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## Thermodynamic behavior of the CO<sub>2</sub> + SO<sub>2</sub> mixture: experimental and Monte Carlo simulation studies

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### Abstract

Accurate knowledge of the thermodynamic properties of CO<sub>2</sub> + contaminant mixtures is required in order to develop optimized carbon dioxide capture and storage solutions. In the present work, the thermodynamic behavior of the CO<sub>2</sub> + SO<sub>2</sub> binary system has been investigated using two different approaches: experimental measurements and molecular simulation calculations. Isothermal vapor-liquid equilibrium (VLE) data have been measured at 263 K and 333 K. The composition of both the gaseous and the liquid phases were measured by gas chromatography once equilibrium had been achieved. Molecular simulation calculations of phase equilibrium were performed on the same binary mixture under the same temperature conditions using the Gibbs Ensemble Monte Carlo method. No calibrations on experimental binary data were performed for these calculations. The experiments and simulations appear consistent as the obtained results are in excellent agreement. As a result, molecular simulation could be used as an attractive and cost-efficient alternative to experimental techniques for generating new thermodynamic data for this mixture.

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**Keywords:** Carbon dioxide ; Sulfur dioxide ; Thermodynamics ; Experiments, Monte Carlo simulations

### 1. Introduction

The risks associated with climate change have been the subject of much debate in recent years. Today, most experts think that these risks are real and directly linked to the increase in greenhouse gas emissions, especially CO<sub>2</sub>. Among the various options for mitigating these emissions, large-scale CO<sub>2</sub> capture and storage into underground formations like deep saline aquifers or depleted oil and gas fields is a promising option [1]. One economical and energetic limitation of such capture and storage operations might be the required purity of the CO<sub>2</sub> stream. The quality of the CO<sub>2</sub> captured from power plants or industrial installations depends on several factors, like the nature of the fossil combustible involved, the processes used for combustion and capture, as well as the possible use of

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further treatments. Depending on these factors, the CO<sub>2</sub> stream will account for a variable amount of gas contaminants, such as SO<sub>2</sub>, NO<sub>x</sub>, H<sub>2</sub>S, N<sub>2</sub>, O<sub>2</sub>, Ar... that can reach up to a few mol %. A detailed inventory of the nature and concentration of contaminants has been proposed by Anheden et al. in 2004 [2]. However, only a few studies have up till now investigated the impact of these contaminants on capture, transportation, injection and storage operations. Therefore, it is not yet possible to define precise maximum amounts of contaminants that can be tolerated in CO<sub>2</sub> flues. Obtaining accurate knowledge of the thermodynamic behavior of CO<sub>2</sub>-contaminant mixtures is part of the studies that are necessary in order to address the impact of these contaminants and to develop optimized carbon dioxide capture and storage solutions. Some of these CO<sub>2</sub>-contaminant mixtures, like CO<sub>2</sub> + O<sub>2</sub> and CO<sub>2</sub> + N<sub>2</sub> for instance, have already been studied over a large range of pressure and temperature conditions. In the case of CO<sub>2</sub> + SO<sub>2</sub> and CO<sub>2</sub> + NO<sub>2</sub> mixtures, thermodynamic data are very scarce. To the best of our knowledge, the only experimental data available for the CO<sub>2</sub> + SO<sub>2</sub> mixture is that reported by Caubet (1904) [3] and Bluemcke (1888) [4] more than one hundred years ago. This lack of experimental data is certainly related to the toxicity of sulfur dioxide, which makes any experimentation delicate and expensive.

In the present study, the thermodynamic behavior of the CO<sub>2</sub> + SO<sub>2</sub> binary system has been investigated using two different approaches: experimental measurements and molecular simulation calculations. Isothermal vapor-liquid equilibrium (VLE) data have been measured at 263 K and 333 K. The composition of both the gaseous and the liquid phases were measured by gas chromatography once equilibrium had been achieved. Molecular simulation calculations of phase equilibrium have been performed on the same binary mixture under the same temperature conditions using the Gibbs Ensemble Monte Carlo method. No calibrations on experimental binary data were performed for these calculations, that are thus fully predictive.

