

Prediction of liquid–liquid phase equilibria of He+H₂ mixtures by NpT molecular dynamics simulations

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Thermodynamic quantities of the classical He+H₂ mixtures were simulated in the isothermal–isobaric ensemble at $T=300$ K, $P=54$ kbar, and several concentrations. The chemical potentials were extrapolated in three directions (T, P, x) with their derivatives calculated by the energy difference method in combination with a modified Kirkwood–Buff fluctuation theory. The phase equilibria at different pressures and temperatures were successfully determined. © 1996 American Institute of Physics. [S0021-9606(96)50828-7]

I. INTRODUCTION

Recently a new method for calculation of the chemical potential difference of a mixture at high density has been developed¹ and successfully extended to quantum mixtures.² The method is based on distribution functions of fictively inflating and shrinking real particles in the system. To determine excess Gibbs free energies and phase equilibria of mixtures, a number of simulations at the same temperature and pressure or volume but different concentrations are needed to fit the coefficients of an equation assumed for the mixtures.³ To reduce the number of simulations for the fitting, a new procedure has been proposed to calculate the composition dependence of the chemical potentials,⁴ which utilizes the assumption that there exists a linearity among the integrals of the direct correlation functions of the mixture,⁵ e.g., water + methanol, water + ethanol, etc. That is, if the closure parameters of those integrals can be found, the composition dependencies of the chemical potentials can then be determined at any concentration in a single simulation with the help of the partial molar volumes and the isothermal compressibility of the mixture. The partial molar volumes and enthalpies of a mixture can be accurately obtained by the energy difference method⁶ and the isothermal compressibility can be calculated by the fluctuation of the volume of the system.⁷ As a result, the simulated data at one point can be extrapolated in three different dimensions with the composition, pressure, and temperature dependencies. The unique advantages of such an approach are apparent over other methods of calculation of chemical potentials. In this paper we have applied this approach to He+H₂ mixtures.

The classical mixtures of He+H₂ were chosen as a test of such an approach, since there are many experimental, theoretical, and simulation works done on these mixtures.

Furthermore, these mixtures exhibit liquid–liquid phase separation at high pressures. In calculation of phase equilibria by molecular simulation there are right now two popular methods of practical interest, i.e. the Gibbs ensemble method⁸ and the NPT+test particle method.⁹ For liquid–liquid phase equilibria it seems that only the Gibbs ensemble method works.^{10,11} But it is known that the insertion of particles from one box into the other in the Gibbs method becomes more difficult with an increase of the density. Finally, the choice of He+H₂ mixtures is consistent with our effort to study quantum mixtures. He and H₂ have small masses and quantum effects become significant at lower temperatures. We have generalized the “ $f_A - f_B$ ” method for the isotopic quantum mixtures of ³He+⁴He by path integral Monte Carlo simulations,² where paths of ³He and ⁴He were fictively switched according to the difference in the masses. For the mixtures of He+H₂ there are not only the difference in masses but also differences in potential parameters. It is very interesting to see how well the method will work for these dense mixtures.

In this paper we report some classical simulation results for the He+H₂ mixtures at $T=300$ K, $P=54$ kbar, and $x_A=0.1, 0.15, 0.3, 0.7, 0.85,$ and 0.9 with the α -exp-6 potentials.¹² The simulation results were also extrapolated to $P=52, 56, 58, 60$ kbar, and $P=42, 44,$ and 46 kbar at $T=250$ K. The corresponding phase equilibria were obtained by determination of the double tangent on the curve of Gibbs free energy of mixing.

