equation is also used.

INTRODUCTION

The calculation of the vapor–liquid phase equilibrium constants for multicomponent gases is the central theoretical problem of studying the condensation and evaporation of real gas mixtures. Several commercial programs for oil and gas applications, such as HYSYS, Chemcad, and PRO/II, have recently appeared, and the calculation of the vapor–liquid phase equilibrium for multicomponent gas mixtures is one of the problems that these programs are designed to solve. However, due to their closed nature, it is impossible to use any of these

programs as a subprogram for calculating any more or less complex process, where phase equilibrium changes from point to point, and condensation and evaporation are only part of changes occurring in a medium. Attempts to reconstruct algorithms according to which such programs work or even any of their informative parts from the materials of open press turn out to be unpromising, since authors either conceal the slightest important points or refer to studies such as [1], where only some of the equations, rather than a calculation algorithm, are described. Below, we will describe the algorithm stated in the abstract and compare the calculation results of the program that implements this algorithm with the results obtained in the HYSYS program, which is most commonly used in practice. In addition, we will specify some of the major difficulties that researchers face when they write such a program on their own for the first time.

EQUATION OF STATE AND INITIAL ASSUMPTIONS

A typical vapor–liquid phase diagram in the p–T axes for a mixture is presented in Fig. 1.
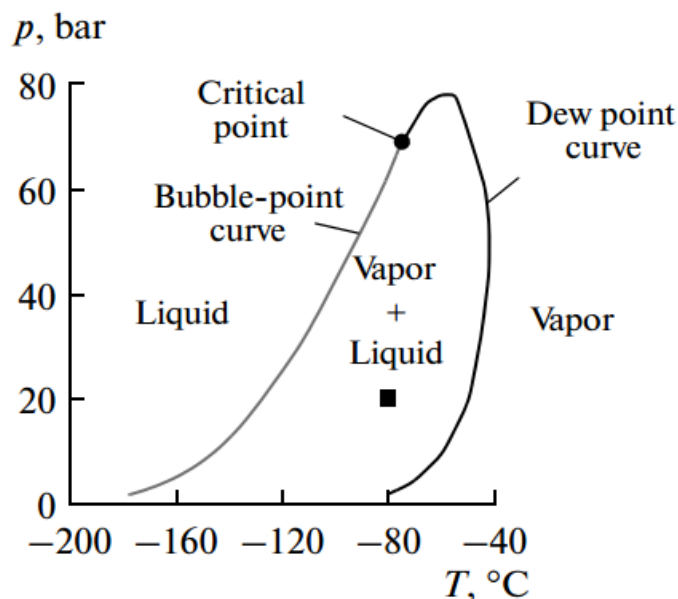

Fig. 1. Phase diagram for the mixture from Table 1. The square symbol marks a point at which phase equilibrium is calculated ($p = 20$ bar, $T = -80°C$).

After the first famous van der Waals equation of state, the studies of real gas mixtures have led to more accurate, but, at the same time, more complex equations of state for real gases, among which the Soave–Redlich–Kwong (SRK) [2, 3] and Peng–Robinson [4] equations of state are most commonly used. Below, we will use the SRK equation:

$$p = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)}. \tag{1}$$

Here, the parameter a takes into account intermolecular attraction forces and b takes into account the volume occupied by molecules; α is the dimensionless coefficient defined by the expression where the parameter m is calculated by the formula $m=0.48+1.574\omega-0.176\omega^2$, $T_r=T/T_c$ is the reduced temperature; T is the temperature of the system in Rankine degrees; T_c is the critical temperature in Rankine degrees; and ω is the acentric factor of a substance, which was first introduced by Pitzer et al. [5] and is an indicator of the nonsphericity of the field of intermolecular forces. For any pure substance, the constants a and b can be written in terms of pressure and temperature at the critical point as $a = \Omega_a R^2 T_c^2 / p_c$ and $b = \Omega_b RT_c / p_c$, where Ω_a and Ω_b are the dimensionless Redlich–Kwong parameters, which have values of $\Omega_a = 0.42747$ and $\Omega_b = 0.08664$ [2]. The above equations are applicable for describing the phase equilibrium of a pure substance, but they give incorrect values for mixtures.

