CHEMICAL THERMODYNAMICS
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Limits of the Applicability of the Effective One-Fluid Model

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Abstracts—The limits of the applicability of the effective one-fluid model are investigated. Thermodynamic parameters of two-component mixtures are calculated in both the field of high and the field of moderate pressures and temperatures. Calculations are performed using the effective one-fluid model (vdW1f) and on the basis of the precise two-component model (2f-model). It is shown that the 2f-model agrees better with the experimental data and with the results from Monte Carlo simulations than the vdW1f model. The difference in the accuracies of these models grows upon an increase in the $\varepsilon_1/\varepsilon_2$ ratio between the energy parameters of the intermolecular potentials. The limiting value of $\varepsilon_1/\varepsilon_2$ is 3, above which the use of the effective one-fluid model for calculating the thermodynamic parameters of mixtures can lead to completely incorrect results.

Keywords: equation of state, two-component fluid, thermodynamic perturbation theory, effective one-fluid model, Exp-6 potential of intermolecular interactions, shock Hugoniot.

INTRODUCTION

The need for calculations of the composition and thermodynamic parameters of multicomponent fluid systems with different chemical compositions at high pressures and temperatures arises when solving different problems in geophysics and astrophysics for simulating states of matter in atmospheres and internal layers of planets, and in the physics and chemistry of detonation and shock waves. In these kinds of problems, the multicomponent mixtures are under supercritical conditions and must be considered supercritical fluids. Derivating the equation of state (EOS) of a multicomponent fluid thus plays an important role in building a theoretical model for calculating the thermodynamic parameters of multicomponent systems. At present, there are a number of methods and theories for deriving the equation of state.

Most of the theoretically substantiated models that exist today and allow us to predict the thermodynamic parameters of fluids and fluid mixtures are based on the perturbation theory [1, 2] and variational theory [3]. The fundamental idea behind each of these theories is to express the excessive Helmholtz energy of a mixture in the form of a Taylor series with respect to a basis hard sphere fluid.

As was shown by many authors [1, 2, 4], the logic of using the perturbation theory as a basis in the theoretical models for the calculation of thermodynamic parameters of a pure fluid is confirmed by the good agreement between the calculation results and the experimental data, along with the results from Monte Carlo (MC) and molecular dynamics (MD) simulations.

In [5], the van der Waals effective one-fluid model (vdW1f) was suggested for describing multicomponent systems, since it allows us to calculate the thermodynamic parameters of multicomponent fluid mixtures. The multicomponent mixture of fluids in this model is represented by a hypothetical (effective) one-component fluid whose properties can be calculated using the EOS for a one-component fluid. The parameters of the effective fluid potential are determined through the parameters of the intermolecular interaction potentials between molecules of a multicomponent mixture, which depend on the composition of the mixture.

The vdW1f model is simple and easy to use, and it provides a compromise between the accuracy of calculated thermodynamic values and calculation performance. This model is now widely used for calculating the thermodynamic properties of multicomponent fluid mixtures.

RESULTS AND DISCUSSION

Applying the vdw1f Model for the Two-Parameter Lennard–Jones Potential

The vdW1f model was described theoretically by Smith in [5]. This method allows us to express the parameters of the Lennard–Jones potential of an

effective one-component fluid through the parameters of the intermolecular potentials of the mixture components. The van der Waals model [5, 6] can be expressed in the form

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

where r_m is the size parameter; ε is the well depth; x_i and x_j are molar fractions of the ith and jth components of the mixture, respectively; and double summation is performed over all of the mixture's components.

McDonald concluded in [7] that the results from calculating the excess properties of a thermodynamic system on the basis of the vdW1f model agree with the MD simulation results at a ratio of potential parameters r_m ranging from 1 to 1.134 and a ratio of energy parameters ε ranging from 0.56 to 2.275.

As was shown in [8], the Lennard–Jones effective one-fluid model for mixtures is applicable only when $\varepsilon_{jj}/\varepsilon_{ii} \leqslant 1.5$ and $r_{m,jj}/r_{m,ii} \leqslant 1.1$.