This paper is organized as follows. The experimental technique is described in section 2, including the presentation of the apparatus used as well as the experimental procedure followed. The simulation technique is presented in section 3 along with all simulation details. Experimental and simulated results are discussed in section 4. Finally, section 5 gives our conclusions.

## 2. Experimental technique

### 2.1. Materials

The two compounds of the studied mixture were obtained from Air Liquide with a certified purity higher than 99.995 vol % for the CO<sub>2</sub> and 99.9 vol % for the SO<sub>2</sub>. No further purification was performed before use.

### 2.2. Apparatus

The apparatus used in this work is based on a “static-analytic” method with sampling of the liquid and vapor phases. It is similar to that described by Laugier and Richon [5]. The equilibrium cell is the same as that described by Coquelet et al. [6], its internal volume is around 28 cm<sup>3</sup>. For accurate thermal regulation, it is immersed inside a thermoregulated liquid bath. Temperatures are measured with two Pt100 platinum resistance thermometer probes inside the walls of the equilibrium cell. These probes are calibrated against a 25 Ω reference probe (TINSLEY Precision Instrument) certified by the Laboratoire National d'Essais (Paris) following the International Temperature Scale 1990 protocol. Pressures are measured using a pressure transducer (Druck, type PTX611, range: 0 – 1.6 MPa). This sensor is calibrated against a dead weight pressure balance (5202S model from Desgranges & Huot). Pressure and temperature data acquisition is performed with a computer linked to a Hewlett Packard unit (HP34970A). The estimated uncertainties in this work are ± 0.02 K and ± 0.0002 MPa as a result of careful calibrations.

The analytical work was carried out using a gas chromatograph (VARIAN model CP-3800) equipped with a thermal conductivity detector (TCD) connected to a data acquisition system (BORWIN ver 1.5, from JMBS). The

analytical column is Porapak Q model, 80/100 Mesh (1/8" silcosteel tube, 2 m length, from Resteck France). The TCD was repeatedly calibrated by introducing known amounts of each pure compound through a syringe in the injector of the gas chromatograph. Taking into account the uncertainties due to calibrations and dispersions of analyses, resulting uncertainties on vapor and liquid mole numbers are estimated to be less than  $\pm 1.5\%$  and  $\pm 2\%$  for  $\text{SO}_2$  and  $\text{CO}_2$  respectively. Resulting uncertainties on compositions are less than  $3.5\%$ .

### 2.3. Experimental procedure

Before transfer, the internal volumes of the cell and of the loading lines are carefully maintained free of air. At room temperature, the equilibrium cell and its loading lines are evacuated down to 0.1 Pa. The cell is first loaded with liquid  $\text{SO}_2$  (about  $5\text{ cm}^3$ ). The equilibrium temperature is assumed to be reached when the two Pt100 probes (one located at top of equilibrium cell, the other at the bottom) give equivalent temperature values within the experimental uncertainty for at least 10 minutes. After recording the vapor pressure of the  $\text{SO}_2$  (the heavier component) at the equilibrium temperature, the two-phase envelopes are determined with generally much more than six isothermal P, x, y data points. For these purposes,  $\text{CO}_2$  (the lighter component) is introduced step by step, leading to successive equilibrium mixtures of increasing overall  $\text{CO}_2$  content. After each new  $\text{CO}_2$  loading, equilibrium is assumed to have been reached when the total pressure remains unchanged within  $\pm 1.0\text{ kPa}$  during a period of 10 min under efficient stirring.

For each equilibrium condition, at least five samples of both vapor and liquid phases are withdrawn using the pneumatic ROLSI<sup>TM</sup> samplers [7] and analyzed in order to check the repeatability of the measurements (deviations are much less than 1%).

## 3. Simulation technique

### 3.1. Monte Carlo algorithm

Monte Carlo simulations allow the calculation of macroscopic equilibrium properties from a microscopic description of a system involving typically a few hundreds of molecules. The principle of these methods is to generate successive configurations of the simulated system. On the basis of these simulations, appropriate statistical averages are performed to derive fluid properties that can be compared with experimental measurements. The present section aims to provide just a brief summary of the Monte Carlo algorithms used in this work, the reader being referred to textbooks in which they are explained in more details [8-10].