Let us point out the limitations for the SRK equation. The SRK equation cannot be applied at temperatures below $-143°C$ and pressures above 350 bar, and it cannot be used for describing systems with methanol and glycols and for calculating vapor–liquid–liquid equilibrium (from the documentation of the HYSYS package). In addition, it cannot be used for calculations near the critical point of a mixture. This study considers a dehydrated gas in which there are no hydrate formation processes, only one liquid phase forms, and pressure and temperature satisfy the specified limitations. Thus, the use of the SRK equation in this study is justified. We consider the condensation process; it can be stated that the proposed algorithm is adapted for an apparatus in which phase separation occurs: from a gas mixture to a vapor and a liquid. Phase transition through the bubble-point curve is calculated in a similar manner.

VARIABLES AND INITIAL APPROXIMATION

The calculation of the vapor–liquid phase equilibrium means the determination of the mixture compositions of both phases at the required point p-T on the phase diagram. It is assumed that the liquid phase is originally absent. The mole fractions z_i of all n components in an original gas mixture, as well as the pressure p and temperature T to which the gas mixture is cooled, are considered the known quantities. It is necessary to determine the mole fractions of all components in the vapor phase y_i and in the liquid phase x_i at these p and T. It is evident that in a two-phase region we have

$$\sum_{i=1}^{n} z_i = \sum_{i=1}^{n} y_i = \sum_{i=1}^{n} x_i = 1. \tag{2}$$

The calculated total vapor fraction φ in a vapor-liquid medium that forms upon condensation is related to z_i, y_i, and x_i as follows:

$$z_i = \varphi\, y_i + (1 - \varphi) x_i, \tag{3}$$

where φ is in the interval $0 \le \varphi \le 1$. We have $\varphi=0$ on the bubble-point curve, $\varphi=1$ on the dew point curve, and $0<\varphi<1$ in the two-phase region. Since it is assumed that phase equilibrium is attained at the considered point p-T of the two-phase region, we can assume that the fugacities of the ith component of a mixture from the vapor phase to the liquid phase and vice versa are identical, i.e. $f_{li} = f_{vi}$. Expressing the fugacity of the ith component in terms of a fugacity coefficient and a mole fraction, we derive the equality $\Phi_{li} x_i\, p = \Phi_{vi} y_i\, p$, from which it follows that

$$K_i = \frac{\Phi_{li}}{\Phi_{vi}} = \frac{y_i}{x_i}. \tag{4}$$

Our problem is to find the phase equilibrium constants K_i; then, the fractions y_i and x_i can be obtained by solving the following equations (12), (13), and (14).

We use the reduced pressure and temperature for the ith component of a mixture: $p_{ri} = p / p_{ci}$ and $T_{ri} = T / T_{ci}$. Here, T is measured in Rankine degrees, and p is measured in pounds per square inch absolute (psia). The conversion of pressure units from kilopascals to pounds per square inch absolute and temperature units from Celsius degrees to Rankine degrees is performed by the following formulas: $p_{ci} = 0.145\, p_{ci}^{*}$ and $T_{ci} = 1.8\, T_{c\,i}^{*} + 491.67$, where the values of p_{ci}^{*} and $T_{c\,i}^{*}$ are specified for each of the gas components (these values in the computational model for all of the six components of the gas under consideration are given in Table 1). These units are conventionally used in such calculations [1].

The initial values for the algorithm of the phase equilibrium constants K_i are calculated by the Wilson correlation. The Wilson correlation for finding the estimated values of the constants K_i appears as [6]

$$K_i = \frac{p_{ci}}{p} \exp\!\left(5.37\, (1 + \omega_i) \left(1 - \frac{T_{ci}}{T} \right) \right). \tag{5}$$

SRK EQUATION FOR COMPRESSIBILITY FACTORS

From the SRK equation of state by substituting $Z_v = pV/RT$, we can derive a cubic equation for determining the compressibility factor Z_v for a vapor. In fact, the equality $Z_v = pV/RT$ can be regarded as one more equation of state for real gases. For a gas mixture, the SRK equation can then be written as

$$Z_v{}^3 - Z_v{}^2 + Z_v\left(A_v - B_v - B_v{}^2\right) - A_v B_v = 0. \tag{6}$$