Thermodynamic parameters of binary mixtures were analyzed in [9] that allow us to expand the range of asymmetry of the potential parameters up to 4 : 1 for both the potential well depth and the radius of the intermolecular interaction of components. It was concluded that the $\varepsilon_{jj}/\varepsilon_{ii}$ ratio affects the results from calculations with the vdW1f model more strongly than the $r_{m,jj}/r_{m,ii}$ ratio.

In [10, 11], Fotouh and Shukla investigated the accuracy of a modified perturbation theory and a vdW1f model in which EOS of a one-component fluid is used. The vdW1f model was successful in predicting the thermodynamic parameters of some fluid mixtures whose components have close potential parameters. However, this model becomes less reliable upon an increase in the difference between the potential parameters of the mixture components. The main conclusion of [10, 11] was that a modification of the existing perturbation theory and a model much more precise than the effective one-fluid model are needed for calculating the thermodynamic parameters of multicomponent fluid mixtures. All of the above studies were performed using the two-parameter Lennard–Jones potential in the area of low temperatures and pressures.

The results from numerous studies indicate that the spherically symmetric Exp-6 potential (modified Buckingham potential) provides a reasonable compromise between reality of the description of intermolecular forces and simplicity of the potential functional form in the area of high pressures.

The effective one-fluid model with the Exp-6 interaction potential is successfully used for calculating the thermodynamic parameters of complex chemically reacting mixtures [4], though the area of applicability of this model has not yet been defined. Analysis of the results from performed studies raises the following question: under what conditions and for what composition of components does the effective one-fluid model with the Exp-6 potential yield realistic results, and in which cases is the use of this model unreasonable?

The aim of the this work was thus to determine the area of applicability of the vdW1f model in the case of using the Exp-6 potential, the practicality of which over a broad range of pressures and temperatures has been proved by many studies.

Applying the vdW1f Effective One-Fluid Model for the Exp-6 Potential

In the area of high temperatures and pressures, the predominant role in intermolecular interactions is played by the repulsive forces between molecules. Ab initio quantum-mechanical calculations and a whole range of experimental data pertaining to the properties of simple chemical systems show the physical validity of exponential repulsion. The spherically symmetric Exp-6 potential can therefore be used to describe interactions between the molecules of fluid mixture components:

$$\varphi_{ij}(r) = \varepsilon_{ij}/(\alpha_{ij} - 6)(6\exp[\alpha_{ij}(1 - r/r_{m,ij})] \\ - \alpha_{ij}(r/r_{m,ij})^6), \quad r \geq c_{ij}, \tag{1}$$

$$\varphi_{ij}(r) = +\infty, \quad r < c_{ij}, \tag{2}$$

where $\varepsilon_{ij} > 0$ and corresponds to the potential well depth (min $[\varphi_{ij}(r)] = -\varepsilon_{ij}$), $r_{m,ij}$ is the distance between the centers of molecules at which the potential energy takes the minimum value ($\varphi_{ij}(r_{m,ij}) = -\varepsilon_{ij}$), and α_{ij} is the parameter determining the repulsive stiffness.

Smith's vdW1f model [5] was developed for the two-parameter Lennard–Jones potential. In [12], Ree added a formula for calculating the stiffness of the effective one-fluid potential with the aim of using the vdW1f model for the three-parameter Exp-6 potential. Final formulas for calculating the parameters of an effective fluid whose properties coincide with the corresponding properties of a multicomponent fluid phase have the form

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

$$\varepsilon = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \varepsilon_{ij} r_{m,ij}^3 / (r_m^3), \tag{3}$$

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

In Eq. (3), x_i is the molar fraction of the ith component, and n is the number of components. The effec-

tive Exp-6 potential parameters α, r_m, and ε, also depend on the composition of a mixture and on the given parameters of potentials of the mixture components.

The reliability of model (3) in its joint use with the precise EOS model of a one-component fluid with the Exp-6 potential is confirmed by the good agreement between thermodynamic predictions made on the basis of the vdW1f model with the Monte Carlo computer simulation results. This was shown in [12] by Ree, the author of the mixing rule for calculating effective potential parameter α. Successful use of this model in practical thermodynamic calculations for various multicomponent systems (e.g., in [13–15]) also demonstrates the physical validity of the vdW1f model.

