

# Experimental Verification of a Numerical Model for Predicting the Adsorption of Mixed Gases

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## ABSTRACT

An ongoing effort is invested on developing a sorption compressor to drive Joule-Thomson cryocoolers with mixed-refrigerants. In previous work a numerical model is presented for determining the adsorption of mixed-gases based on the pure component adsorption characteristics. In the present paper an experimental verification of the numerical results is described. The experimental setup is suitable for simulating the sorption cycle in a compressor. The current research is focused on binary mixtures containing nitrogen and alkanes.

## INTRODUCTION

Sorption Joule-Thomson (JT) cryocoolers are thermally driven and have no moving parts, both at the cold end and at the compressor (except for some check valves), which results in a high reliability, long operating life, and a vibration-free system.

Operating JT cryocoolers with Mixed-Refrigerants (MR) instead of pure refrigerants allows lower pressure ratios and higher coefficients of performance (COP). Mixed-Refrigerant Joule-Thomson (MRJT) cryocooling driven by mechanical compressors has been widely investigated with a variety of suggested MRs [1, 2].

The research presented in this paper is part of the effort to develop a sorption compressor for driving MRJTs. The basis for this study is a fundamental understanding of mixed-gas adsorption and developing the ability to predict the processes in a sorption compressor which contains mixed-gases. In a previous work [3] an analysis of a sorption compressor operating with mixed-gases is presented based on a model using only pure gas adsorption parameters. Recently, we performed a wider set of adsorption measurements and an advanced procedure for fitting the experimental results to the Sips isotherm model [4]. In the current paper we present the experimental verification of the numerical model and the pure gas adsorption measurements we performed at the University of Twente.

## METHOD

### Mixed gas adsorption model

A model, which has been presented elsewhere [3], predicts the adsorption of mixed-gases based on adsorption experimental data of the pure components. The model is based on the Sips isotherm and enables the prediction of the adsorbed phase composition as a function of temperature,

pressure, and vapor-phase composition. The adsorption concentration of pure gases as a function of pressure and temperature for nitrogen, methane, ethane, and propane on three different adsorbents has been recently published [4], based on a modified Sips isotherm:

$$C = C_0 \frac{(ap)^{1/n}}{1+(ap)^{1/n}} \tag{1}$$

where

$$C_0 = C_A T + C_B \tag{2}$$

$$a = a_A \exp(a_B T) \tag{3}$$

$$n = n_A T + n_B \tag{4}$$

$C$  is the adsorption concentration,  $T$  is the temperature, and  $p$  is the pressure.  $C_A$ ,  $C_B$ ,  $a_A$ ,  $a_B$ ,  $n_A$ , and  $n_B$  are fitting parameters. Based on the pure gas parameters, the adsorption of mixed gases is determined using the following relation, depending also on the vapor phase composition,  $y_i$  [3]:

$$C_i = C_{0,i} \frac{(a_i y_i p)^{1/n_i}}{1 + \sum_{j=1}^N (a_j y_j p)^{1/n_j}} \tag{5}$$

In order to analyze sorption compressors, an algorithm for calculating the isochoric adsorption of mixed-gases is developed [3]. The sorption cell contains a known amount of adsorbent and a void volume. The composition of the vapor phase is known at a single state (a given temperature and a given pressure), which enables the calculation of the total mass for each component in the system. Then, the algorithm allows finding the equilibrium pressure, vapor phase composition, and adsorbed phase composition at any other temperature at the constant volume. The algorithm consists of the mixed-gas adsorption model, equation (5), and preserves the mass of each component in the system. The vapor phase is calculated by the Peng-Robinson equation of state (PR-EOS) with the classical van der Waals mixing rules and binary interaction parameters. A detailed description of the analysis is provided in [3]. The current research phase also includes an improvement of the numerical code to allow better convergence of the calculations.

