International Journal of Thermophysics, Vol. 27, No. 2, March 2006 (© 2006)
DOI: 10.1007/s10765-006-0059-9

Equation of State of He-H_2 and He-D_2 Dense Fluid Mixtures at High Pressures and Temperatures

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Received July 5, 2005

The fluid variational theory is used to calculate the Hugoniot equation of state (EOS) of He, D_2, He + H_2, and He + D_2 fluid mixtures with different He:H_2 and He:D_2 compositions at high pressures and temperatures. He, H_2, and D_2 are the lightest elements. Therefore, the quantum effect is included via a first-order quantum correction in the framework of the Wigner-Kirkwood expansion. An examination of the reliability of the above computations is performed by comparing experiments and calculations, in which the calculation procedure used for He and D_2 is adopted also for He + D_2 and He + H_2, since no experimental data for the mixtures are available to conduct these comparisons. Good agreement in both comparisons is found. This result may be seen as an indirect verification of the calculation procedures used here, at least, in the pressure and temperature domains covered by the experimental data for He and D_2 used for comparisons, which is nearly up to 40 GPa and 10^5 K. Also, the equation of state of He + H_2 fluid mixtures with different compositions is predicted over a wide range of temperatures and pressures.

KEY WORDS: deuterium; equation of state; fluid variational theory; helium; hydrogen; mixtures.

1. INTRODUCTION

Hydrogen and helium are the simplest and most abundant elements in the universe and also major constituents of some planets, such as Jupiter and Saturn. Yet at high pressures, they are some of the most difficult to understand. From low to moderately high pressures, hydrogen is a molecular fluid (or solid) with a wide bandgap [1,2]. The high-pressure equation

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of state of hydrogen and its isotopes is a subject of considerable interest, principally due to the importance of the EOS to such areas as inertial confinement fusion, planetary astrophysics, and a fundamental understanding of warm dense matter. In the past several years, some significant advances have been made in the experimental and theoretical Hugoniot equation of state of liquid deuterium and helium [3–9]. He–H_2 mixtures enjoy special significance due to their cosmological relevance and the challenge they pose due to the complex nature of interactions among the constituent species.

Recently, Ali et al. [10] have studied the effect of pressure and temperature on the properties of mixing of helium-hydrogen fluid mixtures based on statistical perturbation theory. The constituent species are considered to be interacting by a pair potential consisting of a short-range repulsion and a long-range attraction which is included through a double Yukawa (DY) potential. Studies involving these mixtures are relatively rare both theoretically and experimentally. In spite of the simple electronic structure of helium and deuterium, it is difficult to make a precise description of the properties of helium and deuterium at high pressures and temperatures, but it can only be made with the help of some approximate models. Although variational free energy calculations have been done for over 30 years, there is still an interest to carry out such calculations.

In some of our previous studies on shock-compressed liquid H_2+D_2 and fluid He + H_2, Chen et al. [11,12] reported the calculation results of an EOS by the use of a one-component variational fluid theory with a quantum correction, and the theoretical results are in excellent agreement with the existing experimental data. Therefore, in this work, we have applied the two-component variational fluid theory method to $\mathrm{He}+D_2$ and $\mathrm{He}+H_2$ fluid mixtures. The interactions of the mixture species were described by using the effective pair potential of the exponential-six form. The equation of state of the $\mathrm{He}+H_2$ fluid mixtures with different compositions is predicted over a wide range of temperatures and pressures.

2. FREE ENERGY MODEL

Based on the fluid variational theory model [13], the free energy is given as a sum of the ideal contributions of the pure components F_i^{id} (with $i=1,2,1=\mathrm{He},2=\mathrm{D}_2$) and a term for the correlations among all particles F_i^{cor}. The thermophysical properties of the mixtures for deuterium and helium are calculated using the following Helmholtz free energy for a system of N_{D_2} molecules and N_{He} atoms:

$$F^{\mathrm{tot}}=F_{\mathrm{He}}^{\mathrm{id}}+F_{\mathrm{D}_2}^{\mathrm{id}}+F_{\mathrm{He-D}_2}^{\mathrm{cor}}+F_{\mathrm{QM}}. \tag{1}$$