Multicomponent EOSs using the vdW1f model should be based on the use of a reliable one-component EOS model. The new version of the perturbation theory, KLRR [16], which improves the accuracy of the calculation of thermodynamic parameters of a fluid at high densities, was used in [4].

Theoretical EOS Model of a Two-Component Fluid

To calculate the thermodynamic properties of a fluid system at a given temperature T and volume V, it is sufficient to know the Helmholtz energy of this system. The values of all the required thermodynamic parameters can be found by calculating the corresponding Helmholtz energy derivatives.

The method, which allows us to calculate with a high level of accuracy the excessive Helmholtz energy of a two-component system consisting of two kinds of molecules that interact with each other through a spherically symmetric intermolecular pair potential, was described in detail in [17, 18]. The reliability and efficiency of the theoretical EOS model of a two-component fluid proposed in [17, 18] is proved by the good agreement between the MC simulation results over a wide range of a fluid's thermodynamic states [17, 18].

Calculation Results and Comparison to the Data from Experiments and Monte Carlo Simulations

Two-component mixtures that are formed as a result of dissociation under the strong compression in a shock wave were chosen for our studies. These were of molecular and atomic nitrogen, and of molecular and atomic oxygen as well. One factor considered in choosing these particular mixtures is that the energy potential parameters ε/k in an N_2–N mixture are quite close, and their ratio is somewhat less than 3 in an O_2–O mixture.

In addition, we examined the parameters of the products of the shock compression of ammonia, even though the mixture formed as a result of dissociation of ammonia is a three-component mixture. This poses

some difficulties for us at present, since the developed theoretical EOS model [18] allows us to calculate only the parameters of one- and two-component mixtures. Therefore, a NH_3–H_2 mixture whose components were ones of the dissociation products yielded upon compression in a shock wave was chosen. The two-component NH_3–H_2 mixture is of particular interest to researchers for the following reasons. First, experimental data with different contents of ammonia are available for this mixture [19]. Second, the covered temperature area is substantially lower than in the shock-wave experiments used for selecting the ammonia potential parameters. This allows us to demonstrate fully the wide area of applicability of the developed EOS model. Third, the ammonia molecule is polar and poorly described by a three-parameter potential of the types (1) and (2). Therefore, a potential in accordance with [13], i.e., a modified form of the Exp-6 potential, for which the potential well depth depends on temperature, was used for the calculations in this work:

$$\varepsilon_{ii}(T) = \varepsilon_{0,ii}\left(1 + \frac{\lambda_{ii}}{T}\right), \qquad (4)$$

where λ_{ii} is the parameter needed for considering the electrostatic effects in polar molecules (for example, NH_3 and H_2O).

Supplementing the potential with its temperature dependence allows us to consider the contribution from dipole interactions at temperatures of around λ_{ii} and lower. The Exp-6 potential (Eqs. (1), (2), and (4)) modified in this way has four parameters (α_{ii}, $r_{m,ii}$, $\varepsilon_{0,ii}$, and λ_{ii}), while $\lambda_{ii} = 0$ for non-polar substances.

The parameters of the Exp-6 potential for various molecules were found in [16]. The parameters of the Exp-6 potential for the molecules comprising the mixtures investigated in this work are given in Table 1.

Thermodynamic parameters of N_2–N and O_2–O mixtures that are the products of the compression of N_2 and O_2 in a shock wave, and of the NH_3–H_2 mixture, were calculated on the basis of the two-component EOS model (2f-model) using the potentials from Table 1 in accordance with the vdW1f model; in addition, MC simulations were performed using the Towhee program [20–25].

Our calculation results are presented in Figs. 1 and 2. The solid line shows the results obtained using the two-component EOS model (2f-model), the dashed line shows the results on the basis of the effective one-fluid model (vdW1f), and the symbols designate the experimental values and the MC simulation data.