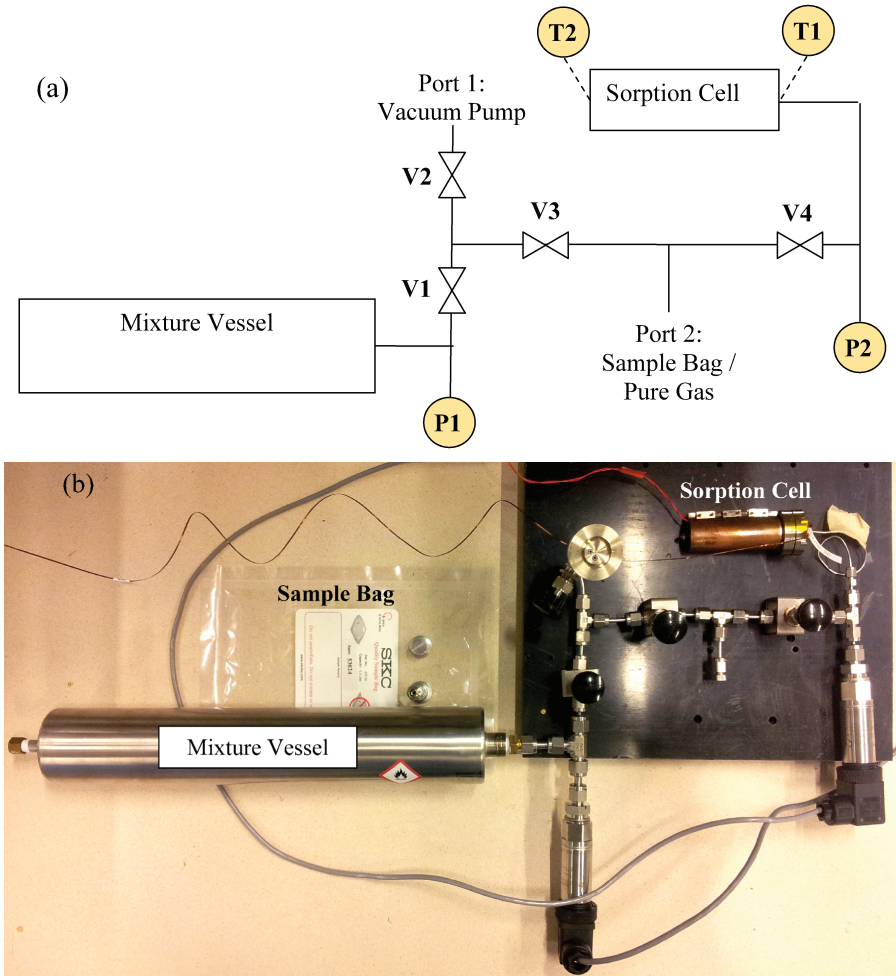
**Experimental Setup**

The objective of the experimental investigation is to validate the currently used numerical model which is based on the recently measured adsorption characteristics of pure gases [4] and the latest sorption compressor model [5].

The experimental setup, depicted in Figure 1, consists of a sorption cell, a mixture vessel, a sample bag, two pressure transducers, and connections to a vacuum pump, port 1, and pure gas sources, port 2. The sorption cell contains 5.9 g of Chemviron AP 4-60 activated carbon, an outer electric heater, and two temperature sensors at the edges. The surrounding heater is wrapped with a copper sheet to obtain a uniform temperature in the sorption cell. Four valves are used for creating the mixture in the mixture vessel out of the pure gas sources, filling the sorption cell with a mixture, and sampling the mixture at different stages of the cycle. A gas chromatograph (GC) is used for determining the composition of the sampled mixture collected in the sample bag. Steady state is defined by obtaining stable temperatures at T1 and T2. A pressure transducer, p1, is connected to the mixture vessel to allow creating mixtures at low pressures. A second pressure transducer, p2, is measuring the pressure in the sorption cell.

**Experimental Procedure**

In order to prepare a new mixture in the experimental setup, first the mixture vessel is evacuated through port 1 when valves 1 and 2 are open. The other valves are closed (in this section valves that are not mentioned explicitly are closed). Then the source of the heaviest component is connected to port 2 (with its own valve closed), and all the tubing is evacuated, where valves 2 and 3 are open.



