Theoretical model of the equation of state for ternary fluid mixtures with exp-6 potential

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Abstract. A new effective two-fluid model is presented. This model is based on the developed equation of state of binary mixtures. In this model division of all components of mixture into two groups with close well-depth parameters is supposed. Thus, the multicomponent mixture is presented in the form of effective two-component fluid. This technique precludes mistake made by effective one-fluid model in calculation of thermodynamic parameters of multicomponent mixture with considerably different well-depth parameters of components. Calculations of the ternary mixtures of various compositions are carried out. It is shown that the results of calculations obtained with the presented method are in better agreement with the experimental data as compared to the similar calculations based on the effective one-fluid model.

1. Introduction
Constructing the equation of state (EOS) of multicomponent fluid plays an important role in creation of theoretical model of calculation of thermodynamic parameters of multicomponent systems. The interest in theoretically reasonable EOS increased considerably. Primarily, in the potential equations constructed on the basis of statistical physics and intermolecular interaction potentials. The equations of such type have strict physical rationale, and they can be applicable to calculations in wide area of pressures and temperatures. The majority of theoretically reasonable models existing today allow predicting thermodynamic parameters of fluids and fluid mixtures. These models are based on the perturbation theory [1,2] and the variation theory [3]. The main idea of each of these theories consists in expression of excess Helmholtz energy of a mixture in the form of a Taylor series of rather basic hard sphere fluid. One of the best theories allowing receiving EOS of fluids both at high pressures and temperatures, and at lower temperatures and density is the perturbation theory of Kang et al (KLRR) [1]. This theory reproduces results of Monte-Carlo (MC) simulation with a good accuracy for different types of interaction potentials, including potentials of exp-6 which adequacy is confirmed by many researches. Van der Waals’s model of an effective one-fluid (vdW1f) [4] allowing to calculate thermodynamic parameters of multicomponent fluid mixtures is widely applied to the description of multicomponent gas systems. In this model the multicomponent mixture of fluids is considered as a hypothetical (effective) one-component fluid which properties can be calculated by means of an EOS of the one-component fluid. Potential parameters of an effective fluid are defined by parameters of intermolecular interaction potentials of multicomponent mixture and depend on its composition. In [5] the analysis of influence of an effective one-fluid model on the accuracy of
2. Intermolecular interaction potential
The modified Buckingham model potential is used. This model is known to provide a sufficiently realistic description of intermolecular interactions at high pressures and, in particular, under high-pressure high-temperature conditions relevant to detonation and shock-wave problems. It is assumed that the molecules $i$ and $j$ of a binary fluid interact via a spherically symmetric exp-6 potential:

$$
\phi_{ij}(r) = \frac{\varepsilon_{ij}}{\alpha_{ij} - 6} \left( 6 \exp \left[ \alpha_{ij} \left( 1 - \frac{r}{r_{m,ij}} \right) \right] - \alpha_{ij} \left( \frac{r_{m,ij}}{r} \right)^6 \right), \quad r \geq c_{ij},
$$

$$
\phi_{ij}(r) = +\infty, \quad r \leq c_{ij},
$$

where $r$ is the intermolecular separation, $\varepsilon_{ij}$ is the well-depth of the attractive, $r_{m,ij}$ is the position of the potential well minimum, and $\alpha_{ij}$ controls the stiffness of the repulsive part of the potential. For polar molecules in [7, 8] the modified form of exp-6 potential considering electrostatic interactions of molecules in which the well-depth depends on temperature was offered:

$$
\varepsilon_{ii}(T) = \varepsilon_{0,ii} \left( 1 + \frac{\lambda_{ii}}{T} \right),
$$

where $\lambda_{ii}$ is the parameter which is responsible for the accounting of electrostatic effects. In [9] it was shown that thermodynamic calculation of isotherms of ammonia and its mixtures with hydrogen using an EOS on the basis of potentials (1)–(2) agrees with the experimental data better as compared for the standard three-parametrical potential of exp-6 (1). Potential parameters for the molecules investigated in the work, are calculated in [10] and presented in table 1. The parameters of unlike-interaction potential are calculated by the Lorentz-Berthelot rule [11].

3. The effective one-fluid model
To calculate thermodynamic properties of a multicomponent fluid phase in [4] an improved van der Waals one fluid (vdW1f) model is proposed, which assumes a mixture of chemical species,

| Molecule | $\varepsilon/k$, K | $r_m$, A | $\alpha$ | $\lambda$, K |
|----------|--------------------|----------|---------|-------------|
| N$_2$    | 100.6              | 4.25     | 12.3    | 0           |
| NH$_3$   | 207.0              | 3.69     | 12.8    | 199.0       |
| H$_2$    | 36.9               | 3.67     | 10.6    | 0           |
| CO$_2$   | 230.2              | 4.22     | 13.8    | 0           |
| CH$_4$   | 145.0              | 4.28     | 12.7    | 0           |
interacting via potentials (1), to be a hypothetical one-component fluid with an effective exp-6 potential. The composition-dependent parameters of the effective potential are given by

\[ r_m = \left[ \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j r_{m,ij}^3 \right]^{1/3}, \]

\[ \varepsilon = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \varepsilon_{ij} r_{m,ij}^3 \left/ \left( r_m^3 \right) \right. \]

\[ \alpha = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \alpha_{ij} \varepsilon_{ij} r_{m,ij}^3 \left/ \left( \varepsilon r_m^3 \right) \right. \]

where the summation extends over all \( ij \) pairs, \( n \) is the number of the components, and \( x_i \) is the mole fraction of species \( i \). The reliability of the vdW1f model in predicting the excess thermodynamic parameters of multicomponent fluid has been shown by Ree [4], who is the author of the \( \alpha \)-mixing rule. Now this model is widely used for calculations of thermodynamic properties of multicomponent fluid mixtures [2, 3].