II. THEORY

The chemical potential difference of a mixture at any $T, P,$ and x can be calculated by its Taylor’s expansion at a reference state

$$\begin{aligned} \Delta\mu_{BA}(T, P, x) = & \Delta\mu_{BA}(T_0, P_0, x_0) + \frac{\partial\Delta\mu_{BA}}{\partial T} (T - T_0) + \frac{\partial\Delta\mu_{BA}}{\partial P} (P - P_0) + \frac{\partial\Delta\mu_{BA}}{\partial x} (x - x_0) \\ & + \frac{1}{2} \frac{\partial^2\Delta\mu_{BA}}{\partial T^2} (T - T_0)^2 + \frac{1}{2} \frac{\partial^2\Delta\mu_{BA}}{\partial P^2} (P - P_0)^2 + \frac{1}{2} \frac{\partial^2\Delta\mu_{BA}}{\partial x^2} (x - x_0)^2 + \frac{\partial^2\Delta\mu_{BA}}{\partial T \partial P} (T - T_0)(P - P_0) \\ & + \frac{\partial^2\Delta\mu_{BA}}{\partial T \partial x} (T - T_0)(x - x_0) + \frac{\partial^2\Delta\mu_{BA}}{\partial P \partial x} (P - P_0)(x - x_0) + \dots \end{aligned} \quad (1)$$

If we neglect the second orders of the temperature and composition dependencies and any higher order term for simplicity, Eq. (1) can be written as

$$\begin{aligned} \Delta\mu_{BA}(T,P,x) = & \Delta\mu_{BA}(T_0,P_0,x_0) + \frac{\Delta\mu_{BA} - \Delta h_{BA}}{T_0} (T - T_0) + \Delta\nu_{BA}(P - P_0) + \frac{\partial\Delta\mu_{BA}}{\partial x} (x - x_0) \\ & - \frac{1}{2} \left[\Delta\nu_{BA}\beta_T - v \frac{\partial\beta_T}{\partial x} \right] (P - P_0)^2 + \left[a\Delta\nu_{BA} - v \frac{\partial a}{\partial x} \right] (T - T_0)(P - P_0) \\ & + \frac{\partial(\Delta\mu_{BA} - \Delta h_{BA})/T_0}{\partial x} \cdot (T - T_0)(x - x_0) + \frac{\partial\Delta\nu_{BA}}{\partial x} (P - P_0)(x - x_0) + \dots, \end{aligned} \quad (2a)$$

where $\Delta\mu_{BA}$ is the residual chemical potential difference between species B and species A of a binary mixture. Δh_{BA} and $\Delta\nu_{BA}$ are the partial molar enthalpy difference and the partial molar volume difference, respectively, β_T is the isothermal compressibility of the system, v is the total volume divided by the total number of mols, and a is the isothermal expansion coefficient. In Eq. (2a) the following thermodynamic relations are used:

$$\frac{\partial\Delta\mu}{\partial T} = \frac{\Delta\mu - \Delta h}{T}; \quad \frac{\partial\Delta\mu}{\partial P} = \Delta\nu;$$

$$\frac{\partial^2\Delta\mu}{\partial P^2} = - \left[\Delta\nu\beta_T - v \frac{\partial\beta_T}{\partial x} \right]; \quad \frac{\partial^2\Delta\mu}{\partial T \partial P} = \left[a\Delta\nu - v \frac{\partial a}{\partial x} \right]; \quad (2b)$$

$$\frac{\partial^2\Delta\mu}{\partial T \partial x} = \frac{\partial((\Delta\mu - \Delta h)/T)}{\partial x}; \quad \frac{\partial^2\Delta\mu}{\partial P \partial x} = \frac{\partial\Delta\nu}{\partial x}.$$

The composition derivatives of β_T and a are very small in the present work. There are three ways to calculate chemical potential differences, i.e., by fictive transformation of an A particle into a B particle or vice versa by the energy difference method,⁶ or by the “ $f_A - f_B$ ” method combining these two fictive transformations.¹ The formulas for the three ways are as follows:

$$\Delta\mu_{BA} = -\beta^{-1} \ln \langle \exp(-\beta\Delta U_{BA}) \rangle_{N_A, N_B} \quad (3)$$

$$= \beta^{-1} \ln \langle \exp(-\beta\Delta U_{AB}) \rangle_{N_A, N_B} \quad (4)$$

and

$$\Delta\mu_{BA} = \beta^{-1} \left[\ln \frac{f_A(-\Delta U_{AB})}{f_B(\Delta U_{BA})} + \beta\Delta U_{BA} \right], \quad (5)$$