The ideal free energies for the atomic and molecular components are given by

$$F_{\mathrm{He}}^{\mathrm{id}}(n,T) = F_{\mathrm{He}}^{\mathrm{trans}}(N,T), \tag{2}$$

$$F_{\mathrm{D}_2}^{\mathrm{id}}(n,T) = F_{\mathrm{D}_2}^{\mathrm{trans}}(N,T) + F_{\mathrm{D}_2}^{\mathrm{rot}}(N,T) + F_{\mathrm{D}_2}^{\mathrm{vib}}(N,T) - D_0. \tag{3}$$

Here D_0 = 4.478 eV is the dissociation energy of isolated deuterium molecules and T and n are the temperature and particle number density, respectively. The translational degrees of freedom for each component can be integrated and yield

$$F_i^{\mathrm{trans}}(n,T) = N_i \mathrm{k}_B T \ln(\Lambda_i^2 n_i), \tag{4}$$

where $\Lambda_i = \mathrm{h}/\sqrt{2\pi m_i \mathrm{k}_B T}$ is the thermal wavelength and $n_i = N_i/V$ is the particle number density. The rotational and vibrational states of the D_2 molecule can be integrated and give [14]

$$F_{\mathrm{D}_2}^{\mathrm{rot}}(N,T) = N_{D_2} \mathrm{k_B} T \left[\ln\left(\frac{T_{\mathrm{r}}}{T}\right) - \frac{T_{\mathrm{r}}}{3T} - \frac{1}{90}\left(\frac{T_{\mathrm{r}}}{2T}\right)^2 \right], \tag{5}$$

$$F_{\mathrm{D}_2}^{\mathrm{vib}}(N,T) = N_{\mathrm{D}_2} \mathrm{k_B} T \left[\ln(1 - \exp(-T_{\mathrm{v}}/T)) + \frac{T_{\mathrm{v}}}{2T} \right]. \tag{6}$$

The rotational temperature of the D_2 molecule is $T_{\mathrm{r}} = 43\,\mathrm{K}$. The vibrational temperature of the D_2 molecule is $T_{\mathrm{v}} = 4395\,\mathrm{K}$.

The correlation parts are determined variationally by using free energy minimization. In particular, in our case with a hard-sphere (HS) reference system we can obtain

$$\begin{aligned} F_{\mathrm{He-D}_2}^{\mathrm{cor}} \approx \min_{d_1,d_2} \{ & F_{\mathrm{HS}}(T, x_1, x_2, \eta_1, \eta_2) + F_{\mathrm{HeHe}}(N_{\mathrm{He}}, \eta_{\mathrm{He}}) \\ & + F_{\mathrm{HeD}_2}(N_{\mathrm{He}}, N_{\mathrm{D}_2}, \eta_1, \eta_2) + F_{\mathrm{D}_2\mathrm{D}_2}(N_{\mathrm{D}_2}, \eta_2) \}, \end{aligned} \tag{7}$$

where $\eta_i = \pi d_i^3 n_i/6$ (d = hard-sphere diameter). The expression for the free energy of a binary HS reference system is given by [15]

$$\begin{aligned} F_{\mathrm{HS}}(n, T, \eta_1, \eta_2) = N \mathrm{k_B} T \Bigg[& \frac{3}{2}(1 - y_1 + y_2 + y_3) + \frac{3y_2 + 2y_3}{1-\eta} \\ & + \frac{3}{2} \frac{1 - y_1 - y_2 - y_3/3}{(1-\eta)^2} + (y_3 - 1)\ln(1-\eta) \Bigg], \end{aligned} \tag{8}$$

where

$$\begin{aligned}
\eta &= \eta_1+\eta_2,\\
y_1 &= (\eta_1^*+\eta_2^*-\eta_{12}-\eta_{21})/\eta,\\
y_2 &= [\eta_1\eta_2+\eta_{21}(\eta_1-2\eta_2)+\eta_{12}(\eta_2-2\eta_1)]/\eta^2,\\
y_3 &= [(x_1\eta_1^2)^{1/3}+(x_2\eta_2^2)^{1/3}]^3/\eta^2,\\
\eta_{12} &= (\eta_1^*\eta_2^{*2})^{1/3}, \quad \eta_{21}=(\eta_2^*\eta_1^{*2})^{1/3},\\
\eta_1^* &= x_1\eta_1, \quad \eta_2^*=x_2\eta_2,\\
x_1 &= N_{\mathrm{He}}/N, \quad x_2=N_{\mathrm{D_2}}/N.
\end{aligned}$$

