Vol 10 No 12, December 2001
1009-1963/2001/10(12)/1144-05
Chinese Physics
© 2001 Chin. Phys. Soc.
and IOP Publishing Ltd

EQUATION OF STATE OF FLUID He+H_2 MIXTURES UNDER HIGH PRESSURE*

Chen Qi-feng(陈其峰)[a)b)c)], Cai Ling-cang(蔡灵仓)[b)], Sun Zhi-hong(孙志红)[c)]
Jing Fu-qian(经福谦)[b)], and Chen Dong-quan(陈栋泉)[d)]

[a)] *Department of Physics, Northwest Normal University, Lanzhou 730070, China*
[b)] *Laboratory for Shock Wave and Detonation Physics Research, Institute of Fluid Physics, CAEP, Mianyang 621900, China*
[c)] *Department of Basic Science, Gansu University of Technology, Lanzhou 730050, China*
[d)] *Institute of Applied Physics and Computational Mathematics, Beijing 100088, China*

(Received 15 March 2001; revised manuscript received 22 July 2001)

A statistical mechanical variational theory and an improved van der Waals one-fluid model have been used to compute the equation of state of fluid He+H_2 mixtures with different H_2:He compositions under high pressure. The first-order quantum correction is included. Comparing the present results with Monte Carlo simulations indicates that the quantum corrections for calculating the thermodynamic properties become increasingly important at lower temperatures.

Keywords: equation of state, fluid He+H_2 mixtures, fluid variational theory, mixing rules
PACC: 6400

I. INTRODUCTION

Hydrogen and helium are the simplest and most abundant elements in the universe. Yet at high pressures, they are the most difficult to understand. From low to moderately high pressures, hydrogen is a molecular solid (or liquid) with a wide bandgap.[1−2] At very high pressures, a metal–insulator transition due to band overlap has been predicted.[3] The pressure at which the metal–insulator transition occurs is still a controversial matter.[4] Solid hydrogen becomes a metal at about 300GPa and liquid hydrogen can become metallic at pressures as low as 140GPa. The cause for such a large difference between the metallization pressures of liquid and solid is not completely understood. Therefore, further high-pressure experimental and theoretical research would be very much desirable in this regard.

The research of mixtures is one of the topics that can count on a great deal of interest from both experimental and theoretical physicists nowadays. Not only the wide abundance of mixtures in our everyday life and in our universe, but also the surprising new phenomena which were detected in the laboratories are responsible for this increased attention. Mixtures, in general, have a much richer phase diagram than their pure constituents and various effects can be observed only in these multi-component systems. The interiors of Jupiter and Saturn are composed of a mixture of hydrogen and helium with a He content of about 10%. Theoretically, the He+H_2 mixtures are challenging systems to study in two respects. Firstly, both H_2 and He have small masses; hence, the quantum effect must be considered in the equation of state (EOS) calculations. Secondly, according to quantum mechanical calculations,[5] the H_2–H_2 repulsion is much softer than the intermolecular repulsion of other species. Physically, the softness occurs because H_2 molecules, despite their large size, do not have inner-shell electrons. Hence the electrons in a hydrogen molecule are loosely bound to the nuclei and can easily change their charge density when a second H_2 molecule approaches. The soft repulsion introduces a complication in describing the thermodynamic properties of mixtures of hydrogen. Namely, one must employ different stiffnesses for intermolecular repulsion of different constituent species in the mixture system. Such a description requires a poten-

*Project supported by the National Natural Science Foundation of China (Grant No. 10032040), and the Science and Technology Foundation of the China Academy of Engineering Physics (Grant No. 97Z011).

tial with at least three parameters, i.e. the range of interaction, the attraction well depth and the stiffness of repulsion. The one-fluid van der Waals model[6] is a widely used mixture theory that uses a simplified potential to represent the intermolecular potential of the mixture; that is, the mixture potentials are replaced by an effective one-component potential. Molecular dynamics (MD) or Monte Carlo (MC) calculations are extremely useful for testing theoretical approximations on a model system. Moreover, the general behaviour or the physical reason for certain characteristic features of phase behaviour can be examined by changing the parameter in the model system.[7,14] In this work, we will employ the van der Waals model and the mixing rules for calculation of the equation of state of fluid He+H_2 mixtures under high pressures.