As is seen from Fig. 1, the shock Hugoniots for N_2 and O_2 that were calculated on the basis of the 2f-model of EOS conform better to the MC simulation

Table 1. Parameters of the Exp-6 potential for the investigated substances

Molecule	α	ε/k, K	r_m, A	λ, K
N_2	12.3	100.6	4.25	0
N	10.4	120.0	2.65	0
O_2	14.7	96.2	3.79	0
O	11.5	277.0	2.57	0
NH_3	12.8	207	3.69	199
H_2	10.6	36.9	3.67	0

Table 2. Statistical deviations of the results from calculations with MC simulation data

Model	N_2-N	O_2-O	NH_3-H_2
Average value of the absolute deviation, %			
vdW1f	2.26	5.04	7.76
2f	1.15	1.69	1.83
Maximum value of the absolute deviation, %			
vdW1f	3.32	6.97	17.99
2f	2.61	2.17	4.73

data than in the case of using the vdW1f model at high pressures ($p > 50$ GPa).

At low pressures ($p < 35$ GPa) and temperatures, both models show good conformity with the experimental and MC simulation data. This is not surprising, since the degree of dissociation is insignificant in these conditions, and only a small amount of the sec-

ond component is present in the mixture. Upon an increase in the degree of dissociation, the difference between the two-component and vdW1f models increases.

For the area of moderate pressures (tens MPa), the calculation results for the binary NH_3-H_2 mixture are more precise when we used the 2f-model of EOS, compared to the results obtained on the basis of the vdW1f model. This is illustrated in Fig. 2, where significant deviations of the dashed lines corresponding to the results of calculations using the effective vdW1f model from the solid lines that correspond to the precise two-component model, and from the symbols showing the experimental data points [19] and MC simulation results, are observed.

Table 2 gives the total statistics of deviations of the pressure values calculated with using both the effective one-fluid model (the row denoted by vdW1f) and the two-component EOS model (the row denoted by 2f) from the MC simulation data for the investigated binary mixtures.

Analyzing all of our calculation results and comparing them to the available experimental data and the MC simulation results, we may conclude that the potential parameter values for the N_2-N mixture are quite close ($\varepsilon_N/\varepsilon_{N_2} = 1.2$), and, according to Table 2, the difference between the accuracies of the 2f- and vdW1f models is also slight.

The $\varepsilon_O/\varepsilon_{O_2}$ value for the O_2-O mixture is ~3 ($\varepsilon_O/\varepsilon_{O_2} = 2.88$). A greater difference in the calculation results is observed in this case.
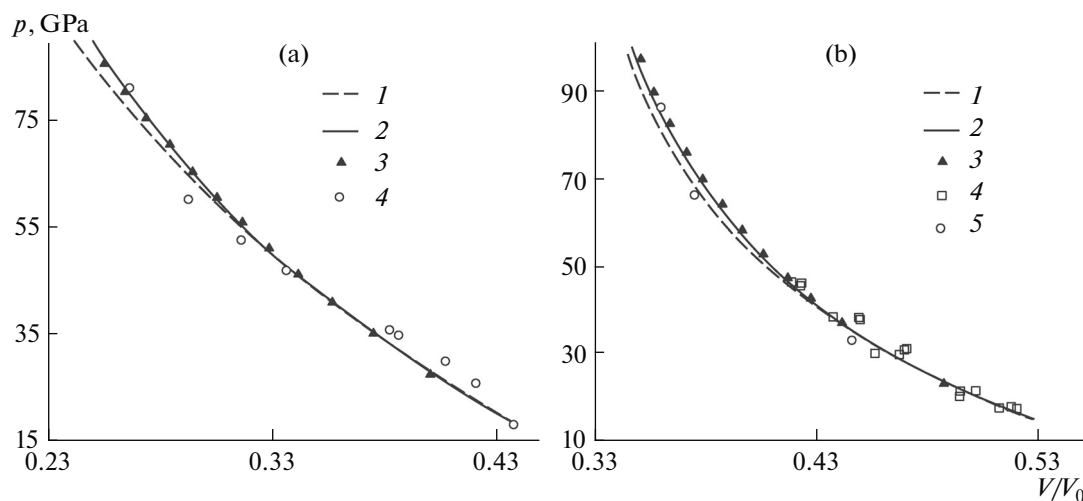

