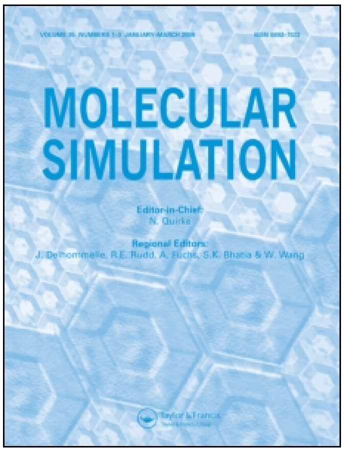

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EXCESS THERMODYNAMIC PROPERTIES OF $CO_2 + C_2H_6$ MIXTURES FROM MD SIMULATIONS

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This paper reports excess Gibbs free energy, excess enthalpy, and excess volume from isothermal-isobaric molecular dynamics simulations of carbon dioxide + ethane mixtures at $T = 230$ K, 260 K, $P = 15.5$ MPa, and $x = 0.1$, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9. The overall agreement of our calculations with experiments is excellent. The excess Gibbs free energies were calculated by two different methods. They showed that the energy difference method for swapping particles of CO_2 into particles of C_2H_6 yields more reliable values.

KEY WORDS: Excess properties, carbon dioxide, ethane, mixtures.

1 INTRODUCTION

Carbon dioxide and ethane are two of the most important components in many industries, *e.g.*, liquefaction of natural gas or extraction of oil, etc. Since it is of fundamental industrial interest to understand their thermodynamic properties, many experimental and theoretical works have been done for pure fluids and mixtures of these two components. With the rapid development of computer technology, computer simulations have become more and more important and widely used in the study of fluids. Because of the relatively simple shapes of CO_2 and C_2H_6, accurate intermolecular potentials and the combining rules for both molecules and their mixtures can be well-established [1–5]. Since carbon dioxide has a strong quadrupole moment whereas ethane has only a relatively weak one, carbon dioxide can be modeled by an effective pair potential of two-center Lennard-Jones plus point quadrupole moment and ethane by the same type of model without quadrupole moment. In comparison with data of excess enthalpy and excess molar volumes, less data of excess Gibbs free energy are reported for these mixtures from simulations. In this paper we report some simulation results of excess Gibbs free energy besides excess enthalpy and excess molar volume at two different temperatures, at which simulations were already done for excess enthalpy and excess volume [5]. The aims are to complete the set of data and test different methods for calculation of excess Gibbs free energy. Fincham *et al.* [3] successfully calculated the chemical potentials of these mixtures using the Widom test particle method [6] and the '*f-g*' method [7,8] at $T = 269.25$ K. Therefore, we also use two methods for computing chemical potentials in this paper: Widom's test particle [6] and the energy difference method [9–11], in which test particles are randomly inserted to obtain absolute values of the residual chemical potentials or real particles are fictively swapped into particles of another component to obtain the chemical potential differences of the mixtures. In general, the energy difference method is more accurate and consumes much less computer time than other methods. From our results it can be seen that the difference method yields better results than Widom's method, and swapping particles of CO_2 into C_2H_6 produces more reliable values. In comparison with experimental data the effective potential functions and combining rules used for the mixtures are accurate and produce results within experimental uncertainties.

2 COMPUTATIONAL METHOD

We can directly evaluate excess properties of v^E and h^E from the definitions

$$v^E = v_{\mathrm{mix}} - x_A v_A^0 - x_B v_B^0 \tag{1}$$

$$h^E = U_{\mathrm{mix}}^c - x_A U_A^0 - x_B U_B^0 + P v^E \tag{2}$$

where $^\circ$ indicates the pure component and the superscript c the configurational internal energy. The mixture and each pure component are at the same temperature and pressure. To obtain excess property g^E, we apply the Widom test particle [6] and the difference method [9–11]. According to Widom's test particle method, the residual chemical potentials of a mixture in the NpT ensemble can be obtained

$$\mu_i^{\mathrm{res}}/kT = -\ln\langle V \exp(-\beta\psi_i)\rangle / N_i \tag{3}$$