**Figure 1.** The experimental setup. (a) a schematic view, (b) a photo.

The gas is introduced to the mixture vessel with valves 3 and 1 open, where the pressure is monitored by p1 and controlled by valve 1. The total pressure of the mixture is designed to be of a few bars only; therefore, the pressure of the first component, divided by the total pressure, is about its molar fraction in the targeted mixture, due to the low operating pressures. When introducing the next component, it is important to maintain a relatively high pressure behind valve 1, to avoid back flow of the fluid that is already in the mixture vessel. This procedure provides a rough estimation of the mixture composition in the mixture vessel. This, however, is satisfying, since the actual composition is measured by a GC. The sample is taken with a sample bag that is connected to port 2, which is evacuated (valves 2 and 3 are open) prior to filling (valves 1 and 3 are open).

The sorption cell is vacuum baked at 400 K for at least 24 hours, with port 2 plugged and valves 2, 3, and 4 open. Then, valve 4 is closed and the heater is switched off to let the sorption cell reach room temperature. The mixture is introduced to the sorption cell by opening valves 1, 3, and 4 and waiting for the temperature sensors to reach steady state. Valve 4 is then closed and the pressure, p2, and temperatures, T1 and T2, are recorded. To enable charging the sorption cell with a pressure higher than 1 bar, the sample bag is disconnected (because its use is limited to 1 bar) and port 2 is plugged. The sorption cell is then heated to reach a higher stable temperature. When that temperature is reached, the corresponding pressure is recorded. In this way the dependency on pressure and temperature, at constant volume, is obtained.

To mimic the cycle of a sorption compressor, the closed volume is heated to obtain a desired high pressure. The temperature is further increased and the pressure is maintained constant by letting the mixture to flow out of the sorption cell into the sample bag. This flow is controlled by valve 4 which functions in a similar manner as a check valve: it is opened in a given “cracking pressure” and closed when the pressures on its two sides are equal. The sample composition is measured by the GC, and it represents the mixture composition to be circulated by a sorption compressor which operates in these conditions.

The remaining mixture in the sorption cell is then cooled back to room temperature, and thus the pressure decreases. At a certain state, the pressure equals to the initial pressure at a temperature above room temperature. This is the state where the intake valve of a compressor shall be opened.

### Measurement Accuracies

In this study we measure three parameters: temperature, pressure, and mixture composition. The pressure measurements have the sensor accuracies of  $\pm 0.1\%$ . The temperature sensors have accuracy of about  $\pm 1.5\%$ ; however, during operation we never have reached a complete uniform temperature over the sorption cell and a difference of about  $5^\circ$  has been obtained. Therefore, the accuracy of the temperature measurement is assumed to be  $\pm 3\%$ . The accuracy of the measured volumes is  $\pm 2.5\%$ , and the accuracy of the adsorbent mass is  $\pm 0.3\%$ . The void volume is considered as the volume between the pellets and any other volume in the sorption cell that doesn't contain adsorbent. It does not consider the micro- and nano- pore volumes in the adsorbent. The GC that we use with the existing calibration curves has an accuracy of  $\pm 2\%$ .