The coefficients A_v and B_v for a mixture of components in the vapor phase are determined using certain rules for mixing. Here, we use the Soave rules [3]:

$$A_v = \sum_{i=1}^{n}\sum_{j=1}^{n} y_i\, y_j A_{b_{ij}} \quad \text{and} \quad B_v = \sum_{i=1}^{n} y_i\, B_{p_i}, \tag{7}$$

where

$$B_{p_i} = 0.08664\frac{p_{r_i}}{T_{r_i}}, \quad A_{b_{ij}} = \left(1 - k_{ij}\right)\sqrt{A_{p_i} A_{p_j}}, \quad A_{p_i} = 0.42747\alpha_i\frac{p_{r_i}}{T_{r_i}{}^2}, \quad \alpha_i = \left[1 + m_i\left(1 - \sqrt{T_{r_i}}\right)\right]^2,$$

$m_i = 0.48 + 1.574\omega_i - 0.176\omega_i{}^2$, k_{ij} is the symmetrical matrix containing binary interaction coefficients for the components of a gas mixture. In our calculations, to simplify the calculation algorithm, we neglect these coefficients on the grounds that, for hydrocarbon mixtures, their values are close to zero, and when there are nonhydrocarbon components in the mixture, these coefficients affect an increase in the accuracy of calculation, but insignificantly, and no nonlinear effects are observed here [7]. Equation (6) can have three real roots in the two-phase region. In this case, it is necessary to take the largest root.

The similar cubic equation for the compressibility factor for a liquid phase can be derived in a similar manner to the equation for a vapor. It has the same form

$$Z_l{}^3 - Z_l{}^2 + Z_l\left(A_l - B_l - B_l{}^2\right) - A_l B_l = 0, \tag{6a}$$

where the coefficients A_l and B_l for the liquid phase are determined in a similar manner to A_v and B_v, replacing y by x in the respective expressions (7):

$$A_l = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i\, x_j A_{b_{ij}} \quad \text{and} \quad B_l = \sum_{i=1}^{n} x_i\, B_{p_i}. \tag{7a}$$

As in the case of the compressibility factor for the vapor phase, Eq. (6a) can also have three real roots in the two-phase region. In contrast to the equation for Z_v, in this case it is necessary to take the smallest root of the three real roots, rather than the largest one. The middle root has no physical meaning in both cases.

FINDING FUGACITY COEFFICIENTS FOR A VAPOR AND A LIQUID

Fugacity coefficients for a vapor and a liquid for the SRK equation of state are determined by the following expressions:

$$\Phi_{v_i} = \exp\left((Z_v - 1)\frac{B_{p_i}}{B_v} - \ln(Z_v - B_v) - \frac{A_v}{B_v}\left(\frac{2\sqrt{A_{p_i}}}{\sqrt{A_v}} - \frac{B_{p_i}}{B_v} \right)\ln\left(\frac{Z_v + B_v}{Z_v} \right) \right),\qquad(8)$$

$$\Phi_{l_i} = \exp\left((Z_l - 1)\frac{B_{p_i}}{B_l} - \ln(Z_l - B_l) - \frac{A_l}{B_l}\left(\frac{2\sqrt{A_{p_i}}}{\sqrt{A_l}} - \frac{B_{p_i}}{B_l} \right)\ln\left(\frac{Z_l + B_l}{Z_l} \right) \right).\qquad(9)$$

The derivation of these equations is rather cumbersome, and it is not given here for reasons of space. Some details of this derivation can be found in [7].

ALGORITHM

To calculate the phase equilibrium constants K_i, the method of successive approximations to the solution of a problem is used. Mathematically, the problem lies in finding the vector of the solution $K = (K_1, K_2,..., K_n)$ to the equation

$$K = \psi(K),\qquad(10)$$

where the vector function ψ will be specified below. The method of successive approximations to the solution of Eq. (10) consists in calculating the sequence of vectors $\{ K^s \}$, s=1, 2, … using the recurrence formula $K^{s+1} = \psi(K^s)$, beginning from a given initial vector K^0. The convergence of the sequence $\{ K^s \}$ at $s\to\infty$ to the solution $\overline{K}$ of Eq. (10) is ensured by the estimation

$$\lambda = \max_{K\in\Omega} \left\| D\psi(K) \right\| < 1,\qquad(11)$$

where $D\psi(K)$ is the Jacobian matrix of the mapping ψ that is calculated at the point K, $\left\| D\psi(K) \right\|$ is its norm defined through the maximum of the moduli of eigenvalues. Here, Ω is some range of the vector parameter K that lies with its boundary in the maximum region of $\overline{\Omega}$ where the inequality $\left\| D\psi(K) \right\| < 1$ holds true, and is invariant with respect to the mapping ψ with $K^0 \in \Omega$. It will be recalled that, by virtue of the contraction mapping principle [8], under these assumptions, there is a unique solution $\overline{K} \in \Omega$ of Eq. (10) (the fixed point of the contraction mapping ψ), and the error estimation $\left| K^{s+1} - \overline{K} \right| < \lambda^s \left| K^1 - K^0 \right|$ is valid. In the