The correlation contributions F_{ij} are given by integrals over the pair potentials $\phi_{\mathrm{ij}}(\mathrm{r})$ and the respective radial distribution function $g_{\mathrm{ij}}(\mathrm{r},\eta)$ which are approximated by the Percus-Yevick equation of a hard-sphere reference system, e.g.,

$$F_{ij}=2\pi Nn\int_d^\infty r^2\phi_{ij}(r)g_{ij}(r,\eta)\mathrm{d}r. \tag{9}$$

The pair distribution functions of the hard-sphere reference system use the Percus-Yevick analytical expression [16],

$$g(r,\eta)=\frac{1}{24\pi\eta ri}\int_{\delta-i\infty}^{\delta+i\infty}\frac{tL(t)e^{rt}\mathrm{d}t}{[L(t)+S(t)\mathrm{e}^t]}, \tag{10}$$

where

$$S(t)=(1-\eta)^2t^3+6\eta(1-\eta)t^2+18\eta^2t-12\eta(1+2\eta),$$

$$L(t)=12\eta\left[\left(1+\frac{1}{2}\eta\right)t+(1+2\eta)\right].$$

The integrals in Eq. (10) can thus be evaluated by means of the residue theorem. F_{QM} is a first-order quantum correction to the Wigner-Kirkwood expansion [17]:

$$F_{\mathrm{QM}}=\frac{\beta\mathrm{h}^2nN}{24\pi m^*}\int_d^\infty g_{ij}(r,\eta)\nabla^2\phi_{ij}(r)r^2\mathrm{d}r, \tag{11}$$

where m^* is the effective mass. The expression for this effective mass m^* is [18]

$$\frac{1}{m^*}=\sum_{i,j}\frac{1}{m_i}x_ix_j\varepsilon_{ij}r_{ij}^*\,/\,\varepsilon r^*. \tag{12}$$

The parameters (ε, r^*) are expressed in terms of the exp-6 parameters $(\varepsilon_{\mathrm{ij}}, r_{ij}^*)$ of constituent species of the mixture system [12], and x_i denotes the mole fraction of species i. Here F^{cor} is calculated by adjusting d_i until F^{cor} attains a minimum, and we take this F^{cor} minimum as the value of F^{cor}. Then the pressure (P) and the internal energy (E) of the system may be calculated by

$$p = -\frac{\partial F^{\mathrm{tot}}}{\partial V} = \frac{1}{N}\rho^2 \frac{\partial F^{\mathrm{tot}}}{\partial \rho}, \tag{13}$$

$$E = \frac{\partial(\beta F^{\mathrm{tot}})}{\partial \beta} = -T^2 \frac{\partial}{\partial T}\left(\frac{F^{\mathrm{tot}}}{T}\right). \tag{14}$$

To verify the reliability of the theoretical high-pressure and high-temperature EOS, we think that it is better to conduct experiments under shock compression conditions, because experimental data are generally easy to obtain in that case. Hugoniot calculations could be made by the above equations combined with the Rankine-Hugoniot relation [19],

$$E_{\mathrm{H}} - E_0 = \frac{1}{2}(P_{\mathrm{H}} + P_0)(V_0 - V_{\mathrm{H}}), \tag{15}$$

which connects a thermodynamic state $(P_{\mathrm{H}}, E_{\mathrm{H}}, V_{\mathrm{H}})$ achieved behind the shock front with the initial state (P_0, E_0, V_0) ahead of the shock front. The initial states (P_0, E_0, V_0) of He and D$_2$ are taken as (10^{-4} GPa, 0.1 kJ·mol^{-1}, 32.4 cm^3· mol^{-1}) [20] and (10^{-4} GPa, 0.1146 kJ· mol^{-1}, 23.64 cm^3· mol^{-1}) [14], respectively. The values of P_0, E_0, and V_0 may be computed from the mole fractions of the mixture components by using the following forms:

$$E(p) = \sum_i c_i E_i(p), \tag{16}$$

$$V(p) = \sum_i c_i V_i(p). \tag{17}$$

Here c_i is the mass fraction of the ith component, and $\sum_i c_i = 1$.