where ΔU_{BA} denotes the change in potential energy that results from the fictive transformation of an A particle into a B particle, likewise ΔU_{AB} for a B particle. $\beta = 1/kT$. The brackets mean the isothermal–isobaric ensemble average. The differences in partial molar enthalpies and volumes can also be obtained at the same time⁶

$$\begin{aligned} \Delta h_{BA} = & \frac{\langle [\Delta U_{BA} + U + PV] \exp(-\beta\Delta U_{BA}) \rangle_{N_A, N_B}}{\langle \exp(-\beta\Delta U_{BA}) \rangle_{N_A, N_B}} \\ & - \langle U + PV \rangle_{N_A, N_B} \end{aligned} \quad (6)$$

$$\begin{aligned} = & - \frac{\langle [\Delta U_{AB} + U + PV] \exp(-\beta\Delta U_{AB}) \rangle_{N_A, N_B}}{\langle \exp(-\beta\Delta U_{AB}) \rangle_{N_A, N_B}} \\ & + \langle U + PV \rangle_{N_A, N_B}, \end{aligned} \quad (7)$$

$$\Delta\nu_{BA} = \frac{\langle V \exp(-\beta\Delta U_{BA}) \rangle_{N_A, N_B}}{\langle \exp(-\beta\Delta U_{BA}) \rangle_{N_A, N_B}} - \langle V \rangle_{N_A, N_B} \quad (8)$$

$$= \frac{\langle V \exp(-\beta\Delta U_{AB}) \rangle_{N_A, N_B}}{\langle \exp(-\beta\Delta U_{AB}) \rangle_{N_A, N_B}} - \langle V \rangle_{N_A, N_B}. \quad (9)$$

The isothermal compressibility and isothermal expansion coefficient in an NPT ensemble can be expressed as

$$\beta_T = \frac{1}{kT} \left\{ \frac{\langle V^2 \rangle - \langle V \rangle^2}{\langle V \rangle} \right\}, \quad (10)$$

$$a = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = - \frac{1}{TV} \left(\frac{\partial U}{\partial P} \right)_T + \frac{P\beta_T}{T}, \quad (11)$$

and

$$\left(\frac{\partial U}{\partial P} \right)_T = - \frac{1}{NkT} \{ \langle V \cdot U \rangle - \langle V \rangle \langle U \rangle \}. \quad (12)$$

Until here, the temperature and pressure derivatives of the chemical potential difference can be determined without many problems. To determine the composition derivative is more cumbersome. The Kirkwood–Buff theory is a useful tool to meet this end, since the Kirkwood–Buff fluctuation theory provides simple relations between thermodynamic quantities and integrals over the system’s pair distribution functions.¹³ The composition derivative of the chemical potential difference can be calculated by the KB integrals

$$\frac{\partial\Delta\mu_{BA}}{\partial x_A} = \frac{1}{kT} \frac{\rho\Delta}{1 + x_A x_B \rho \Delta}, \quad (13)$$

where ρ is the density and $\Delta = G_{AA} + G_{BB} - 2G_{AB}$. But unfortunately, the KB integrals can not be easily obtained because of the long-range and oscillatory nature of the distri-

bution functions. Hamad *et al.*⁵ found that in many organic mixtures such as water+alkanol, CCl₄+alkanol, etc., there are simple relations among the integrals of the direct correlation functions.¹⁴ If a weighted arithmetic mean closure $C_{AB} = \alpha_{BA}C_{AA} + \alpha_{AB}C_{BB}$ is assumed, C_{AA} and C_{BB} can be determined by the equations

$$(x_A + x_B \alpha_{BA}) \rho C_{AA} + x_B \alpha_{AB} \rho C_{BB} = 1 - \frac{\nu_A}{kT\beta_T}, \quad (14)$$

$$x_A \alpha_{BA} \rho C_{AA} + (x_A \alpha_{AB} + x_B) \rho C_{BB} = 1 - \frac{\nu_B}{kT\beta_T},$$