small neighborhood of the solution $\overline{K}$, there is the ordinary expansion $\psi(K + \Delta K) = \psi(K) + D\psi(K)\Delta K + o(|K|)$, which at $K = \overline{K}$ gives $\Delta K^{s+1} = \psi(K^s) - \psi(\overline{K}) = D\psi(\overline{K})\Delta K^s$, $\Delta K^s = K^s - \overline{K}$, which makes it possible to draw inferences about the convergence of the process without calculating the derivative $D\psi(K)$. Indeed, if the matrix $D\psi(K)$ had eigenvalues that are higher than unity in absolute value, the iteration of almost any approximation K^0 would take us away from the solution at an exponential rate (the so-called hyperbolic singular point of the mapping ψ), except for the case where the approximation K^0 randomly falls on the proper subspace with the smaller dimension that corresponds to eigenvalues lower than unity in absolute value. However, real calculations stably show rapid convergence to the solution, beginning from different initial points. Therefore, in evaluating convergence, we restrict ourselves only to the comparison of the vectors K^s by comparing the numbers $\Delta^s = |K^{s+1} - K^s|/|K^s|$ up to values of 10^{-5}. A block diagram of the algorithm is presented in Fig. 2.

Let us now characterize calculations at each stage.

1. Finding the total vapor fraction. Using the values of z_i and K_i, the total vapor fraction φ is calculated from the Rachford–Rice equation [9]:

$$\sum_{i=1}^{n} \frac{z_i(K_i - 1)}{1 + \varphi(K_i - 1)} = 0, \tag{12}$$

where n is the number of components in the system ($n = 6$ for the mixture from Table 1). The Rachford–Rice equation is derived from Eqs. (2), (3), and (4). This equation can have several real roots for φ, but, by virtue of equality (3), only the root from the range [0, 1] is meaningful. The Rachford–Rice equation is solved by the bisection method. We designate the function of finding such a root as $\varphi(z, K)$.

2. Finding the molar fractions of components y_i and x_i for a vapor and a liquid:

$$x_i = z_i/(1 + \varphi(K_i - 1)), \tag{13}$$

$$y_i = K_i x_i. \tag{14}$$

3. Finding the compressibility factors Z_v and Z_l for the vapor and the liquid. We use expressions (6) and (6a).

4. Finding the fugacity coefficients Φ_v and Φ_l for the vapor and the liquid. The fugacity coefficients Φ_v and Φ_l for the vapor and the liquid for the SRK equation of state are determined by expressions (8) and (9). After calculating the fugacity coefficients, we find the

phase equilibrium constants K_i by formula (4) [10]. In the literature, such a technique for updating Ki is called the phi–phi method, which, according to [10], is convenient in that it does not require any additional information about a substance, unlike the other two frequently used methods for updating K_i: gamma–phi and gamma–gamma.
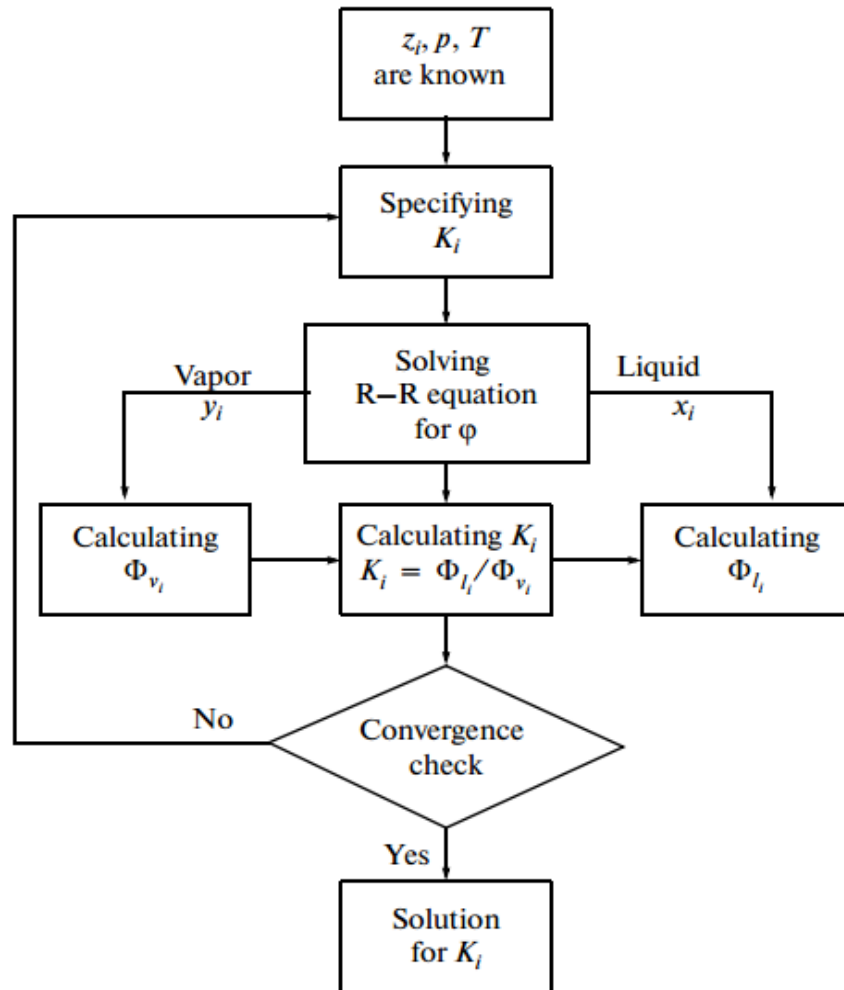