II. METHOD OF CALCULATION

A. Calculation of the Helmholtz free energy for pure fluids

Thermodynamic properties are calculated by using the Helmholtz free energy A for pure H_2 and He systems[13]

$$A = 1.5Nk_{\mathrm{B}}T + A_{\mathrm{int}} + A_{\mathrm{PE}} + Nk_{\mathrm{B}}T\ \mathrm{in}\rho + \mathrm{const}, \quad (1)$$

where T is temperature, and ρ is the number density. A_{int} is the contribution to A from rotational and vibrational degrees of freedom in H_2

$$A_{\mathrm{int}} = Nk_{\mathrm{B}}T + N\{0.5hv + k_{\mathrm{B}}T\ln[1-\exp(-\beta hv)]\}, \quad (2)$$

where the first term is due to the kinetic energy of rotation and the second term within the bracket represents the contribution of the bond vibration of the H_2 molecule with a frequency hv/k_{B}=6340 K. A_{int} is zero for He. The term A_{PE} in Eq.(1) is the contribution from the intermolecular potential energy $\phi(r)$. It is evaluated by using the Ross fluid variational theory[8]

$$A_{\mathrm{PE}} \le A_{\mathrm{HS}}(\eta) + F(\eta)Nk_{\mathrm{B}}T + 2\pi N\rho\int_{\mathrm{d}}^{\infty} g_{\mathrm{HS}}(r,\eta)\phi(r)r^2\mathrm{d}r + A_{\mathrm{QM}}, \quad (3)$$

where $\eta = \pi \mathrm{d}^3\rho/6$ (d is the hard-sphere diameter), A_{HS} is the hard-sphere excess free energy, and $g_{\mathrm{HS}}(r,\eta)$ is the hard-sphere radial distribution function.[9] The factor $F(\eta)$ is the soft-sphere correction function. A_{QM} is the first-order quantum correction in the Wigner–Kirwood expansion[10]

$$A_{\mathrm{QM}} = \frac{\beta h^2\rho N}{24\pi m}\int g_{\mathrm{HS}}(r,\eta)\nabla^2\phi(r)r^2\mathrm{d}r. \quad (4)$$

The hard-sphere diameter d, which is the only adjustable parameter in Eq.(3), is determined by minimizing the right-hand side of Eq.(3). The pressure P is calculated by numerically taking the appropriate derivative of Eq.(1), i.e.,

$$P = -\frac{\partial A}{\partial V} = \frac{1}{N}\rho^2\frac{\partial A}{\partial \rho}. \quad (5)$$

B. Effective one-component system and mixing rules

The potential used in Eq.(3) to calculate the excess Helmholtz free energy A_{PE} is an exp-6 potential of the form

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

The parameter ε represents the attractive well depth, r^* indicates the range of interaction, while parameter α regulates the stiffness of repulsion. For pure components we use the parameters listed in Table 1. The one-fluid van der Waals model is a well-known theory for mixtures, which represents the intermolecular interaction in the mixture by an effective one-component potential. If the potential is of the form $\varepsilon f(r/r^*)$, the replacement can be carried out by making use of the principle of corresponding states. The new effective potential parameters $(\varepsilon, r^*, \alpha)$ are expressed in term of the exp-6 parameter $(\varepsilon_{ij}, r^*_{ij}, \alpha_{ij})$ of the constituent species of the mixture system by[6]

$$(r^*)^3 = \sum_{i,j} x_i x_j (r^*_{ij})^3, \quad (7)$$

$$\varepsilon = \sum_{i,j} x_i x_j \varepsilon_{ij} (r^*_{ij})^3/(r^*)^3, \quad (8)$$

$$\alpha = \sum_{i,j} x_i x_j \alpha_{ij}\varepsilon_{ij} (r^*_{ij})^3/\varepsilon(r^*)^3. \quad (9)$$

Table 1. Values of the parameters used for the system He+H_2 , taken from Ref.[11].