Fig. 1. Shock adiabatic curves of liquid nitrogen in pV-coordinates; the initial state of the substance is characterized by the following parameters: $T_0 = 77$ K, ρ_0 equals (a) 0.808 and (b) 1.202 g/cm^3, U_0 equals (a) -2.84 and (b) -1.41 kcal/mol; (*1*) corresponds to the results from calculations based on the vdW1f model [16]; (*2*) corresponds to the results from calculations using the 2f-model [17]; (*3*) corresponds to the MC simulation results [20–25]; (*4*) corresponds to experimental data from (a) [26] and (b) [27]; (*5*) corresponds to experimental data from [28].
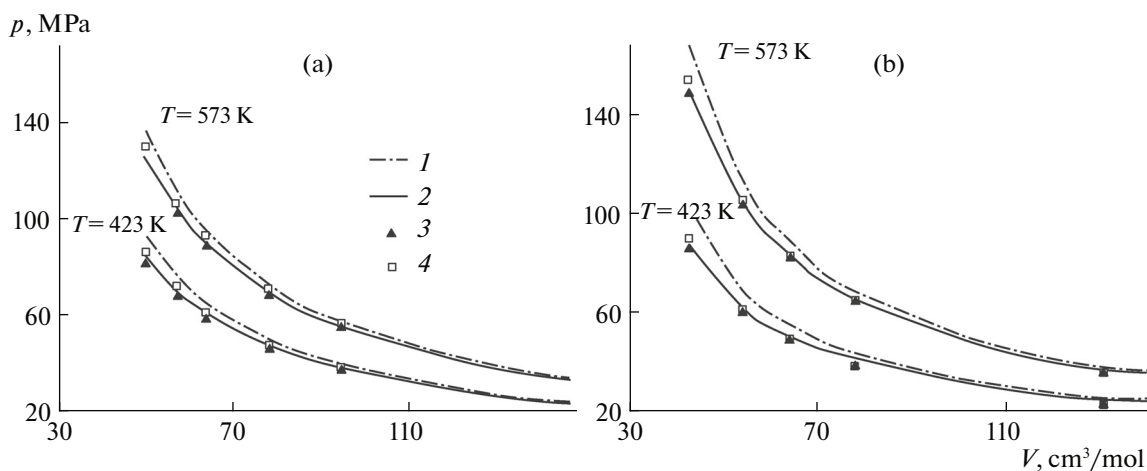
Fig. 2. Isotherms of NH_3-H_2 mixtures with ammonia contents of (a) 34.75 and (b) 57.49%; (*1*) corresponds to the results from calculations based on of the vdW1f model [16]; (*2*) corresponds to the results from calculations using the 2f-model [17]; (*3*) corresponds to the MC simulation results [20–25]; (*4*) corresponds to the experimental data [19].

The $\varepsilon_{NH_3}/\varepsilon_{H_2}$ value for the NH_3-H_2 mixture is 5.6 ($\varepsilon_{NH_3}/\varepsilon_{H_2} > 3$). The error of the calculations performed in accordance with the vdW1f model is rather high in this case. This allows us to conclude that the vdW1f model cannot be applied to the NH_3-H_2 mixture. The calculations based on the 2f-model in turn conform to the MC simulation data.

CONCLUSIONS

The thermodynamic parameters for three binary mixtures were calculated using the intermolecular Exp-6 potential. The calculation area covered both the range of high pressures (20 to 80 GPa) and temperatures (2000 to 12 000 K) that correspond to shock waves and the region of moderate pressures (20 to 100 MPa). This demonstrates the wide area of applicability of our equation of state for a two-component fluid. The calculations were performed both on the basis of EOS for a two-component fluid and on the basis of the effective one-fluid model (vdW1f). MC simulation was also performed.

Based on our studies, we may conclude that the 2f-model yields the calculation results that are in better agreement with the experimental data and MC simulations than does the vdW1f model. The difference between the accuracies of these models increases along with the ratio $\varepsilon_1/\varepsilon_2$ of their energy parameters, while the vdW1f model remains accurate up to $\varepsilon_1/\varepsilon_2 \leqslant$ 3. Hence, the effective one-fluid model can be used for calculations of the thermodynamic parameters of mixtures whose components have a ratio of the well depth not exceeding 3. Otherwise, the EOS model of a two-component fluid should be used.

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