The liquid-vapor phase equilibrium of the  $\text{CO}_2 + \text{SO}_2$  mixture has been simulated with the Gibbs Ensemble technique in which two simulation boxes without explicit interfaces represent the coexisting phases. Calculations have been performed at constant temperature and constant pressure. The following Monte Carlo moves are used to sample the possible coexisting configurations: rigid body translations and rotations of the molecules, volume changes and transfers of molecules between the two phases. In order to improve the efficiency of the sampling, a pre-insertion bias [11] has been used during the transfer move. This statistical bias involves two steps: first the selection of a suitable location for inserting a new molecule by testing several locations with a simplified potential and then the selection of a suitable molecular orientation. The lengths of the simulations performed are typically about 50 million steps, one step corresponding to one Monte Carlo move. The desired equilibrium properties (molar composition and density of each phase) are computed by taking the average value, after an equilibration period of around 10 million steps.

These simulations have been performed with the GIBBS software [10] that has been developed conjointly by IFP and the Laboratory of Chemical Physics at Université Paris-Sud.

### 3.2. Potential model

The potential energy of the system is considered to be the sum of the energy related to the dispersion - repulsion interactions and electrostatic energy. Intramolecular energy has not been taken into account as all molecules are considered to be rigid. Dispersion-repulsion energy between two force centers  $i$  and  $j$  belonging to different molecules is calculated with a Lennard-Jones potential, in which  $r_{ij}$  represents the distance between the two centers, and the electrostatic energy between charges  $q_i$  and  $q_j$  is computed from Coulomb's law:

$$U_{ij} = U_{rep} + U_{disp} + U_{elec} = 4\epsilon_{ij} \left( \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right) + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (1)$$

where  $\sigma_{ij}$  and  $\epsilon_{ij}$  are the Lennard-Jones parameters. The Lorentz-Berthelot combining rules have been used to calculate these Lennard-Jones parameters for the cross interactions:

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \quad (2)$$

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (3)$$

The Lennard-Jones intermolecular energy was computed with a cutoff radius equal to half of the box length, and a classical long distance correction was applied. Periodic boundary conditions have been added, and the reaction field method [12] has been used to calculate long range electrostatic interactions.

The potential model used to represent the CO<sub>2</sub> molecule is the rigid version EPM2 of the force field proposed by Harris and Yung [13]. According to this model, each carbon dioxide molecule consists of three Lennard-Jones centers and three electrostatic charges centered at each atom. The carbon-oxygen bond lengths are fixed and equal to 1.163 Å, and the molecule has a fixed OCO angle of 180°. This potential is known to reproduce correctly both thermodynamic and transport properties of carbon dioxide [14].

The SO<sub>2</sub> molecule is represented by three Lennard-Jones sites and three electrostatic point charges, using an original parameterization. In this model the three Lennard-Jones centers are centered on the atoms of the molecule, two negative charges are centered on the two oxygen atoms, whereas the third charge (the positive one) is located on the bisector of the OSO angle rather than on the sulfur atom. The Lennard-Jones parameters and the charge distribution have been optimized to reproduce the experimental dipole moment of the molecule and the liquid-vapor phase envelope of pure SO<sub>2</sub>. Like CO<sub>2</sub>, the SO<sub>2</sub> molecule is considered as rigid body with a sulfur-oxygen bond length of 1.434 Å and a OSO angle of 119.5°.

## 4. Results

Measured and calculated phase diagrams at 263 K and 333 K are shown in Figure 1. In the two graphs of this figure, open squares represent our experimental results, while filled squares refer to our Monte Carlo simulation results. Diamonds represent the experimental results of either Caubet or Bluemcke available in the literature. The lowest studied temperature, 263 K, is below the critical temperature of CO<sub>2</sub> ( $T_c = 304.21$  K), explaining why the phase diagram ends up at the vapor pressure of pure CO<sub>2</sub> at this imposed temperature. The other temperature studied is above the critical temperature of CO<sub>2</sub>; the corresponding phase diagram is thus displaying a liquid-vapor critical point.

