Equations for calculation of liquid-vapor equilibrium in binary mixtures containing methane

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Abstract. Equations describing the experimental data on liquid-vapor equilibrium in binary mixtures of methane with argon, carbon dioxide and helium have been compiled. The equations describe the dependence of pressure of liquid or vapor on temperature and composition. When compiling them, the program selected most significant coefficients of the equations. The standard deviations of experimental values of pressure from the calculated values range from 1.8 to 5.0%. The equations make it possible to determine the composition or temperature of the phases at known values of other parameters of phase equilibrium.

1. Introduction
Some authors have investigated experimentally the liquid-vapor phase equilibrium in binary mixtures containing methane, but they did not describe analytically obtained data. Therefore we have performed analytical description of the experimental data on phase equilibrium in binary mixtures of helium-methane, argon-methane and carbon dioxide-methane.

2. Analytical description
At compiling equations describing the phase equilibrium in mixtures of helium-methane and carbon dioxide-methane it was taken into account that these mixtures are characterized by sharp increase in pressure on the isotherms. For such mixtures it is advisable to use the form of equation proposed in [1]:

\[
\ln p' = \ln p_{\text{min}} + \sum_{k=1}^{n} M'_k x_i T_j,
\]

where \( p' \) and \( p_{\text{min}} \) are pressures of liquid and the high-boiling component at phase equilibrium; \( x \) is molar concentration of the low-boiling component in the liquid phase; \( T \) – temperature; \( M'_k \) – coefficients.

The equation for vapor pressure \( p'' \) has an identical form, but the concentration \( x \) is replaced by \( y \) (the concentration of the low-boiling component in the vapor phase).

The form of equation (1) satisfies the limiting condition \( p' \rightarrow p_{\text{min}} \) as \( x \rightarrow 0 \) and \( y \rightarrow 0 \) and is suitable for any ratios of mixture temperatures and critical temperatures of the components [1,2].
To describe the data on phase equilibrium in mixture argon-methane obtained at temperatures below the critical temperatures of components an improved form of the equation [14] was used:

\[ p' = p_a + (p_{s2} - p_{s1}) \sum_{k=1}^{n} M'_k x^i k (1 - x)^j k T^l k. \] (2)

Here \( p_a \) is the mixture pressure, calculated as a linear combination of the saturation pressures \( p_{s1} \) and \( p_{s2} \) of components:

\[ p_a = p_{s1} x + p_{s2} (1 - x). \] (3)

The equation for the vapor pressure \( p'' \) has an identical form, provided that the concentration \( x \) is replaced by \( y \).

Equations in the form (2) satisfy two limiting conditions, and when they are compiled, the differences \( p_{\text{max}} - p_a \) are approximated, which for medium and large values of \( x \) and \( y \) are less than the differences \( p_{\text{max}} - p_{\text{min}} \). These circumstances contribute to improving the accuracy of the description of experimental data.

Using equation (1), the data for mixtures He – CH\(_4\) and CO\(_2\) – CH\(_4\) are approximated, and using equation (2) – the data for mixture Ar – CH\(_4\). Information about the experimental data used at compiling of the equations is given in Table 1.

At compiling equations the program was used that optimizes the number of coefficients of equations without significantly reducing the accuracy of approximation of experimental data. It provides a choice of the most significant coefficients of equation. First 30 coefficients are determined by the least squares method. Then are calculated the weights \( w_k \) of all coefficients and their errors \( \sigma_k \) [15]:

\[ \sigma_k = \sqrt{\frac{D}{w_k}}. \] (4)

Here \( D \) is the variance, which is calculated by the formula:
Table 2. The coefficients $M'$ and $M''$ of equations for calculation of the equilibrium pressure of liquid and vapor

| Equation(1) | Mixture He – CH$_4$ | Mixture CO$_2$ – CH$_4$ |
|-------------|---------------------|-------------------------|
| $k$ | $M'_k$ | $i_k$ | $j_k$ | $M''_k$ | $i_k$ | $j_k$ |
| 1 | $-2.1213 \times 10^3$ | 0.1 | 0 | $7.4930 \times 10^6$ | 0.35 | 0.35 |
| 2 | $-4.7546 \times 10^{-4}$ | 0.25 | 2 | $-1.6875 \times 10^4$ | 0.25 | -1.5 |
| 3 | $-9.1070 \times 10^2$ | 0.1 | 0.1 | $8.1929 \times 10^2$ | 1 | -0.75 |
| 4 | $2.3892 \times 10^1$ | 0.25 | 0 | $-1.4590 \times 10^4$ | 1 | -1.25 |
| 5 | $2.1483 \times 10^1$ | 0.1 | -0.25 | $7.1671 \times 10^2$ | 0.1 | 0.25 |

