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# Molecular simulations of thermodynamic properties for $N_2$–$CO_2$–$CH_4$ mixtures at saturation conditions

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## Abstract

Enthalpy of vaporization and coexistence densities for nitrogen–carbon dioxide–methane mixtures at low temperature and high pressure saturation conditions were calculated by the Gibbs ensemble Monte Carlo method. Values of the pure component Lennard–Jones (12, 6) pair-potential reported by van Leeuwen et al. [7] were employed to describe the intermolecular interactions. The total number of molecules adopted in all simulations was 300. Comparisons of the simulated data with the results predicted from the Peng–Robinson equation of state, utilizing the three binary interaction parameters reported in the literature, yield a fair agreement. © 1997 Elsevier Science B.V.

*Keywords:* Coexistence densities; Enthalpy of vaporization; Equilibrium compositions; Gibbs ensemble Monte Carlo method; Lennard–Jones potential; Simulation; Ternary system

## 1. Introduction

Further to our previous investigation, molecular simulation of thermodynamic properties has been extended to (nitrogen + carbon dioxide + methane) mixtures. Phase equilibrium behavior of carbon dioxide with the hydrocarbon and the non-hydrocarbon components of natural gas is of interest to future processing of natural gases with high carbon dioxide and non-hydrocarbon contents. Al-Sahhaf et al. [1] also pointed out that emphasis on ethane recovery from natural gas by cryogenic processing and the use of liquified natural gas peak-shaving facilities by public utilities, both require knowledge of phase equilibrium behavior of a carbon dioxide-containing system. Thermodynamic properties for mixtures at saturation conditions, such as the equilibrium-phase compositions, coexistence densities and enthalpy of vaporization, are essential for the process design. However, experimental measurements at saturation conditions, especially coexistence densities and enthalpies of vaporization, are difficult to perform. It is for these reasons that this investigation was made.

It has been shown that the Gibbs ensemble Monte Carlo (GEMC) method [2] is an efficient tool for simulation of not only phase equilibria but also of enthalpies of both binary [3] and ternary [4] systems. In this work, several mixtures of $N_2(1)$–$CO_2$ (2)–$CH_4(3)$, at 220 and 240 K and at pressures from 6.0 to 9.0 MPa were investigated by the GEMC method. Comparisons of the enthalpy of vaporization, coexistence densities and vapor composition values have been made between the simulation results and the

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values calculated by the Peng–Robinson equation of state [5].

## 2. Simulation method

The simulation procedure adopted in this work has been described previously [3,4]. The molecules of nitrogen and carbon dioxide were treated as spherical particles [4]. In this work, the molecules of methane were also treated in the same manner. The structure of dry ice, namely, alpha-face-centred cubic lattice [6] was adopted as the starting configuration in this work. In all simulations, the total number of molecules employed was 300. As before, the simulations were performed in cycles, with each cycle consisting of 500 attempted particle displacements, a single volume change attempt and 500 attempted particle interchanges. For each run, an overall configuration of $1.2 \times 10^6$ was produced in which the first $3 \times 10^5$ states were used for equilibration and the remainder for obtaining the averages of properties.

## 3. Potential function

For close-packed molecules with no or weak polarities, the Lennard–Jones (12,6) potential function

$$u_{ij}(r) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] \tag{1}$$

has been found to be a reasonable approximation for describing their intermolecular interactions. In Eq. (1), $r_{ij}$ is the distance between molecules $i$ and $j$, $\varepsilon_{ij}$ and $\sigma_{ij}$ are the energy and size parameters, respectively. Values of the pair-potential parameters for five pure components (including $N_2$, $CO_2$, and $CH_4$) have been determined by van Leeuwen et al. [7] from an optimization procedure, using the statistical-mechanical virial equation of state of Peters and Lichtenthaler [8]. The experimental data compiled by Angus et al. [9–11] were used in the determination of the values for $N_2$, $CO_2$, and $CH_4$. In their dealings with the phase behavior of several binary systems, the simulation results show that the optimized pure-component parameters are physically meaningful. The parameter values reported by van Leeuwen et al. [7] have been adopted in this work in view of their success and are listed in Table 1. It should be mentioned that identical values for $N_2$ and $CO_2$ were employed in Ref. [4]. The Lorentz–Berthelot combination rules

$$\sigma_{ij} = \frac{(\sigma_{ii} + \sigma_{jj})}{2} \qquad \varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \tag{2}$$

were applied to calculate the cross parameters.