where ψ_i denotes the potential energy of the test particle of species i, N_i the number of particles of species i, V the instantaneous volume, and the brackets ensemble averaging in the isobaric-isothermal ensemble. $\beta = 1/kT$. This method is easily implemented and yields reliable results for up to medium density fluids, but failed in dense systems because of the difficulty of insertion of test particles [12]. Instead of sampling the potential energy changes resulting from particle insertion, the energy difference method samples the potential energy changes associated with the virtual transformation of a real particle of one species into another species. For a two-component mixture of species A and B, this method directly provides values of the differences between the two residual chemical potentials of A and B. For swapping A into B, we have the following equation

$$\Delta\mu_{BA}^{\mathrm{res}}/kT = -\ln\langle \exp(-\beta\Delta U_{BA})\rangle_{N_A, N_B - 1} \tag{4}$$

Analogously for swapping B into A, we have

$$\Delta\mu_{AB}^{\mathrm{res}}/kT = -\ln\langle \exp(-\beta\Delta U_{AB})\rangle_{N_A - 1, N_B} \tag{5}$$

where the brackets refer to a $(N-1)$ phase space sampling in a NpT-ensemble with N particles. In general, excess Gibbs free energy of a non ideal mixture can well be presented by the Redlich-Kister equation with three parameters

$$g^E/RT = x_A x_B[A + B(x_A - x_B) + C(x_A - x_B)] \tag{6}$$

The residual chemical potential differences are related to the Redlich-Kister equation as follows [13]

$$A(x_A - x_B) + B(1 - 6x_Ax_B) + C(x_B - x_A)(8x_Ax_B - 1) + \beta(\mu_B^0 - \mu_A^0)^{\mathrm{res}} = \beta\Delta\mu_{BA}^{\mathrm{res}} \quad (7)$$

In (7) there are four unknown parameters, A, B, C, and the difference of the pure residual chemical potentials $\beta(\mu^0 B - \mu^0 A)^{\mathrm{res}}$. If we have sufficient data of $\beta\Delta\mu_{BA}^{\mathrm{res}}$, the four unknown parameters can be determined through mean square regression, thus, excess Gibbs free energy at any concentration can be calculated.

3 THE SIMULATION

Molecular dynamics simulations were performed for $CO_2 + C_2H_6$ mixtures in the NpT-ensemble at two different temperatures. For the solution of the translational equations of motion a fifth order Gear predictor-corrector algorithm was used. Periodic boundary conditions and a neighborhood list, which was updated at every 10 time steps, were applied. The temperature was kept constant by momentum scaling. The pressure was controlled by using the Andersen's method [14], with the value of the volume inertial parameter $M = 10^{-4}$. A number of 256 particles were used with a cut-off radius $r_{cr} = 2.5\sigma_{AA} + L_{\max}$ for real particles and $r_{cr} = 4.0\sigma_{AA} + L_{\max}$ for test particles, where $L_{\max}$ is the longest elongation of the two components. The starting configuration was the standard fcc lattice sites. At the beginning of the simulation the system was allowed to equilibrate for a period of 3000 time steps. Production runs were 30,000–50,000 time steps. The time step was $\Delta t^* = 0.0015$. All units were reduced with respect to the parameters of component A. At every 10 time steps 500 test particles of each component were randomly inserted and each real particle was fictively switched to the other type of particle by turns at the same time. The simulations reported here were performed on a Cyber 205 at Ruhr-University Bochum, Germany. Table 1 shows the parameters of the intermolecular potentials and the combining rules based on Lorentz-Berthelot rules used in the simulations.

The parameters of the intermolecular potentials of pure CO_2 and C_2H_6 were determined through fitting two vapor pressures and one saturation density by Fischer *et al.* [1], and values of h^E and v^E at $T = 248.1$ K, $P = 3$ MPa, and $x_A = 0.5078$ from [15] were used to fit the adjustable parameters ζ and η by Möller [4]. Table 2 shows the simulation results at $T = 230$ K, 260 K, and $P = 15.5$ MPa. Our simulation data are in excellent agreement with the simulation data from Möller [4], within 0.3% in density and 0.4% in internal energy for equimolar

Table 1 Parameters of intermolecular potential functions and combining rules of the components.