where $\nu_A = V/N - x_B \Delta \nu_{BA}$ and $\nu_B = \Delta \nu_{BA} + \nu_A$. The KB integrals can then be calculated by

$$\rho G_{ii} = \frac{\rho C_{ii} - (1 - x_i) \rho^2 (C_{AA} C_{BB} - C_{BB}^2)}{1 - x_A \rho C_{AA} - x_B \rho C_{BB} + x_A x_B \rho^2 (C_{AA} C_{BB} - C_{AB}^2)}, \quad (15)$$

$$\rho G_{ij} = \frac{\rho C_{AB}}{1 - x_A \rho C_{AA} - x_B \rho C_{BB} + x_A x_B \rho^2 (C_{AA} C_{BB} - C_{AB}^2)}, \quad (16)$$

where $i, j = A, B$. The crucial point here is to determine the closure parameters α_{AB} and α_{BA} . The inversion procedure of the Kirkwood-Buff theory¹⁵ may be utilized for this purpose

$$\Delta = G_{AA} + G_{BB} - 2G_{AB} = \frac{\partial(\beta \Delta \mu_{BA}) / \partial x_A}{\rho(1 - x_A x_B (\partial \beta \Delta \mu_{BA} / \partial x_A))}, \quad (17)$$

$$\Delta_A = G_{AA} - G_{AB} = \Delta \nu_{BA} + (x_B + \rho x_A x_B \Delta \nu_{BA}) \Delta, \quad (18)$$

$$\Delta_B = G_{BB} - G_{AB} = \Delta - \Delta_A, \quad (19)$$

$$G_{AB} = kT \cdot \beta_T - \frac{1 + x_A \rho \Delta_A + x_B \rho \Delta_B + x_A x_B \rho^2 \Delta_A \Delta_B}{\rho + x_A x_B \rho^2 \Delta}. \quad (20)$$

The integrals of the direct correlation functions can then be determined by the KB integrals⁵

$$\rho C_{ii} = \frac{\rho G_{ii} + (1 - x_i) \rho^2 (G_{AA} G_{BB} - G_{BB}^2)}{1 + x_A \rho G_{AA} + x_B \rho G_{BB} + x_A x_B \rho^2 (G_{AA} G_{BB} - G_{AB}^2)}, \quad (21)$$

$$\rho C_{AB} = \frac{\rho G_{AB}}{1 + x_A \rho G_{AA} + x_B \rho G_{BB} + x_A x_B \rho^2 (G_{AA} G_{BB} - G_{AB}^2)}. \quad (22)$$

Using the inversion procedure to determine the closure parameters, we may simulate the mixture at several different concentrations to build up the composition dependencies of the chemical potential difference by numerical differentiation and calculate the integrals from Eqs. (17)–(22). Once the closure parameters are known, all derivatives of $\Delta \mu$ can be obtained at any concentration with a single simulation. If the extrapolations from Eq. (2) are just within a small region around the simulated point, the uncertainties of such an approach will be small. For the He+H₂ mixtures at $T=300$ K and $P=54$ kbar studied in this work, we may first simulate four points at $x=0.1, 0.15, 0.85,$ and 0.9 to build up the composition derivatives of the chemical potential difference

TABLE I. Intermolecular (α -exp-6) potential parameters for the He-H₂ system (Ref. 12). $\phi(r) = [\epsilon/(\alpha-6)]\{6 \exp[\alpha(1-r/r^*)] - \alpha(r^*/r)^6\}$.

	ϵ/k (K)	r^* (Å)	α
He-He	10.8	2.9673	13.1
H ₂ -H ₂	36.4	3.43	11.1
He-H ₂	17.3	3.28	12.49

at $x=0.125$ and 0.875 , respectively. The integrals of the distribution functions G_{ij} and C_{ij} at these two concentrations can be calculated using Eqs. (17)–(22). Thus, the closure parameters can be determined by solving two equations with two unknown parameters. Knowing the closure parameters, the composition derivatives of the chemical potential difference at those simulated concentrations can then be evaluated by Eqs. (14)–(16). Now we have the temperature, pressure, and composition derivatives of the chemical potential difference at these concentrations. In order to ensure the fitting procedure, we may simulate additional points in the middle range of the concentration. The simulation data at each point may be extrapolated in three directions using Eq. (2) and the corresponding excess Gibbs free energy can be determined by fitting those data.³ In the next section we demonstrate such an application described above.