Table 1
Potential parameters for different groups

| Component | $\sigma$, Å | $\varepsilon/k$, K |
|---|---|---|
| $N_2$ | 3.624 | 97.9 |
| $CO_2$ | 4.694 | 243.4 |
| $CH_4$ | 3.725 | 147.8 |

## 4. Thermodynamic properties

With component 1 (nitrogen) as the reference, the following reduced properties

$$T^* = \frac{kT}{\varepsilon_{11}} \quad U^* = \frac{U}{\varepsilon_{11}} \quad \rho^* = \rho\sigma_{11}^3$$
$$P^* = \frac{P\sigma_{11}^3}{\varepsilon_{11}} \quad \varepsilon_{ij}^* = \frac{\varepsilon_{ij}}{\varepsilon_{11}} \quad L^* = \frac{L}{\sigma_{11}} \tag{3}$$

were used in the course of simulation. In Eq. (3), $T$, $P$ and $U$ represent temperature, pressure, and configurational energy, respectively. $\rho$ is the density of the system and $L$ is the side length of the central simulation box. The configurational energy and pressure are expressed by

$$U_c^* = \sum_i \sum_{j>i} \frac{u_{ij}}{\varepsilon_{11}} + U_{\mathrm{LRC}}^* \tag{4}$$

and

$$P^* = \rho^* T^* + \frac{8}{L^{*3}} \sum_i \sum_{j>i} \varepsilon_{ij}^* \left[2\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + P_{\mathrm{LRC}}^*. \tag{5}$$

As in Ref. [4], the usual spherical cut-off was made to save computation time, and long-range corrections (LRC) to thermodynamic properties in the course of simulation were calculated by

$$U^*_{\mathrm{LRC}} = \frac{8\pi}{3} N\rho^* \sum_i \sum_j x_i x_j \varepsilon^*_{ij} \sigma^{*3}_{ij} \times \left[\frac{1}{3}\left(\frac{\sigma_{ij}}{r_c}\right)^9 - \left(\frac{\sigma_{ij}}{r_c}\right)^3\right]$$

$$P^*_{\mathrm{LRC}} = \frac{16\pi}{3} \rho^{*2} \sum_i \sum_j x_i x_j \varepsilon^*_{ij} \sigma^{*3}_{ij} \times \left[\frac{2}{3}\left(\frac{\sigma_{ij}}{r_c}\right)^9 - \left(\frac{\sigma_{ij}}{r_c}\right)^3\right]$$

where $r_c$ is the cut-off radius, taken to be one-half of the side length of the simulation box in this work; $x_i$ is the mole fraction of component $i$ and $N$ is the total number of molecules in one phase. The radial distribution function $g(r)$ was taken to be unity for $r > r_c$ in the derivation of Eq. (6).

Enthalpies can be readily obtained from the values of energy, pressure and volume:

$$H^* = (U^*_c + U^*_k) + P^* L^{*3} = (U^*_c + U^*_k) + NzT^* \tag{7}$$

where $U^*_k$ is the dimensionless kinetic energy and $z$ is the compressibility factor. For an ideal gas at the same state conditions,

$$H^*_{id} = U^*_k + NT^*. \tag{8}$$

Subtracting Eq. (8) from Eq. (7) yields the enthalpy departure

$$\Delta H^{\neq *} = H^* - H^*_{id} = U^*_c + N(z-1)T^*. \tag{9}$$

The molar enthalpy of vaporization is the difference of enthalpy departures between the two coexisting phases and is given by

$$\Delta H^*_v = \Delta H^{\neq *}_g - \Delta H^{\neq *}_l = (U^*_{c,g} - U^*_{c,l}) + N_{\mathrm{A}}(z_g - z_l)T^* \tag{10}$$

where $N_A$ represents Avogadro's number, and subscripts $g$ and $l$ denote the vapor and liquid phases, respectively.