Interaction	ε/k_B(K)	r^*(nm)	α
H_2–H_2	36.4	0.343	11.1
He–He	10.8	0.2967	13.1
He–H_2	15.5	0.337	12.7

In these equations x_i denotes the mole fraction of component i, and r^*_{ij} and ε_{ij} are the potential parameters of the interaction between a molecule of species i and a molecule of species j. To accommodate the quantum corrections in the effective one-component fluid, an expression for an effective one-component mass is needed. The expression for this effective mass m is[6]

$$\frac{1}{m} = \sum_{i,j} \frac{1}{m_i} x_i x_j \varepsilon_{ij} r^*_{ij} / (\varepsilon r^*). \tag{10}$$

Statistical mechanical calculations are generally simplified if the effective one-component potential is used.

Ⅲ. COMPUTATIONAL RESULTS

It is more convenient for the procedure of the calculation of the fluid–fluid equilibrium to use the Gibbs free energy $G(P,T,x)$ of the mixture system (here x is a mole per cent of He). At fixed T and x the Helmholtz free energy $A(T,V,x)$ is calculated in a sufficiently large volume interval, thus obtaining $A = A(T,V,x)$. The entropy change due to mixing has been accounted for by adding an ideal entropy of the mixing term $-Nk_B \sum x_i \ln x_i$. Using Eq.(5), the transformation from A to G is achieved by means of a thermodynamic definition, $G = A + PV$. At given (P,T) the coexisting phases of a He–H_2 mixture can be determined by finding the pair of compositions x_1 and x_2, at which the curve of Gibbs free energy of mixing

$$\begin{aligned} &G^m(P,T,x) \\ =&G(P,T,x) - xG(P,T,1) - (1-x)G(P,T,0), \end{aligned} \tag{11}$$

has a common tangent. By varying the pressure, a P–x plot can be constructed, representing the fluid–fluid equilibrium of the mixture at temperature T.

To test our computational procedure, we compare our numerical values for the fluid–fluid isotherms of He–H_2 at 300K with the experimental data of van den Bergh[12] in Fig.1. Good agreement can be found between theoretical calculation and experiment. To test our theoretical calculation method, we have calculated the EOS of He+H_2 mixtures with different He:PH_2 compositions in a wide range of temperatures and pressures. The calculated results are listed in Table 2. In comparison with MC simulations,[6] there is a large difference for pressures at lower temperatures. We think that quantum effects are stronger at low temperature, but quantum effects are not considered in Monto Carlo simulations. We are now studying the systems at lower temperatures and higher pressures, at which quantum effects become significant. The quantum effects are very weak at high temperatures, thus our computational results are very close to the Monto Carlo simulation at temperatures above 300K. It can be shown that our calculated pressures are slightly higher than those of the Monto Carlo simulation as the H_2 composition is larger than that of He in the system from Table 2. Because of the lack of experimental data at higher pressures, the reliability of the present results will be tested in future experiments.

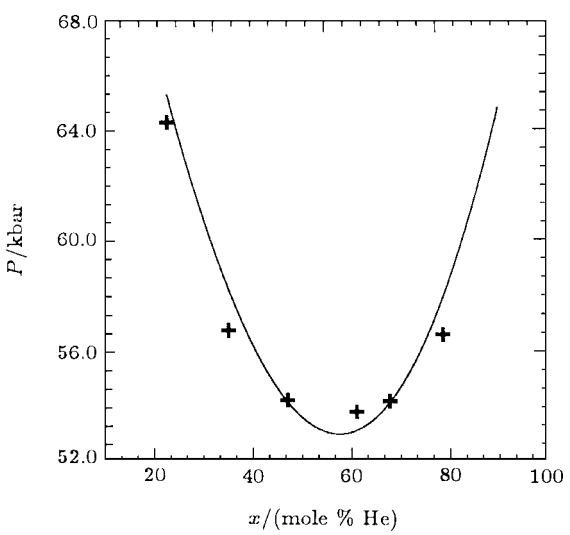


Fig.1. The fluid–fluid isotherms of He–H_2 at 300K: — this work (calc.); + van den Bergh *et al.* [12] (exp.).