Fluid mixtures are of great practical importance but theoretical calculations for them are generally much harder than for single species. Thus, the correlation free energy F^{cor} is calculated by using the effective pair potential. The potential used in Eq. (9) to calculate F^{cor} is taken as the exponential-six form,

$$\phi(r) = \frac{\varepsilon}{\alpha - 6}\left\{6\exp\left[\alpha\left(1 - \frac{r}{r^*}\right)\right] - \alpha\left(\frac{r^*}{r}\right)^6\right\}. \tag{18}$$

Table I. Parameters for the Effective Potentials for the D_2-D_2, He-He, and He-D_2 Systems Used in the Present Work [22].

Parameter	D_2-D_2	He-D_2	He-He
α	11.1	12.7	13.10
ε/k_B (K)	36.4	15.5	10.800
r^* (nm)	0.343	0.337	0.29673
r_a (nm)	0.145855	0.104748	0.085548
A (K)	313369	852692	939318
B (nm^{-1})	0.224478	0.261272	0.307828

The parameter ε represents the attractive well depth, r^* indicates the range of interaction, while parameter α regulates the stiffness of repulsion. The long-range attractive part is similar to the Lennard-Jones potential, while the repulsion at shorter distances is modeled by an exponential function. In the limit $r \to 0$, the exp-6 potential, Eq. (18), becomes attractive again. This unphysical behavior is avoided by replacing the exp-6 potential, Eq. (18), by an exponential function of form $\phi_{ij}(r) = \phi_2(r) = A \exp(-Br)$ for $r \leqslant r_a$ such that repulsion remains for small distances. Here r_a is one of the two inflection points of Eq. (18) and smaller than the equilibrium distance. The parameters A and B are chosen to ensure continuity, i.e., $\phi_1(r_a) = \phi_2(r_a)$ and $\phi_1'(r_a) = \phi_2'(r_a)$, and are given in Table I together with the values for ε, r^*, and α of Eq. (18).

3. RESULTS AND DISCUSSION

The calculated Hugoniots for fluid He, D_2, and He + D_2 mixtures with He:D_2=5:1, 3:1, 1:1, and 1:3 are shown in Figs. 1 and 2, separately in $P_H - V_H$ and $T_H - V_H$ planes. Because there are no experimental data for He + D_2 mixtures that verify the reliability of calculations directly, we have no choice but to make comparisons for He and D_2 between experiment and calculations that use similar procedures as carried out for He + D_2 mixtures. So the data for He and D_2 are given in Figs. 1 and 2. Rather good agreement between experiment and calculations [6,19–21] is shown in these two figures. We think these comparisons may be seen as indirect verification of the reliability of the calculation procedure used here. Both figures also demonstrate that the Hugoniots of fluid He, D_2, and their mixtures tend to coincide when V_H approaches its initial state, but deviate from each other more and more with increasing compression. Also, at a given V the values of P_H and T_H will decrease with decreasing mole fraction of He and approach to values of one-component D_2 when the mole fraction ratio of He: D_2 falls to 1:3 or lower.