| Equation(2) | Mixture Ar – CH$_4$ |
|-------------|---------------------|
| $k$ | $M'_k$ | $i_k$ | $j_k$ | $l_k$ |
| 1 | $-1.6440 \times 10^{-1}$ | 0.25 | 0.25 | 0.25 |
| 2 | $3.6000 \times 10^0$ | 0.25 | 0.25 | -0.5 |
| 3 | $1.4256 \times 10^{-2}$ | 0.25 | 0.25 | 0.5 |
| 4 | $1.3676 \times 10^{-2}$ | 0.5 | 0.5 | 0.5 |

| $k$ | $M''_k$ | $i_k$ | $j_k$ | $l_k$ |
| 1 | $4.7224 \times 10^1$ | 0.2 | 0.25 | 0.8 |
| 2 | $3.4758 \times 10^0$ | 0.25 | 0.1 | -0.1 |
| 3 | $-2.2947 \times 10^{-2}$ | 0.2 | 0.15 | 0.75 |
| 4 | $-6.1985 \times 10^{-1}$ | 0.5 | 0.2 | 1 |
| 5 | $3.6496 \times 10^2$ | 0.15 | 0.6 | 0.5 |

$$D = \frac{1}{N-n} \sum_{i=1}^{N} (\ln p_{io} - \ln p_{iras})$$  \hspace{1cm} (5)

where $N$ is the number of experimental data, $n$ is the number of coefficients, $p_{io}$ is experimental pressure, $p_{iras}$ is calculated pressure.

At compiling the following equation the coefficient, for which the ratio of its absolute value and the error $\sigma_k$ is minimal, is excluded. This process is repeated until the ratio of variances for the given and initial equations is less than the selected value of the Fisher criterion.

The coefficients of equations were determined on the base of data listed in table 1. At calculating the values of saturation pressure of the components the equations of vaporization curves were used, given for carbon dioxide in [16], for helium in [17], for methane in [18]. The coefficients of equations for calculating the equilibrium pressure of liquid and vapor $M'_k$ and $M''_k$ are given in table 2.
Table 3. Characteristics of the experimental data and the accuracy of their approximation

| Mixture    | $\delta p'$, % | $\delta p''$, % | $\Delta x$ | $\Delta y$ | $\Delta T'$, K | $\Delta T''$, K |
|------------|----------------|-----------------|------------|------------|----------------|----------------|
| He–CH$_4$  | 4.6            | 5.0             | 0.004      | 0.021      | 0.73           | 0.90           |
| CO$_2$–CH$_4$ | 3.0            | 3.9             | 0.006      | 0.009      | 0.52           | 0.58           |
| Ar–CH$_4$  | 1.8            | 3.1             | 0.008      | 0.028      | 0.42           | 0.33           |

To assess the accuracy of compiled equations, a comparison was made between the calculated pressure values of liquid $p'$ and vapor $p''$ with the experimental data. In table 3 the mean square relative deviations $\delta p'$ and $\delta p''$ of these data from the calculated ones are presented. The satisfactory accuracy of the composed equations, which contain from 4 to 6 coefficients, is visible from table 3.

Using the composed equations, it is possible to calculate by the methods of iteration any phase equilibrium parameter ($p$, $T$, $x$, or $y$) at given two others. Calculations of composition and temperature of the coexisting phases showed satisfactory agreement of the calculated values of $x$, $y$, $T'$ and $T''$ with the experimental data. This is confirmed by the table 3, where mean square absolute deviations $\Delta x$, $\Delta y$, $\Delta T'$ and $\Delta T''$ of experimental data from the calculated ones are presented.

3. Conclusion

On the basis of experimental data on the phase equilibrium of liquid-vapor in binary mixtures of rare gases between themselves and with methane, equations have been compiled describing data on the equilibrium pressure of a liquid or vapor, depending on temperature and composition. The program of their compilation selected the most significant coefficients of the equations.

The standard deviations of the experimental pressure values from the calculated ones are from 1.8 to 5.0%. The equations make it possible to determine the composition or temperature of the phases for known values of other parameters of phase equilibrium.

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