Fig. 2. Flow chart of the iterative algorithm for determining the phase equilibrium constants K_i for the given mixture composition z_i at the pressure p and temperature T corresponding to the two-phase region.

GAS MIXTURE UNDER CONSIDERATION

The composition of a model mixture (the values of z_i in Table 1) is very close to the composition of natural gas after drying in one of the gas fields in Russia. The physical properties of components are taken from the database of the HYSYS package. Figure 1 shows the phase diagram for this mixture. At the critical point of the mixture, we have $p = 68.29$ bar and $T= -75.08°C$.

Table 1. Composition of a model mixture, pressure and temperature at the critical point, and the acentric factor of components

i	Component	Chemical formula	p^*_{ci}, kPa	T^*_{ci}, °C	ω_i	z_i
1	Methane	CH_4	4640.68	-82.45	0.0115	0.7812
2	Ethane	C_2H_6	4883.85	32.28	0.0986	0.03
3	Propane	C_3H_8	4256.66	96.75	0.1524	0.02
4	Isobutane	$iso\text{-}C_4H_{10}$	3647.62	134.95	0.18479	0.0048
5	n-butane	$n\text{-}C_4H_{10}$	3796.62	152.05	0.201	0.001
6	Nitrogen	N_2	3394.37	-146.96	0.04	0.163

DETERMINING THE POINT OF TRANSITION THROUGH THE DEW POINT CURVE

The above algorithm is applicable only to the two-phase region, where $0 < \varphi < 1$. By virtue of the fact that Eq. (12) for φ contains the unknown K_i, the error in K_i, which is introduced by the use of Wilson correlation (5) in estimating the condition $0 < \varphi < 1$, leads to the fact that the algorithm can be erroneously applied to a single-phase medium or, vice versa, that it is not used in a two-phase medium (see Fig. 3). In the former case, the region between the solid and dashed lines above 5 bar is meant; in the latter case, the region between these lines at $p < 5$ bar is meant. It follows from the figure that the correction is necessary in the first case.

In the open literature, it is stated that for the dew point curve we have $\sum_{i=1}^{n} z_i / K_i = 1$ [7]. Let us transform the condition to the form $\sum_{i=1}^{n} x_i (z_i / y_i) = 1$, which is reduced to the new condition for the point of transition through the dew point curve as follows: $\sum_{i=1}^{n} x_i = 1$, if we take into account that $z_i = y_i$ on the right of the dew point curve. Indeed, the condition $\sum_{i=1}^{n} x_i = 1$ should be satisfied on the left of the dew point curve, whereas on the right of the dew point curve, based on the physics of the process, we have $x_i = 0$ (i.e., any liquid is absent). However, when the Wilson correlation is used, we have $K_i \neq \infty$ and, consequently, on the basis of expression (13), $x_i \neq 0$. Computational experiments have shown that, in the region between the solid and dashed lines at $p > 5$ bar (Fig. 3), the condition $0 < \sum_{i=1}^{n} x_i < 1$ is satisfied (in addition to the condition $0 < \varphi < 1$). If the latter condition is not fulfilled and, instead, the condition