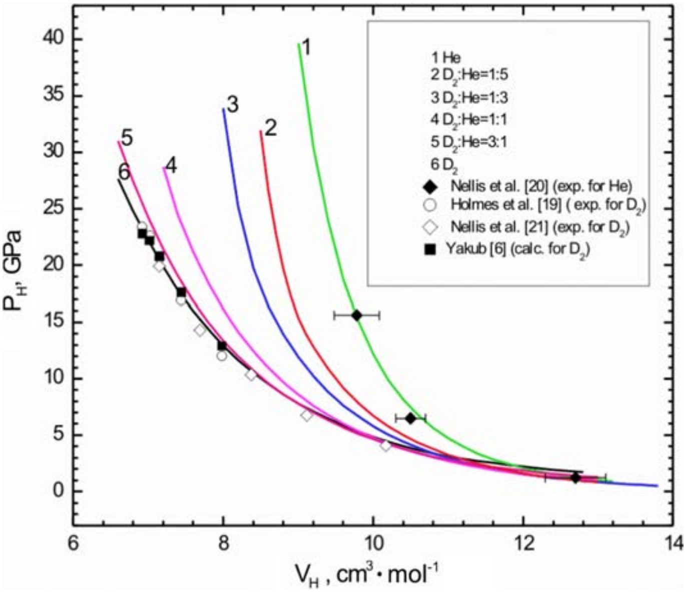

Fig. 1. Comparison of $P_H - V_H$ curves for fluid He, D$_2$, and He + D$_2$ mixtures

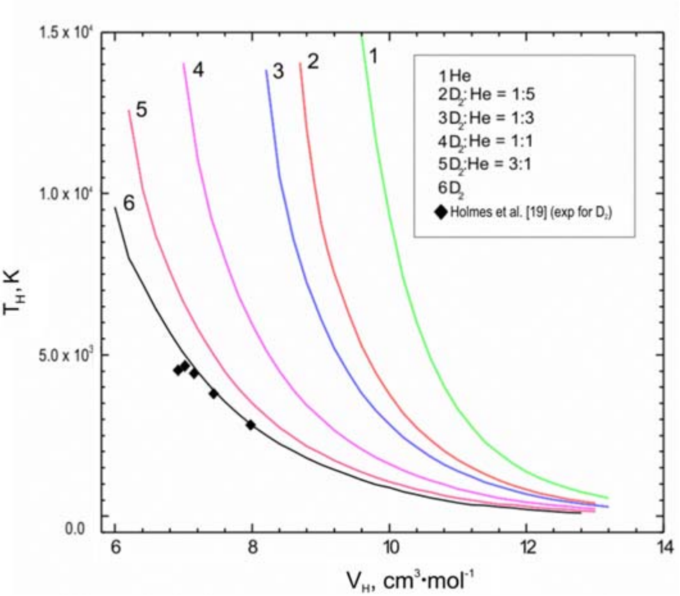

Fig. 2. Comparison of $T_H - V_H$ curves for fluid He, D$_2$, and He + D$_2$ mixtures

As is well known, the difference between isotopes is simply related to the neutron number in each nucleus, but on the hand, there are the same number of electrons around each nucleus which plays an important role in determining the chemical properties of the substance. Therefore, when the inter-particle distance is the same, the interaction and thermal excitation of electrons will be also in both He–H_2 and D_2-He systems. The parameters used for the calculation of He–H_2 mixtures should be also the same as that of He–D_2 mixtures listed in Table I. But the rotational and vibrational temperatures for H_2 and D_2 molecules are different, $T_r = 85\,K$ and $T_v = 6210\,K$ for H_2. Figure 3 shows a comparison of isotherms of fluid helium and hydrogen with the Monto-Carlo (MC) simulations [13], calculations of Ali et al. [10], and the effective one-component model [12]. The present results are in agreement with the MC data and the effective one-component model. Note that the results of Ali et al. are slightly higher than our calculations. The deviations from the pressures by Ali et al. have a tendency to increase with density. This indicates that the DY potential used in their calculations is stiffer than the present potential. The reason is that the many-particle nature of the interaction might not be well approximated by the DY potentials in the higher density region.