Excellent agreement is obtained between our experiments and predictive simulations at both temperatures. At 263 K, both our experimental and simulation results are in good agreement with the experimental bubble pressures of Bluemcke [4]. However, more significant deviations between our results (experimental and simulated results) and

literature data are observed at 333 K, with a systematic overestimate of the bubble and dew pressures reported by Caubet [3] compared to our new data. The validity of Caubet’s data therefore becomes questionable since the two different approaches used in this work lead to very consistent results.

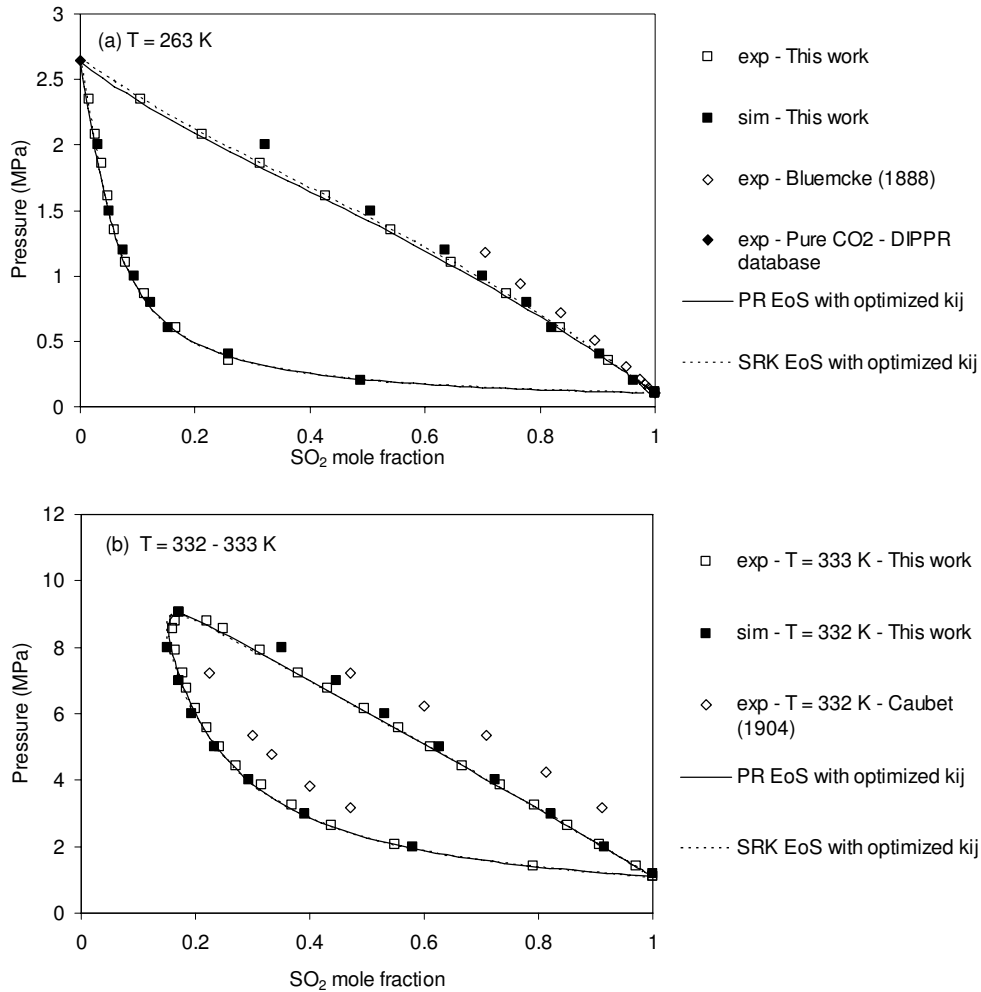


Figure 1: (P,x,y) phase diagrams for the CO<sub>2</sub> + SO<sub>2</sub> mixture at two different temperatures. Open squares represent our experimental results while black squares are our Monte Carlo simulation results. Diamonds represent the experimental results from ref [3] and ref [4]. Solid lines and dotted lines are equation of state results.