## 5. Results and discussions

The enthalpies and densities for the mixtures of $N_2$, $CO_2$ and $CH_4$, were simulated at the vapor–liquid equilibrium compositions previously simulated by means of the GEMC method [2] and performed at 220 and 240 K and at several high pressures. The

Table 2
Simulated enthalpy of vaporization (in KJ/mol) for $N_2(1)$–$CO_2(2)$–$CH_4(3)$ under various conditions

| | | | | $-\Delta H^{\neq PR}$ | | $-\Delta H^{\neq MC}$ | | $-\Delta H_v$ | |
|---|---|---|---|---|---|---|---|---|---|
| $x_1$ | $x_2$ | $y_1$ | $y_2$ | V | L | V | L | PR | MC |
| $T = 220\,K, P = 6.080\,MPa(60\,atm)$ | | | | | | | | | |
| 0.041 | 0.364 | 0.092 | 0.166 | 2.62 | 6.83 | 2.57 | 6.96 | 4.21 | 4.39 |
| 0.072 | 0.544 | 0.255 | 0.179 | 2.18 | 9.22 | 2.00 | 8.56 | 7.04 | 6.56 |
| 0.112 | 0.618 | 0.404 | 0.196 | 1.92 | 10.01 | 1.92 | 8.90 | 8.09 | 6.98 |
| 0.158 | 0.644 | 0.561 | 0.175 | 1.60 | 10.16 | 2.02 | 8.71 | 8.56 | 6.69 |
| $T = 220\,K, P = 9.119\,MPa(90\,atm)$ | | | | | | | | | |
| 0.125 | 0.738 | 0.551 | 0.222 | 2.75 | 11.56 | 1.96 | 9.80 | 8.81 | 7.84 |
| 0.214 | 0.694 | 0.655 | 0.222 | 2.46 | 10.66 | 2.28 | 8.98 | 8.20 | 6.70 |
| 0.308 | 0.521 | 0.596 | 0.217 | 2.59 | 7.97 | 2.61 | 6.84 | 5.38 | 4.23 |
| $T = 240\,K, P = 8.106\,MPa(80\,atm)$ | | | | | | | | | |
| 0.035 | 0.639 | 0.117 | 0.339 | 3.86 | 9.51 | 2.83 | 8.73 | 5.65 | 5.90 |
| 0.054 | 0.783 | 0.259 | 0.400 | 3.69 | 11.40 | 2.81 | 9.99 | 7.71 | 7.18 |
| 0.079 | 0.655 | 0.138 | 0.517 | 6.95 | 9.51 | 6.28 | 8.45 | 2.56 | 2.17 |
| 0.085 | 0.848 | 0.459 | 0.405 | 2.94 | 12.17 | 2.20 | 10.42 | 9.23 | 8.22 |
| 0.116 | 0.694 | 0.418 | 0.296 | 2.45 | 9.89 | 1.98 | 8.97 | 7.44 | 6.99 |

$\Delta H = \Delta H^*(\varepsilon_{11}/k)R$.

Table 3
Simulated molar volumes (in cm$^3$/mol) for $N_2(1)$–$CO_2(2)$–$CH_4(3)$ under various conditions

| | | $V_g$ | | $V_l$ | |
|---|---|---|---|---|---|
| $x_1$ | $x_2$ | PR | MC | PR | MC |
| $T = 220$ K, P = 6.080 MPa(60 atm) | | | | | |
| 0.041 | 0.364 | 175.6 | 169 | 61.8 | 56.6 |
| 0.072 | 0.544 | 198.5 | 202 | 47.0 | 48.1 |
| 0.112 | 0.618 | 213.0 | 200 | 44.2 | 46.8 |
| 0.158 | 0.644 | 230.9 | 235 | 43.7 | 48.0 |
| $T = 220$ K, P = 9.119 MPa(90 atm) | | | | | |
| 0.125 | 0.738 | 127.3 | 166 | 39.7 | 43.2 |
| 0.214 | 0.694 | 135.9 | 136 | 41.3 | 45.2 |
| 0.308 | 0.521 | 132.0 | 122 | 50.2 | 53.3 |
| $T = 240$ K, P = 8.106 MPa(80 atm) | | | | | |
| 0.035 | 0.639 | 122.2 | 129 | 49.3 | 49.8 |
| 0.054 | 0.783 | 127.8 | 140 | 43.3 | 44.9 |
| 0.079 | 0.655 | 65.9 | 73 | 49.2 | 51.2 |
| 0.085 | 0.848 | 151.9 | 189 | 41.5 | 44.1 |
| 0.116 | 0.694 | 168.6 | 199 | 47.6 | 50.1 |