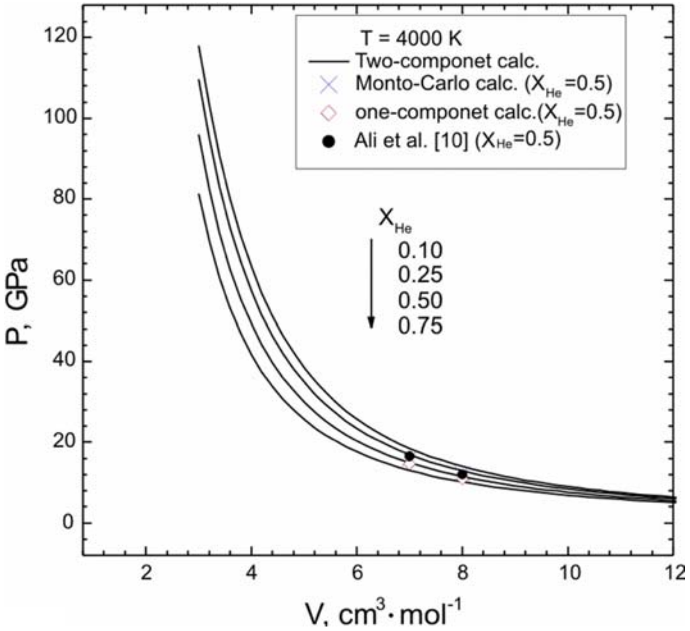

Fig. 3. Comparison of the isotherms of helium and hydrogen fluid mixtures

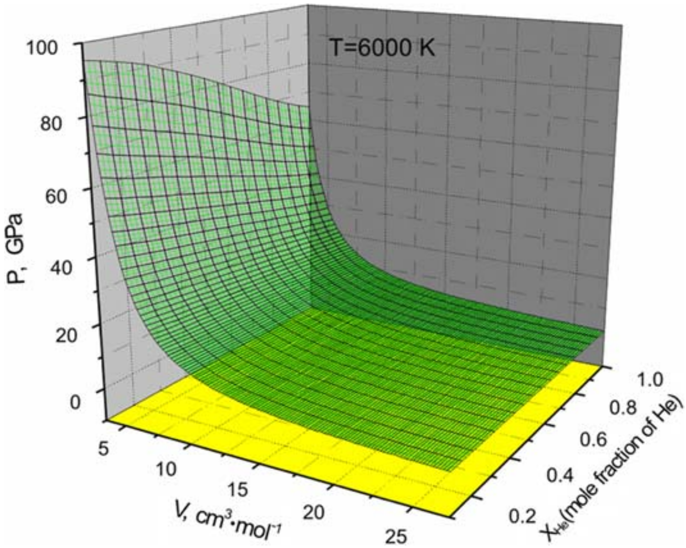

Fig. 4. Isothermal surfaces of mixtures of fluid helium and hydrogen as a function of specific volume and mole fraction of He.

Another effect, the pressure dissociation of hydrogen, should occur under these conditions as well. Therefore, the short-range parts of the effective pair potentials become more and more important for very high densities. The present calculation method is also extended to calculate the isothermal surface for $He + H_2$ fluid mixtures over a wide range of pressure with different compositions. Figure 4 shows the predicted isothermal surface of the helium and hydrogen fluid mixtures with different $He{:}H_2$ compositions at 6000 K. It can be seen that pressures decrease with increasing mole fraction of helium at isothermal conditions. The pressure of the $He + H_2$ fluid mixtures increases with increasing temperature. Based on the calculation procedures and results, the difference in the equation of state between $He–D_2$ and $He–H_2$ fluid mixtures is mainly reflected in the quantum effect due to different masses of H_2 and D_2. It leads to a difference in both vibration and rotation temperatures for H_2 and D_2. Therefore, $He–H_2$ shows the more sensitive quantum effect for volume change than $He–D_2$. The validity of the present predictions needs to be verified by comparisons with experimental data.

4. CONCLUSIONS

The experimental high-pressure data of deuterium and helium are reproduced by the fluid variational theory with a pure molecular (or a pure atom) fluid up to 40 GPa. The EOS for He+H_2 fluid mixtures is in good agreement with MC data and the effective one-component model. The predicted EOSs for the two-component fluid mixtures are extended to pressures up to 100 GPa and temperatures up to 10 kK. However, the many-particle nature of the interactions might not be well approximated by these effective pair potentials at high pressures. Another effect, the pressure dissociation of hydrogen molecules, should occur under these conditions as well. Therefore, the calculated model is restricted to pressures below 100 GPa. The reliability of the calculation procedure proposed in this paper should be clarified through direct comparisons with experimental data for $He + D_2$ and $He + H_2$ mixtures in the future. The present results help to guide the importance for developing shock-compression experiments.

ACKNOWLEDGMENTS

This work has been supported by the Foundation of Laboratory for Shock Wave and Detonation Physics Research of China Academy of Engineering Physics Grant No. 9140C67120206ZS7502.

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