III. SIMULATION RESULTS AND CALCULATION OF LIQUID-LIQUID PHASE EQUILIBRIA

Molecular dynamics simulations were carried out for the He+H₂ mixtures at $T=300$ K, $P=54$ kbar, and six different concentrations in the NPT ensemble. The potential parameters are shown in Table I. The temperature was kept constant by momentum scaling and the pressure was controlled using Andersen's method,¹⁶ with the value of the volume inertial parameter $M=5 \times 10^{-3}$. A number of 500 particles was used with a cut-off radius of about half of the box without the long-range correction. The start configurations were from previous simulations. The equilibration time was 5000 steps and production runs were about 30,000–40,000 steps. The time step was $\Delta t^*=0.002$. After every ten steps particles were fictively switched by turns. The simulation data are presented in Table II. There are several interesting points to be noticed about the data in Table II. First, the values of $\Delta \mu_{BA}$ calculated by transformation of He particles into H₂ particles are away from that calculated by other methods on the rich side of He, where the densities are higher. The reason for this is that inflating the smaller particles (He) into the larger particles (H₂) yielded too much repulsive contributions in the average at those high densities. It means that successful inflation of particles became rare there. This may also explain why the binodal curve of these mixtures calculated by the Gibbs ensemble method¹¹ is shifted systematically to the side of H₂ in comparison with the experimental data. In the Gibbs ensemble method phase separation is reached automatically by keeping equality of the temperature, pressure, and the chemical potentials of each species in the two simu-

TABLE II. Simulation data of the He+H₂ mixtures at $T=300$ K and $P=54$ kbar. The values below are reduced by the parameters of He in Table I. A is He.

x_A	ρ	U	$\beta\Delta\mu_{BA}$ (3)	$\beta\Delta\mu_{BA}$ (4)	$\beta\Delta\mu_{BA}$ (5)	Δh_{BA} (6)	Δh_{BA} (7)	Δv_{BA} (8)	Δv_{BA} (9)	β_T	$(\partial U/\partial P)_T/V$
0.1	1.97317 ± 0.00005	102.815 ± 0.020	5.370 ± 0.010	5.772 ± 0.050	5.373	153.86 ± 3	165.97 ± 5	0.1536 ± 0.005	0.7429 ± 0.08	0.00031 ± 0.00001	0.00044 ± 0.00001
0.15	2.00054 ± 0.00005	101.904 ± 0.050	5.562 ± 0.020	5.610 ± 0.020	5.564	150.334 ± 3	119.68 ± 4	0.0995 ± 0.006	0.0564 ± 0.005	0.00026 ± 0.00001	0.00037 ± 0.00001
0.3	2.09512 ± 0.00020	98.517 ± 0.020	6.162 ± 0.020	6.388 ± 0.030	6.207	161.364 ± 6	222.0 ± 8	0.1105 ± 0.004	0.1777 ± 0.020	0.00027 ± 0.00001	0.00036 ± 0.00001
0.7	2.44322 ± 0.00004	87.089 ± 0.020	-0.393 ± 0.4	7.814 ± 0.020	7.827	307.67 ± 30	219.99 ± 2	-0.6770 ± 0.1	0.1620 ± 0.005	0.0003 ± 0.00001	0.00038 ± 0.00001
0.85	2.62655 ± 0.00015	81.790 ± 0.010	0.692 ± 0.090	8.552 ± 0.020	8.594	467.46 ± 60	255.82 ± 5	-0.4634 ± 0.08	0.1675 ± 0.02	0.0003 ± 0.00002	0.00038 ± 0.00001
0.9	2.70029 ± 0.00005	79.715 ± 0.005	1.350 ± 0.040	8.875 ± 0.050	9.011	461.05 ± 2	267.74 ± 3	-1.177 ± 0.02	0.2126 ± 0.02	0.00027 ± 0.00001	0.00034 ± 0.00001