equilibrium compositions [12] and the simulated enthalpy values expressed in terms of KJ/mol are listed in Table 2. The density values, expressed in terms of molar volumes, are reported in Table 3.

It would be desirable to compare the simulated saturation enthalpies with experimental values which, however, are not available in the literature. It is also for this reason that Eq. (2) was used without introducing any modifications. We are not aware of any equations which are specifically developed for estimating saturation enthalpies for the mixture under consideration. Notwithstanding the uncertainties involved in estimating saturation enthalpies and densities from vapor–liquid equilibrium data by means of an equation of state, such estimations were made to provide some indication of the validity of the simulated values. As the estimated values would only give a qualitative comparison, it was decided to use a simple cubic equation of state for the task.

As in Ref. [4], the Peng–Robinson (PR) equation of state was selected for the calculation. In the calculation, the conventional mixing rules were employed, namely

$$a = \sum_i \sum_j x_i x_j (1 - k_{ij}) \sqrt{a_{ii} a_{jj}}$$

$$b = \sum_i x_i b_{ii} \qquad (11)$$

The enthalpy departure is obtained from Ref. [13]:

$$\Delta H^{\neq} = \frac{a}{2\sqrt{2}b}\left(1 - \frac{T}{a}\frac{\partial a}{\partial T}\right) \ln \frac{z + (1 - \sqrt{2})B^*}{z + (1 + \sqrt{2})B^*} + \mathrm{RT}(z - 1)$$

$$\frac{\partial a}{\partial T} = -\frac{R}{2}\left(\frac{\Omega_a}{T}\right)^{1/2} \sum_i \sum_j x_i x_j (1 - k_{ij}) \times \left[K_j \left(\frac{a_i T_{cj}}{P_{cj}}\right)^{1/2} + \kappa_i \left(\frac{a_j T_{ci}}{P_{ci}}\right)^{1/2}\right] \qquad (12)$$

$$\kappa_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2$$

where

$$B^* = \frac{bP}{\mathrm{RT}} \quad z = \frac{PV}{\mathrm{RT}}$$

It should be mentioned that although the results presented in Ref. [4] were correct, Eqs. (6) and (12) of Ref. [4] should be replaced by Eqs. (6) and (12) presented above.

In Eqs. (11) and (12), values of $k_{ij}$ have been reported by Al-Sahhaf et al. [1]. They were obtained by fitting the PR equation to the vapor–liquid equilibrium values of the three constituent binaries of the mixture. Their reported values for the three parameters are $k_{12} = -0.013$, $k_{13} = 0.034$ and $k_{23} = 0.095$.

The calculated $\Delta H^{\neq}$ using the same $k_{ij}$ values are included for comparison in Table 2. The average absolute percent deviation (AAPD) between the simulated results and those estimated from the PR equation is 11.73 for $\Delta H_v$. The average absolute differences in the vapor compositions, based on the same liquid compositions, between the simulated values and those obtained from the PR equation are $\Delta y_1 = 0.046$, $\Delta y_2 = 0.023$, and $\Delta y_3 = 0.063$. Although it is known that the PR equation may not yield excellent results when simultaneous calculations of densities and vapor pressures are made over large ranges of temperature, the temperature range considered in this work is relatively small and a comparison of densities is made in Table 3, where the simulated results and the calculated values obtained from the PR equation expressed in terms of $V_g$ and $V_l$ are reported. The AAPDs between the two sets of values are 10.12 and 6.84 for $V_g$ and $V_l$, respectively. It appears that the simulated results are reasonable.

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