Table 2. Pressures P of He+H_2 mixtures with different H_2:He compositions.

T (K)	V (cm^3/mol)	H_2:He	P (GPa)	P^*_{qm} (MPa)	$P(M-C)$[6] (GPa)
50	20	1:1	0.1192	48	0.0480
50	20	1:3	0.0648	19	
50	20	3:1	0.1895	93	
100	14	1:1	0.6221	95	0.337
100	14	1:3	0.3598	34	
100	14	3:1	0.9388	193	
300	10	1:1	2.459	107	1.858
300	10	1:3	1.558	54	1.417
300	10	3:1	3.428	166	2.315
1000	9	1:1	4.459		4.416
1000	9	1:3	3.127		3.643
1000	9	3:1	5.708		5.172
4000	8	1:1	10.875		12.15
4000	8	1:3	7.987		
4000	8	3:1	13.269		
4000	7	1:1	14.713		15.96
4000	7	1:3	10.895		
4000	7	3:1	17.812		
7000	4.5	1:1	50.139		52.53
7000	4.5	1:3	39.215		47.70
7000	4.5	3:1	57.447		54.54

* P_{qm} refers to the quantum mechanical contributions.

IV. CONCLUSIONS

In our calculations, the model of fluid perturbation variational theory with quantum corrections is also adopted. Compared with the works of van den Bergh *et al.*[12] and of Ree,[6] the following conclusions can be drawn: (a) at T=300K, the computational P–x relation (here x is the mole fraction of He) is in agreement with experiments given by van den Bergh *et al.*; (b) in the region of $T \geq$ 1000K, the computational P–V relation is in agreement with MC calculations given by Ree, but it fails at and below 300K. The cause of the disagreement in the low-temperature region between the above-mentioned two calculations may be ascribed to the quantum effects that are not considered in the MC computation. Nevertheless, the agreement among our calculations, the experiments at T=300K by van den Bergh *et al.*, and the MC calculations in the range of $T \geq$1000K by Ree demonstrate that the model and the potential parameters adopted in this work are still of practical significance, though attention should be given to the appropriate thermodynamic states in use.

References

[1] Erskine W J and Weir S T 1992 *Phys. Rev. Lett.* **68** 2937

[2] Chacham H and Louie S G 1991 *Phys. Rev. Lett.* **66** 64

[3] Weir S T, Mitchell A C and Nellis W J 1996 *Phys. Rev. Lett.* **76** 1860

[4] Collins G W, DaSilva L B, Celliers P, Gold D M, Foord M E *et al* 1998 *Science* **281** 1178

[5] Burton P G and senff U E 1982 *J. Chem. Phys.* **76** 6073
[6] Ree F H 1983 *J. Chem. Phys.* **78** 409
[7] Wang L, Li H, Bian X F, Sun M H *et al* 2000 *Acta Phys. Sin.* **49** 45 (in Chinese)
[8] Ross M 1979 *J. Chem. Phys.* **71** 1567
[9] Smith W R and Henderson D 1970 *Mol. Phys.* **19** 411
[10] Rosenfeld Y 1980 *J. Chem. Phys.* **73** 5760
[11] Kuijper A D, Smit B, Schouten J A *et al* 1990 *Europhys. Lett.* **13** 679
[12] Van den Bergh L C, Schouten J A and Trappeniers N J 1987 *Physica* **141A** 524
[13] Chen Q F, Cai L C and Jing F Q *et al* 1999 *Acta Phys. Sin.* **48** 485 (in Chinese)
[14] Wang F H, Yang C L, Li X J and Jing F Q 2000 *Acta Phys. Sin.* **49** 114 (in Chinese)