4. The theoretical model of the equation of state for binary fluids

For calculation of thermodynamic properties of chemical system at known temperature \( T \) and volume \( V \) it is enough to determine the Helmholtz energy of this system. Then all necessary thermodynamic parameters can be found by calculation of the corresponding derivatives of the Helmholtz energy. The method by means of which it is possible to calculate with high precision the Helmholtz excess energy of the binary system consisting of molecules of two types which interact with each other with spherically-symmetric intermolecular potentials \( \varphi_{ij}(r) \) (indexes \( i \) and \( j \) correspond to each type of molecules), is described in [6]. The presented technique is based on the thermodynamic perturbation theory KLRR and is generalized to the case of binary mixtures. Reliability and efficiency of theoretical EOS model of binary fluid (2f model) [6] is proved by a good agreement with results of MC simulation in wide area of thermodynamic conditions of fluid [6, 12]. The EOS model of two-component fluid [6] predicts thermodynamic properties of binary mixtures with higher precision as compared to the calculations on the basis of the vdW1f model. For binary mixtures the results of calculations show that such two-component model [6] better agrees with experimental data and results of MC simulation as compared to the vdW1f model [5, 9].

5. The theoretical effective two-fluid model

An effective two-fluid model (vdW2f) is proposed for calculation of thermodynamic properties of multicomponent mixture. In this model the division of all components of mixture into two groups with close well-depth parameters is supposed. Thus, the multicomponent mixture is presented in the form of an effective two-component fluid. This technique diminishes mistakes made by vdW1f model in calculation of thermodynamic parameters of a multicomponent mixture with considerably different well-depth parameters of components. Basis of the offered model is the thermodynamic perturbation theory and the EOS model of a two-component fluid [6] that’s why the vdW2f model possesses high speed in comparison with computer simulation by methods of Monte-Carlo and molecular dynamics.
Table 2. Separation of the mixture components into two groups.

| Group | Composition | $\epsilon/k$ | $x, \%$ |
|-------|-------------|--------------|---------|
| I     | NH$_3$     | 278–304      | 17.4–49.5 |
| II    | N$_2$+H$_2$| 52.37        | 82.6–50.5 |

Table 3. Statistics of relative deviations (average/maximum, percents). Calculation results compared to experimental data [13, 14].

| EOS-model | NH$_3$–N$_2$–H$_2$ | CO$_2$–CH$_4$–N$_2$ |
|-----------|--------------------|---------------------|
| vdW-1f    | 2.05/7.0           | 3.07/12.3           |
| vdW-2f    | 1.9/6.5            | 2.02/9.3            |

6. Results
In [13] the experimental data for ternary mixtures of ammonia-hydrogen-nitrogen of various compositions are published. An advantages of research of this mixture consist in existence of a polar molecule of ammonia for which it is necessary to use temperature dependence (3). It gives good opportunity to verify the offered effective two-fluid model.

By means of the offered technique (vdW2f model) the calculations of thermodynamic parameters of the ternary mixture NH$_3$–N$_2$–H$_2$ at the temperature ranging from 473 to 573 K and pressures from 10 to 150 MPa were carried out. The corresponding calculations on the basis of the vdW1f model were also carried out. Division of components of the mixture NH$_3$–N$_2$–H$_2$ is carried out proceeding from ratios of well-depth parameters of components (see table 1). In this case the ratio of the well-depth parameters is $\epsilon_{N_2}/\epsilon_{H_2} = 2.7$ does not exceed 3. But ratios $\epsilon_{NH_3}/\epsilon_{H_2} = 7.5$–8.2 and $\epsilon_{N_2}/\epsilon_{N_2} = 2.75$–3.1 exceed 3, where the well depth of ammonia depends on temperature (3). For the mixture NH$_3$–N$_2$–H$_2$ division into two groups according to the vdW2f model is shown in table 2. Values of effective well-depth and molar fraction of each group are also shown.

Similar calculations were carried out also for the ternary mixture CO$_2$–CH$_4$–N$_2$ of various compositions at the temperature ranging from 323 to 573 K. Experimental data are presented in [14]. The calculated data discrepancy of pressure according to the offered vdW2f model and the vdW1f model from experimental data is presented in table 3.

7. Conclusion
The new effective two-fluid model is presented. This model is based on the developed equation of state of two-component mixtures. The model has been applied to calculations of thermodynamic parameters of a ternary mixture with various component compositions in a range of moderate pressures and temperatures. Also the corresponding calculations with the use the vdW1f model have been carried out as well. Comparison of calculation results with experimental data shows higher precision of the vdW2f model as compared to the vdW1f model.

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