Component	*Model*	L^*	$(\varepsilon/k)/K$	$\sigma/\mathring{A}$	Q^*	ζ	η
CO_2[4]	2CLJQ	0.699	125.317	3.0354	3.0255	0.946	1.005
C_2H_6[1]	2CLJ	0.67	139.81	3.512			

Table 2 *NpT*-MD simulation results for density, internal energy, chemical potentials, and difference in chemical potentials of $CO_2 + C_2H_6$ mixtures at $T = 230$ K, 260 K, and $P = 15.5$ MPa, with parameters in Table 1.

x_A	ρ^*	U^*	μ_A^* (3)	μ_B^* (3)	$\Delta\mu_{BA}^*$ (4)	$\Delta\mu_{AB}^*$ (5)
		$T = 230$ K				
0.0000	0.2837 ± 0.0003	−12.01 ± 0.01		−3.78 ± 0.17		
0.1016	0.2909 ± 0.0005	−11.67 ± 0.03	−2.33 ± 0.05	−3.54 ± 0.10	−0.90 ± 0.06	1.14 ± 0.05
0.1992	0.2995 ± 0.0003	−11.40 ± 0.01	−2.64 ± 0.03	−3.82 ± 0.15	−0.87 ± 0.07	1.03 ± 0.07
0.3008	0.3101 ± 0.0006	−11.29 ± 0.02	−2.78 ± 0.04	−3.85 ± 0.17	−0.56 ± 0.07	1.04 ± 0.08
0.3984	0.3209 ± 0.0011	−11.19 ± 0.05	−2.94 ± 0.05	−3.71 ± 0.12	−0.41 ± 0.09	0.67 ± 0.10
0.5000	0.3328 ± 0.0008	−11.12 ± 0.03	−3.15 ± 0.05	−3.57 ± 0.08	−0.22 ± 0.05	0.63 ± 0.05
0.6016	0.3482 ± 0.0012	−11.21 ± 0.06	−3.38 ± 0.10	−3.07 ± 0.17	0.01 ± 0.11	0.21 ± 0.10
0.6992	0.3665 ± 0.0002	−11.47 ± 0.01	−3.41 ± 0.06	−3.39 ± 0.06	0.28 ± 0.05	0.19 ± 0.05
0.8008	0.3881 ± 0.0009	−11.81 ± 0.02	−3.53 ± 0.15	−3.44 ± 0.29	0.56 ± 0.06	0.07 ± 0.08
0.8984	0.4132 ± 0.0009	−12.34 ± 0.04	−3.47 ± 0.06	−2.76 ± 0.09	0.96 ± 0.04	−0.32 ± 0.05
1.0000	0.4430 ± 0.0004	−12.95 ± 0.01	−3.68 ± 0.08			
		$T = 260$ K				
0.0000	0.2636 ± 0.0002	−10.96 ± 0.02		−2.97 ± 0.05		
0.1016	0.2697 ± 0.0005	−10.61 ± 0.02	−1.83 ± 0.05	−2.94 ± 0.07	−0.91 ± 0.02	1.21 ± 0.02
0.1992	0.2760 ± 00005	−10.31 ± 0.02	−1.98 ± 0.04	−2.95 ± 0.08	−0.72 ± 0.03	1.06 ± 0.02
0.3008	0.2831 ± 0.0015	−10.07 ± 0.04	−2.19 ± 0.03	−2.95 ± 0.07	−0.56 ± 0.02	0.82 ± 0.03
0.3984	0.2931 ± 0.0008	−9.96 ± 0.04	−2.28 ± 0.03	−2.93 ± 0.06	−0.43 ± 0.03	0.67 ± 0.04
0.5000	0.3031 ± 0.0012	−9.88 ± 0.04	−2.46 ± 0.05	−2.94 ± 0.06	−0.28 ± 0.02	0.59 ± 0.03
0.6016	0.3166 ± 0.0008	−9.94 ± 0.03	−2.59 ± 0.04	−2.79 ± 0.02	−0.10 ± 0.02	0.43 ± 0.03
0.6992	0.3317 ± 0.0004	−10.08 ± 0.01	−2.68 ± 0.03	−2.76 ± 0.04	0.08 ± 0.05	0.27 ± 0.05
0.8008	0.3518 ± 0.0005	−10.36 ± 0.02	−2.74 ± 0.10	−2.59 ± 0.03	0.26 ± 0.04	−0.01 ± 0.05
0.8984	0.3724 ± 0.0022	−10.75 ± 0.09	−3.02 ± 0.14	−2.59 ± 0.10	0.51 ± 0.06	−0.35 ± 0.07
1.0000	0.4029 ± 0.0004	−11.39 ± 0.01	−3.12 ± 0.08			