lation boxes through three steps, i.e., random walk of particles, adjustment of the volume, and exchange of the particles. If even the transformation of the difference of the two particles has difficulty where it is still in the two-phase region, the insertion of a whole particle becomes less possible. Consequently, pseudo equilibria may possibly be reached at lower densities. It is known that the difference method of inflating yields more accurate results than that of shrinking. To our surprise the shrinking of H₂ particles to He particles can still yield relatively good results at such high densities in comparison with the data from the “ f_A-f_B ” sampling method (5). Therefore, in our calculation of the derivatives the partial molar quantities from Eq. (3) for $x_A \leq 0.3$ and from Eq. (4) for $x_A \geq 0.7$, and the chemical potential differences from Eq. (5), were used. We applied the data at $x_A=0.1, 0.15, 0.85$, and 0.9 to build up the numerical composition dependencies of $\Delta\mu$ at $x_A=0.125$ and $x_A=0.875$ for the determination of the closure parameters. To determine the coefficients of the Redlich-Kister equation assumed for the excess Gibbs free energies, several points of $\Delta\mu$ were extrapolated within ($x_0-0.05, x_0+0.05$). Thus, there were about 25 data used for fitting the coefficients. The results are presented in Table III. The Gibbs free energies of mixing of these mixtures are shown in Figs. 1 and 2, from which the phase separations were determined by drawing the double

TABLE III. The coefficients of the Redlich-Kister equation for the excess Gibbs free energy of the He+H₂ mixtures $g^E/RT = x_A x_B [A + B(x_A - x_B) + C(x_A - x_B)^2]$.

P (kbar)	A	B	C
$T=300$ K			
52	2.10893	0.17457	0.27583
54	2.16102	0.23532	0.21883
56	2.20948	0.29021	0.15773
58	2.26309	0.36003	0.09616
60	2.31237	0.40956	0.05098
$T=250$ K			
42	2.32821	-0.03079	0.49722
44	2.38128	0.04248	0.45207
46	2.43965	0.10881	0.40833

tangents. The estimated immiscibility curves together with some literature data are shown in Figs. 3 and 4.

It is amazing that just using six simulation runs the whole immiscibility curve at $T=300$ K can be well predicted and the curve at $T=250$ K can be predicted qualitatively, since the linear temperature dependence of $\Delta\mu$ was assumed. The experimental data of the critical point of these mixtures at 300 K are $x_{A,c}=0.58$ and $P_c=54$ kbar.¹⁷ Although the simulations were done at the critical pressure but at concentrations away from the critical concentration, all quantities seem to be well-behaved. From the point of view of fitting the coefficients of the RK equation, the data in the central region are less important than the data on the sides because of the $x_A x_B$ term in the equation. Therefore, if thermodynamic quantities which cross the critical region are smooth functions, the approach demonstrated here may provide a convenient way to study near critical fluids.

IV. CONCLUSIONS

We have performed a series of simulations on the He+H₂ mixtures at $T=300$ K and $P=54$ kbar. In application

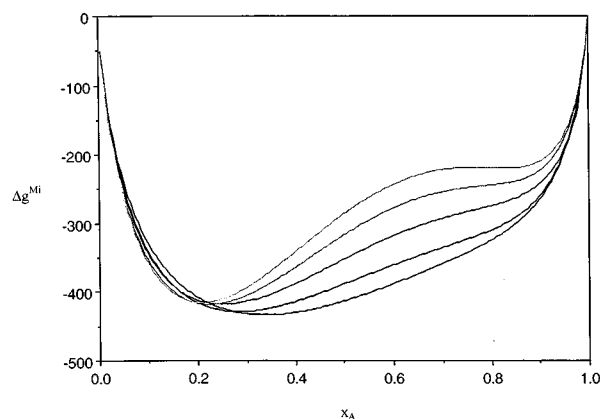


FIG. 1. The Gibbs free energies of mixing of the He+H₂ mixtures at $T=300$ K and $P=52, 54, 56, 58$, and 60 kbar, from bottom to top, respectively. The curve at $P=52, 56, 58$, and 60 kbar are extrapolated from the simulation data at $P=54$ kbar.