At 332 K, the critical coordinates  $P_c$ ,  $\rho_c$  and  $x_c$  (critical pressure, critical density and critical composition) have been determined using some extrapolations of the simulation results based on the following scaling laws (Ungerer et al., 2005):

$$\begin{aligned} \rho_i &= \rho_c + \varepsilon \frac{\gamma}{2} (P_c - P)^\beta + \lambda (P_c - P) \\ x_i &= x_c + \left( \lambda_1 - \varepsilon \frac{\lambda_2}{2} \right) (P_c - P) - \varepsilon \frac{\mu}{2} (P_c - P)^\beta \end{aligned} \quad (4)$$

where  $\varepsilon = 1$  for the liquid phase and  $\varepsilon = -1$  for the vapor phase. The critical coordinates ( $P_c$ ,  $\rho_c$  and  $x_c$ ) as well as the five parameters ( $\gamma$ ,  $\lambda$ ,  $\lambda_1$ ,  $\lambda_2$ ,  $\mu$ ) involved in expressions (4) are regressed from a set of coexistence points ( $P$ ,  $\rho_l$ ,  $\rho_v$ ) and ( $P$ ,  $x_l$ ,  $x_v$ ) below the critical point. Critical coordinates obtained using this procedure are:  $P_c = 9.06$  MPa,  $\rho_c = 552.05$  kg/m<sup>3</sup> and  $x_c$  (SO<sub>2</sub>) = 0.171 at 332 K. No attempts have been undertaken to experimentally determine these critical coordinates in this work. The pressure-density diagram calculated from Monte Carlo simulations at 332 K is shown in Figure 2. To the best of our knowledge, no experimental information on these volumetric properties is available for comparison.

Finally, the CO<sub>2</sub>-SO<sub>2</sub> interaction parameter used in standard cubic equation of states has been optimized. Our experimental data at 263 K and 333 K were simultaneously taken into account in the data regression. The optimization has been performed using a simplex procedure with an objective function defined as the mean relative deviation on bubble pressures. Peng-Robinson [15] and Soave-Redlich-Kwong [16] equations of state have been considered in this work. For both equations of state, the optimization leads to a binary interaction parameter equal to 0.02. Associated deviations on bubble pressures are 2.3 % for Peng-Robinson equation of state and 2.2 % for Soave-Redlich-Kwong equation. The phase envelopes calculated using these two equations of state with the optimized interaction parameter are shown in Figure 1, together with the experimental and molecular simulation results.

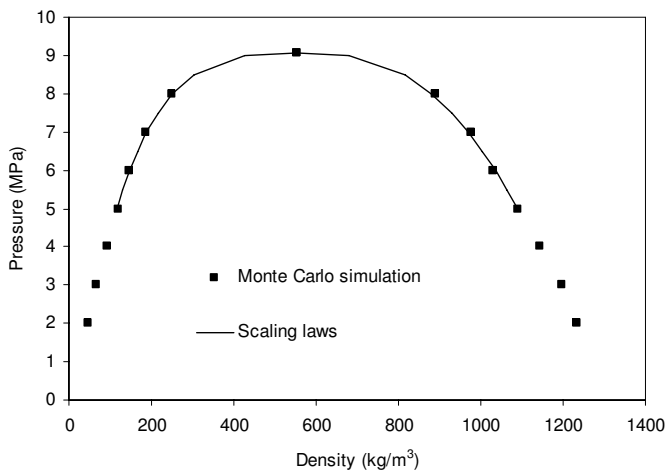


Figure 2: Pressure-density diagram of the CO<sub>2</sub> + SO<sub>2</sub> mixture calculated by Monte Carlo simulations at 332 K.

## 5. Conclusion

Experimental and Monte Carlo simulation studies have been performed on the CO<sub>2</sub> + SO<sub>2</sub> mixture at 263 K and 333 K. The excellent agreement obtained between the Gibbs simulations and experimental results at both temperatures demonstrates the consistency of our experimental set-up design and computational approach. As a result, molecular simulation can be used as an attractive and cost-efficient alternative to experimentation techniques, to generate new thermodynamic data covering a large range of temperature and pressure conditions for this mixture.

## 6. Acknowledgements

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