$\sum_{i=1}^{n} x_i = 1$ is satisfied with an error of less than 0.001, we assume that this is the point of transition through the dew point curve. After the correction, the point of transition through the dew curve at $p > 5$ bar is determined with an error of less than 1°C.
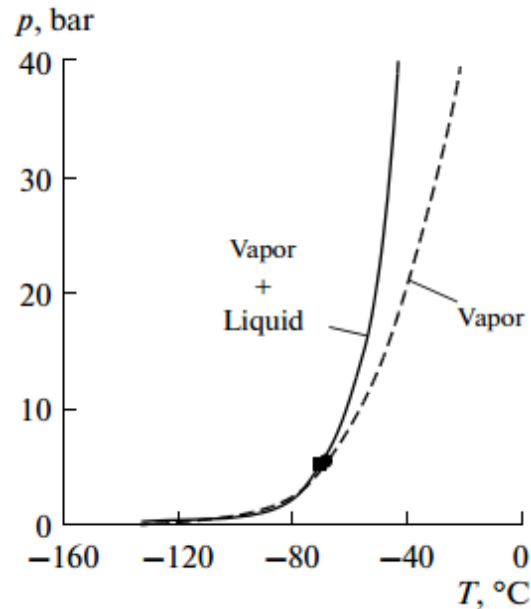

Fig. 3. Comparison of the dew point curves from the HYSYS package (the solid line) and from the developed program determining the transformation point by Eqs. (12) and (5), Wilson correlation (the dashed line) for the mixture from Table 1. The round point is the intersection point of these curves.

RESULTS

The values of K_i, yi, and x_i calculated by the proposed algorithm and the HYSYS package at $T = -80$°C and $p = 20$ bar (the point is marked by a square symbol in Fig. 1) are given in Table 2.

The largest discrepancies in the values of K_i are observed for nitrogen because of the assumption that $k_{ij} = 0$. Using K_i from the third column, it is possible to calculate $\sum_{i=1}^{n} z_i / K_i = 4.2$ and $\sum_{i=1}^{n} z_i K_i = 3.9$. Both sums are larger than unity, from which it follows that the given point p-T lies in the two-phase region [7].

Table 2. Comparison of results for K_i, y_i and x_i , obtained using the developed algorithm and the HYSYS package at T=-80ºC, p=20 bar for the mixture from Table 1

i	K_i, Wilson correlation	K_i, SRK equation, our code	K_i, SRK, HYSYS	y_i, our code	x_i, our code	y_i, HYSYS	x_i, HYSYS
1	2.485845	2.423041	2.506	0.802051	0.331010	0.801825	0.319901
2	0.079132	0.123539	0.1241	0.022830	0.184802	0.023040	0.185669
3	0.007390	0.014078	0.01387	0.004878	0.346500	0.004948	0.356655
4	0.001535	0.003020	0.003116	0.000307	0.101799	0.000327	0.104850
5	0.000819	0.001609	0.001637	0.000035	0.021833	0.000037	0.022540
6	11.764347	12.087532	16.35	0.169898	0.014056	0.169824	0.010386

The quantities φ, Z_v, and Z_l calculated by the developed algorithm have values of 0.9557, 0.8571, and 0.0802, respectively, and those calculated by the HYSYS package have values of 0.9572, 0.8585, and 0.0768, respectively, which gives the difference 0.16, 0.16, and 4.43%, respectively. It should be noted that φ=0.96 in spite of the fact that the considered point p-T is located deep inside the two-phase region. It will be recalled that by virtue of Eq. (3) we have φ=0 on the bubble-point curve and φ=1 on the dew point curve, from which it follows that φ decreases with a decrease in T extremely nonlinearly in the case under consideration because of hardly condensable components: methane and nitrogen.
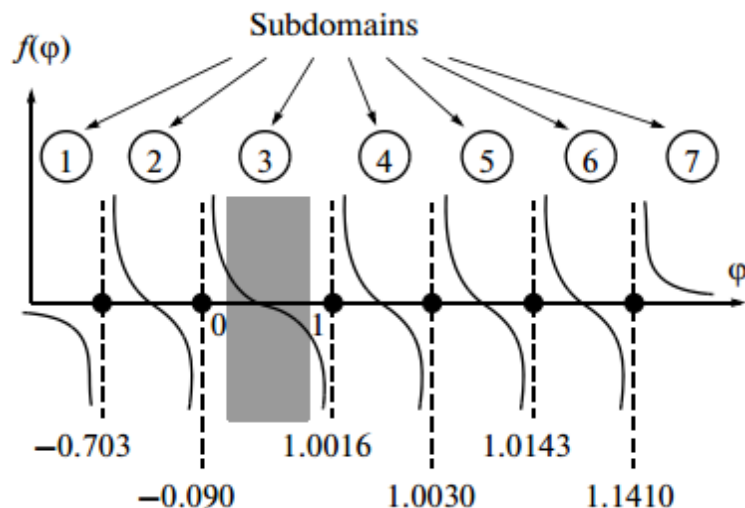