## RESULTS AND DISCUSSION

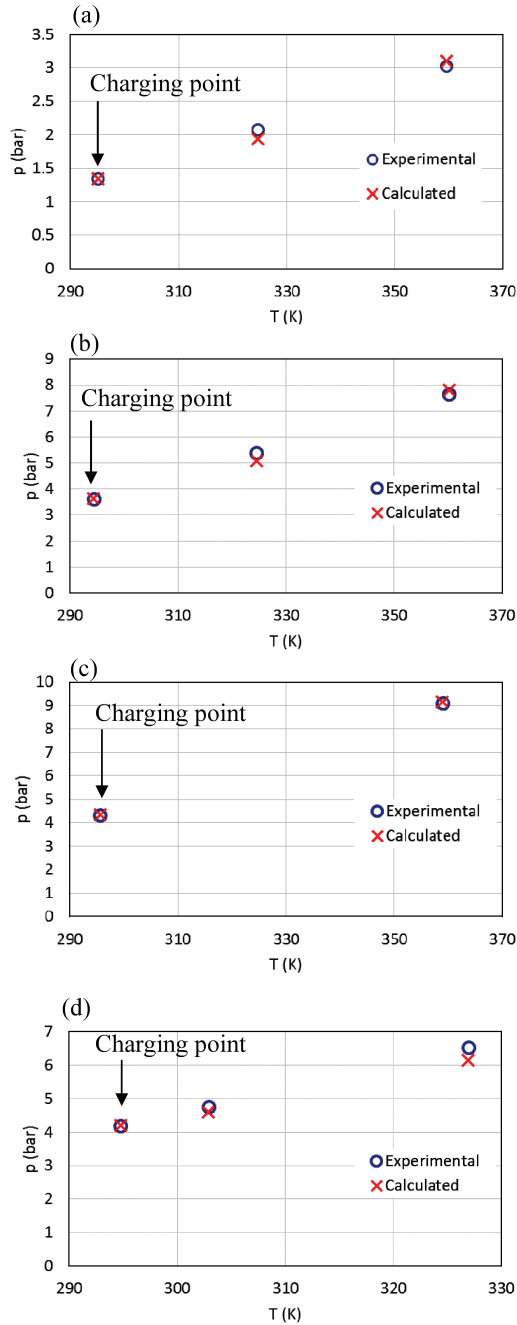
### Isochoric Adsorption of Mixed Gases

Figures 2 (a – d) shows the pressure as a function of temperature for mixtures adsorbed in a constant volume with charging vapor compositions of  $0.5544 \text{ N}_2 / 0.4456 \text{ C1}$ ,  $0.5287 \text{ N}_2 / 0.4713 \text{ C1}$ ,  $0.3885 \text{ N}_2 / 0.6115 \text{ C1}$ , and  $0.288 \text{ N}_2 / 0.712 \text{ C1}$ , respectively. The charging temperatures are about room temperature and the charging pressures are 1.34 bar, 3.62 bar, 4.33 bar, and 4.20 bar, respectively. The calculated and experimental results at the charging point are identical, since the calculations were fitted to simulate the experiment (the temperature, pressure, and vapor-phase composition at the charging point are the inputs to the model). The results in Figure 2 demonstrate the satisfying predictions of the pressure changes caused by temperature changes in a constant volume. The maximum deviation between the experimental and calculated results is 6.3%.

### Outflow from the Sorption Cell

When the desired pressure is obtained in simulating the compressor cycle, the temperature is further increased to provide an out flow while maintaining a constant pressure in the sorption cell. A sufficient amount of out flow is required to fill the sample bag for measuring the composition in the GC. The relatively small sorption cell in use makes it difficult to capture a valid out flow. A non valid out flow is a flow where one of the components is already fully desorbed. In the current setup the amount of mixture that leaves the sorption cell is not directly measured. However, the composition of the out flow and the temperature where the remaining mixture in the sorption cell reaches the initial pressure are measured, and these two parameters provide a complete definition of the sorption cycle.

Figure 3 shows the calculated out flow nitrogen molar fraction as a function of the flow rate for a charging mixture of  $0.5287 \text{ N}_2 / 0.4713 \text{ C1}$  at 294.4 K and 3.62 bar. In this cycle, a high pressure of 7.64 bar is obtained at 369.15 K, and the out flow is provided by further increase in temperature to 393.6 K (and maintaining the pressure equal to 7.64 bar). The dashed line in Figure 3 indicates the measured nitrogen molar fraction of the out flow as measured in the GC:  $0.654 \text{ N}_2 / 0.346 \text{ C1}$ . The



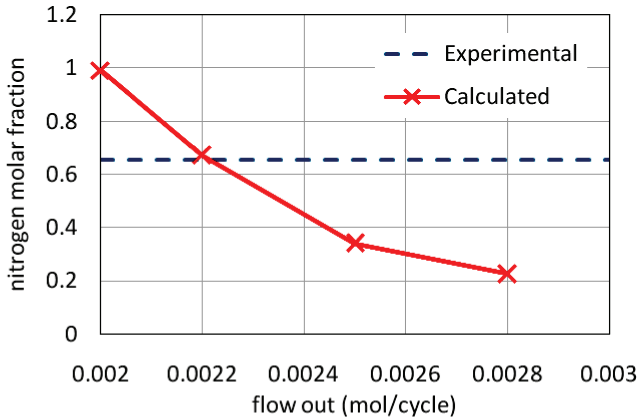
**Figure 2.** A comparison between experimental and calculated pressures as a function of temperature at constant volume.