mixtures. Möller compared his data, gathered from a wide range of temperatures, pressures, and densities, with experimental data and concluded that the uncertainties of his h^E and v^E are within experimental errors, which are 2% and 4% for h^E and v^E [15], respectively.

Figure 1 and Figure 2 show the excess properties of h^E and v^E calculated from data in Table 2 in comparison with experimental data [15, 16, 17] and simulation data from Möller [4]. In consideration of the uncertainty of experiment and pressure correction the agreement is very good. The g^E results from fitting the data of chemical potential differences in Table 2 are summarized in Table 3 and are plotted in Figure 3 and Figure 4 for 230 K and 260 K, respectively. From Figure 3 we can see that the results from (3) and (4) are identical and in excellent agreement with the experimental data. As a comparison, $g^E(x = 0.5)$ from (3), (4), (5), and experiment are 579 J/mol, 554 J/mol, 430 J/mol($P = 15.5$ MPa), and 539 J/mol($P = 0$) at $T = 230$ K, respectively. In contrast to Figure 3 the results in Figure 4 show that (3) produced a less satisfactory prediction of g^E, whereas, (4) still gave a very good prediction. It seems that there are some numerical problems in the calculations using the Widom test particle method. Generally speaking, the uncertainty of Widom's method in calculation of g^E is twice as large as in the difference method. It is interesting that swapping a C_2H_6 into a CO_2 never yielded good results. This is a consequence of the fact that a CO_2 particle is "thinner" than a C_2H_6 particle. We know that

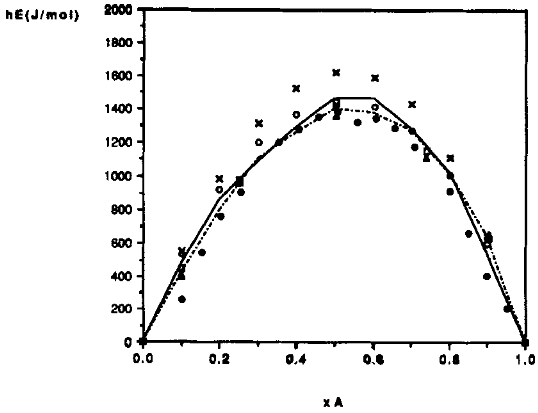

Figure 1 Excess enthalpies versus x_A for mixtures of $CO_2 + C_2H_6$. The solid and dot dashed curves are from this work at $T = 230$ K, 260 K, and $P = 15.5$ MPa, respectively. The squares and triangles are from Möller [4] at the same temperatures and pressures as above. The circles are from Wallis *et al.* [16] at $T = 230$ K and $P = 0$. The crosses are from Guedes *et al.* [17] at $T = 230$ K and $P = 0$. The points are from Wormald *et al.* [15] at $T = 272.1$ K and $P = 11$ MPa.

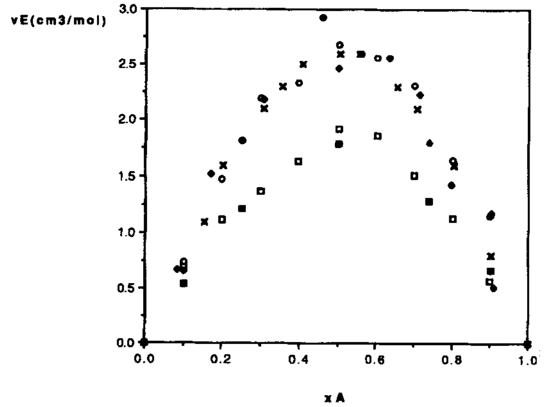

Figure 2 Excess molar volume versus x_A for mixtures of $CO_2 + C_2H_6$. The unfilled squares and circles are from this work at $T = 230$ K, 260 K, and $P = 15.5$ MPa, respectively. The filled squares and diamonds are from Möller [4] at the same temperatures and pressures as above. The unfilled diamonds are from Wallis *et al.* [16] at $T = 241.5$ K and $P = 0$. The crosses are from Wormald *et al.* [15] at $T = 248.1$ K and $P = 10.9$ MPa.