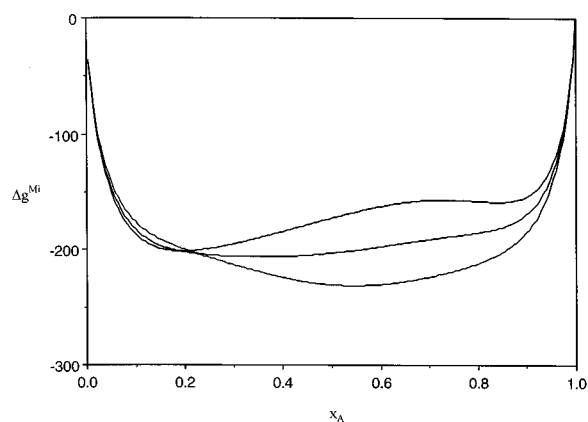


FIG. 2. The Gibbs free energies of mixing of the He+H₂ mixtures at $T=250$ K and $P=42, 44,$ and 46 kbar, from bottom to top, respectively. The curves are extrapolated from the simulation data at $T=300$ K and $P=54$ kbar.

of the modified Kirkwood-Buff theory and the partial molar quantities calculated by the difference method, chemical potential differences were extrapolated in three directions of (T, P, x) space and the excess Gibbs free energies at different temperature and pressures were determined. With a small number of simulations, immiscibility curves were relatively well predicted. The strength of the procedure is the capability of extrapolation and no need to know previously about the mixture. We are in the process of studying the system at lower temperatures and higher pressures, at which quantum effects become significant.

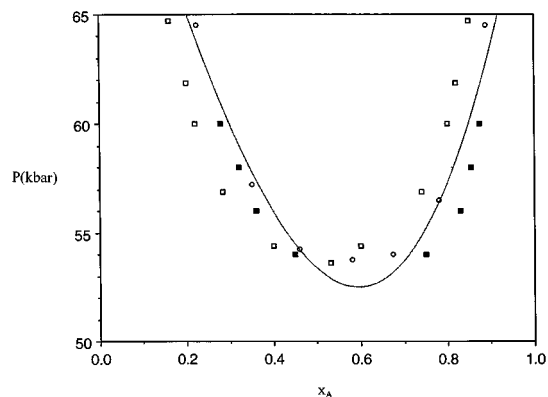


FIG. 3. The estimated immiscibility curve at $T=300$ K from Fig. 1 in comparison with literature data. The solid squares are from this work, the circles the experimental data (Ref. 17), the curve the theoretical calculations (Ref. 12), and the unfilled squares from the Gibbs method (Ref. 11).

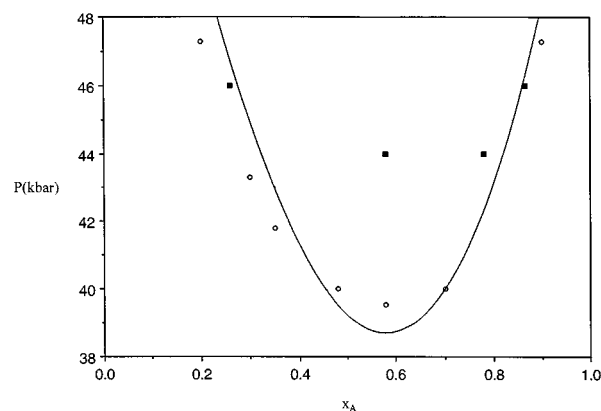


FIG. 4. The estimated immiscibility curve at $T=250$ K from Fig. 2 in comparison with literature data. The solid squares are determined by extrapolations of the simulation data at $T=300$ K and $P=54$ kbar in this work, the circles the experimental data (Ref. 17), and the curve the theoretical calculations. (Ref. 12).

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