Fig. 4. Schematic graph of the function $f(\varphi)$ (the left-hand side of the Rachford–Rice equation) for the mixture from Table 1 at $T = -80°C$ and $p = 20$ bar. The root of interest is in the interval [0,1].

Figure 4 shows a schematic graph of the function for the mixture from Table 1 for the considered point p-T, where $f(\varphi)$ is the left-hand side of the Rachford–Rice equation. Because this function is not defined at the points $\varphi = -1/(K_i - 1)$, the number domain is divided into subdomains: $(1)\,(-\infty;\ [1 - K_{CH_4}]^{-1})$, $(2)\,([1 - K_{CH_4}]^{-1};\ [1 - K_{N_2}]^{-1})$,

$(3)\,([1 - K_{N_2}]^{-1};\ [1 - K_{n-C_4H_{10}}]^{-1})$, $(4)\,([1 - K_{n-C_4H_{10}}]^{-1};\ [1 - K_{iso-C_4H_{10}}]^{-1})$,

$(5)\,([1 - K_{iso-C_4H_{10}}]^{-1};\ [1 - K_{C_3H_8}]^{-1})$, $(6)\,([1 - K_{C_3H_8}]^{-1};\ [1 - K_{C_2H_6}]^{-1})$,

$(7)\,([1 - K_{C_2H_6}]^{-1};\ +\infty)$. The number of subdomains is $n + 1$. The solutions of the Rachford-Rice equation are the following values: –0.1985, 0.9557, 1.0018, 1.0058, and 1.1054, but only the solution 0.9557 is meaningful by virtue of Eq. (3). It can be seen that the expression for the right boundary of subdomain 3 includes K for the most easily condensable component, n-C_4H_{10}; this explains the presence of the range [0, 1] in the given subdomain.

CONCLUSIONS

The proposed algorithm for calculating the vapor–liquid phase equilibrium for multicomponent gases is presented in sufficient details to write a computational subprogram. The results of calculation by the developed algorithm agree with the results from the commercial program HYSYS with an accuracy of several percent. Such a program is indispensable in calculating real processes that occur in gas separators (it is where this program has been used), in the perforated zones of gas–condensate wells, and in the units of gas-processing plants, in calculating emergency situations in a gas transport network, etc.

NOTATION

A_b, A_p – coefficients in the SRK equation;

a – coefficient in van der Waals-type equations of state;

B_p – coefficient in the SRK equation;

b – coefficient in van der Waals-type equations of state;

f – fugacity, kPa;

K – phase equilibrium constant;

k_{ij} – matrix of binary interaction coefficients for a mixture;

m – parameter in the SRK equation;

n – number of components in a mixture;

p – static pressure, bar or psia;

p^* – static pressure, kPa;

R – specific gas constant, J/(kg K);

T – static temperature, °R;

T^* – static temperature, °C;

V – specific volume, m^3/kg;

x – mole fraction of a liquid phase after condensation;

y – mole fraction of a vapor phase after condensation;

Z – compressibility factor;

z – mole fraction of a vapor phase in the original mixture;

α – coefficient in the SRK equation;

λ – compression ratio;

Φ – fugacity coefficient;

φ – total vapor fraction;

ψ – vector-function of contraction mapping;

Ω_a – dimensionless Redlich-Kwong parameter;

Ω_b – dimensionless Redlich-Kwong parameter;

ω – acentric factor.

SUBSCRIPTS AND SUPERSCRIPTS

0 – initial value;

c – critical parameter;

i, j – component numbers;

l – liquid phase;

r – reduced parameter;

s – iteration number;

v – vapor phase.

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