removal of a particle from a system does not sample the configurations correctly [18]. It seems that the quadrupole moment of CO_2 does not have much influence on this behavior. It would be very interesting to apply the difference method to mixtures which have two components, one larger in one dimension but smaller in another dimension than the other, *e.g.* $CO_2(3CLJQ) + C_2H_6$ mixtures. In this case, we could expect that transforming particles from both directions would yield the same results.

Table 3 Parameters of (6) and differences of pure residual chemical potentials determined by curve smoothing for $CO_2 + C_2H_6$ mixtures at $T = 230$ K, 260 K, and $P = 15.5$ MPa.

	$T = 230$ K			$T = 260$ K		
	(3)	*(4)*	*(5)*	*(3)*	*(4)*	*(5)*
A	1.21180	1.15831	0.90040	0.94667	0.86206	0.91494
B	0.05486	0.23690	0.12129	0.11104	0.07557	0.13893
C	−0.31365	0.07993	−0.07477	0.04762	0.09579	0.28051
$\beta(\mu_B^0 - \mu_A^0)^{res}$	−0.38612	−0.10262	−0.50361	−0.39600	−0.23314	−0.50596

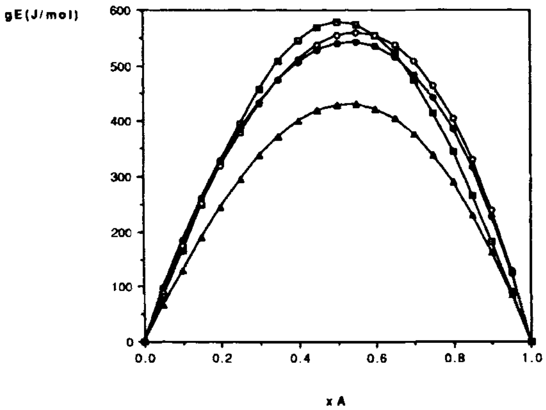

Figure 3 Excess Gibbs free energy versus x_A for mixtures of $CO_2 + C_2H_6$ at $T = 230$ K. The squares, circles, and triangles are from equations (3), (4), and (5) at $P = 15.5$ MPa, respectively. The points are from Wallis *et al.* [16] at $P = 0$.

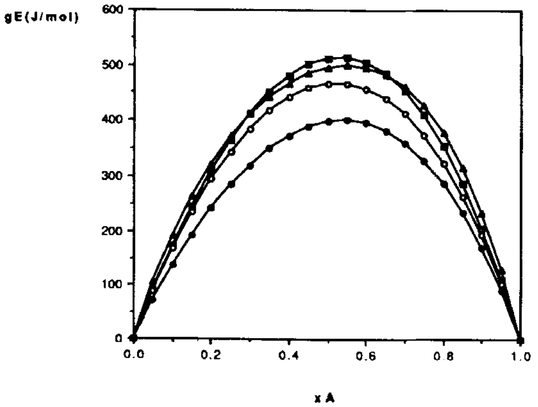

Figure 4 Excess Gibbs free energy versus x_A for mixtures of $CO_2 + C_2H_6$ at $T = 260$ K. The squares, circles, and triangles are from equations (3), (4), and (5) at $P = 15.5$ MPa, respectively. The points are from Wallis *et al.* [16] at $P = 0$.

4 CONCLUSIONS

In this paper we have reported excess thermodynamic properties of g^E, h^E, and v^E for $CO_2 + C_2H_6$ mixtures at two temperatures. The overall agreement of our calculations with experiments is excellent. We used two methods to calculate the excess Gibbs free energies, *i.e.*, the Widom test particle method and the energy difference method. The results showed that swapping a smaller particle into a larger one yields more reliable values. It is obvious that the energy difference method deserves more thorough studies because of its many potential advantages over existing techniques.