(a) molar composition of charging vapor phase 0.5544  $N_2$  and 0.4456  $C1$ , at 295.2 K and 1.34 bar.

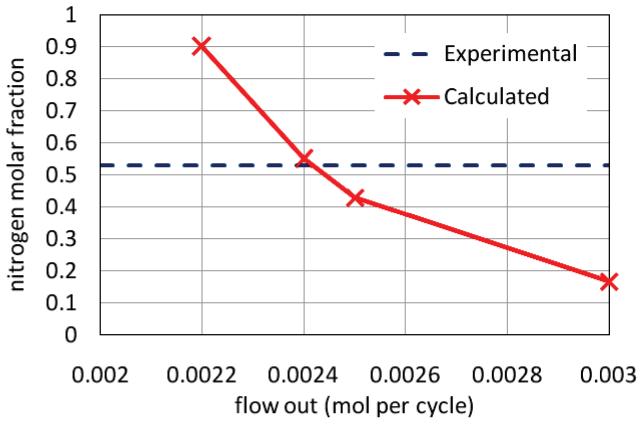
(b) molar composition of charging vapor phase 0.5287  $N_2$  and 0.4713  $C1$ , at 294.4 K and 3.62 bar.

(c) molar composition of charging vapor phase 0.3885  $N_2$  and 0.6115  $C1$ , at 295.6 K and 4.33 bar.

(d) molar composition of charging vapor phase 0.288  $N_2$  and 0.712  $C1$ , at 294.8 K and 4.20 bar.



**Figure 3.** Determining the experimental flow rate using the measured composition of the out flow. The molar composition of the charging vapor phase is 0.5287 N<sub>2</sub> and 0.4713 C1, at 294.4 K and 3.62 bar. A high pressure of 7.64 bar is obtained at 360.15 bar, and the out flow is delivered up to 393.6 K



**Figure 4.** Determining the experimental flow rate using the measured composition of the out flow. The molar composition of the charging vapor phase is 0.3885 N<sub>2</sub> and 0.6115 C1, at 295.6 K and 4.327 bar. A high pressure of 9.1 bar is obtained at 358.9 bar, and the out flow is delivered up to 388.7 K.

intersect between the solid and the dashed lines shows the out flow rate in the experiments, which equals 2.21 mmol per cycle. Since the molar mass of this mixture is 23.85 g/mol and the density at 295 K and 1 bar is 0.97 mg/cc [REFPROP], the out flow is about 53 mg and occupies 54.6 cc. For this flow rate, the calculated pressure in which the remaining mixture in the sorption cell reaches the initial pressure of 3.62 bar is 344 K, whereas the experimental value is 316 K. Taking into consideration the accuracy of the experimental setup and of the numerical model, we find this correspondence reasonable.

Another example is shown in Figure 4. The charged mixture in this case is 0.3885 N<sub>2</sub> / 0.6115 C1 at 295.6 K and 4.327 bar. A high pressure of 9.1 bar is obtained at 358.9 K, and the out flow is provided by further increase in temperature to 388.7 K. The dashed line in Figure 7 indicates the measured nitrogen molar fraction of the out flow: 0.53 N<sub>2</sub> / 0.47 C1. The intersect between the solid and the dashed lines here is at 2.42 mmol per cycle. The calculated pressure in which the remaining mixture in the sorption cell reaches the initial pressure of 4.327 bar is 340 K whereas the experimental value is 301 K.

## CONCLUSION

The current study is part of an ongoing research aiming at the development of sorption compressors for driving mixed-gas Joule-Thomson cryocoolers. Recently, we performed an extensive set of adsorption measurements of four pure gases on three different adsorbents. In addition, an improved procedure for fitting the experimental results to the Sips isotherm model was developed and an advanced algorithm has been developed for analyzing the mixed-gases sorption compressor. The experimental investigation presented in this paper is set up for validating this algorithm and analysis. A good agreement between the calculated results and the experimental results for the isochoric adsorption of mixtures is obtained. The experimental setup and procedure are found to be suitable for validating the complete sorption compressor model. However, further improvements are required for increasing the system sensitivity as well as the overall accuracy. Among other ideas, we plan to increase the volume of the sorption cell, to improve the temperature uniformity within this cell, and to improve the calibration of the GC.

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