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References

[1] J. Fischer, R. Lustig, H. Breitenfelder-Manske and W. Lemming, "Influence of intermolecular potential parameters on orthobaric properties of fluids consisting of spherical and linear molecules," *Mol. Phys.*, **52**, 485–97 (1984).

[2] M. Bohn, R. Lustig and J. Fischer, "Description of polyatomic real substances by two-center Lennard-Johns model fluids," *Fluid Phase Equilibria*, **25**, 251–62 (1986).

[3] D. Fincham, N. Quirke and D. J. Tildesley, "Computer simulation of molecular liquid mixtures I. A diatomic Lennard Jones model mixtures for CO_2/C_2H_6," *J.Chem. Phys.*, **84**, 4535–46 (1986).

[4] D. Möller, dissertation, "Thermodynamik fluider Mischungen: Kalorimetrie und Computersimulationen," Ruhr-Universität Bochum, Germany (Reihe 3, Nr. 260, VDI), 1991.

[5] R. Lustig, A. Toro-Labbé and W. A. Steele, "A molecular dynamics study of the thermodynamics of liquid ethane," *Fluid Phase Equilibria*, **48**, 1–10 (1989).

[6] B. Widom, "Some topics in the theory of fluids," *J. Chem. Phys.*, **39**, 2808–12 (1963).

[7] K. S. Shing and K. E. Gubbins, "The chemical potential from computer simulation: Test particle method with umbrella sampling," *Mol. Phys.*, **43**, 717–21 (1981).

[8] J. G. Powles, W. A. B. Evans and N. Quirke, "Non-destructive molecular dynamics simulation of the chemical potential of a liquid," *Mol. Phys.*, **46**, 1347–70 (1982).

[9] K. S. Shing, "Infinite-dilution activity coefficients from computer simulation," *Chem. Phys. Letts.*, **119**, 149–51 (1986).

[10] P. Sindzingre, G. Ciccotti, C. Massobrio and D. Frenkel, "Partial enthalpies and related quantities in mixtures from computer simulation," *Chem. Phys. Letts.*, **136**, 35–41 (1987).

[11] P. Sindzingre, C. Massobrio, G. Ciccotti and D. Frenkel," Calculation of partial enthalpies of an argon-krypton mixture by NpT molecular dynamics," *Chem. Phys.*, **129**, 213–24 (1989).

[12] K. S. Shing and K. E. Gubbins, "A Review of Methods for Predicting Fluif Phase Equilibria: Theory and Computer Simulation," in Molecular-based Study of Fluid, ACS Advances in Chemistry Series, 1983, Chapter 4.

[13] J. M. Prausnitz, R. N. Lichtenthaler and E. G. de Azevedo," Molecular thermodynamics of fluid phase equilibria," Prentice-Hall, Inc., Englewood Cliffs, New Jerdey, 1986.

[14] H. C. Andersen, "Molecular dynamics simulation at constant pressure and/or temperature," *J. Chem. Phys.*, **72**, 2384–93 (1980).

[15] C. J. Wormald and J. M. Eyears, "Excess molar enthalpies and excess molar volumes of $\{xCO_2 + (1-x)C_2H_6\}$ up to 308.4 K and 11,0 MPa," *J. Chem. Thermodynamics*, **20**, 323–31 (1988).

[16] K. P. Wallis, P. Clancy, J. A. Zollweg and W. B. Streett, "Excess thermodynamic properties for $\{xCO_2 + (1-x)C_2H_6\}$: experiment and theory," *J. Chem. Thermodynamics*, **16**, 811–23 (1984).

[17] H. J. R. Guedes, J. A. Zollweg and W. B. Streett, "Enthalpy of mixing of liquid (carbon dioxide + ethane) at 230.8 K and of liquid (carbon dioxide + *n*-butane) at 221.4 and 241.4 K," *J. Chem. Thermodynamics*, **23**, 239–45 (1991).

[18] B. Guillot and Y. Guissani, "Investigation of the chemical potential by molecular dynamics simulation," *Mol. Phys.*, **54**, 455–65 (1985).