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Citation for published version:

Shade, D, Mounfield III, WP, Huang, Y, Marszalek, B & Walton, KS 2021, 'An Automated Multi-Component Gas Adsorption System (MC GAS)', *Review of Scientific Instruments*, vol. 92, no. 5, 054102. <https://doi.org/10.1063/5.0031579>

Digital Object Identifier (DOI):

[10.1063/5.0031579](https://doi.org/10.1063/5.0031579)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Review of Scientific Instruments

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An Automated Multi-Component Gas Adsorption System (MC GAS)

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Abstract

The knowledge gap on adsorption of complex mixtures in the literature relative to single component data represents a persistent obstacle to developing accurate process models for adsorption separations. The collection of mixed gas adsorption data is an imminent need for improved understanding of the behavior of adsorbent systems in these diverse adsorption applications. Current approaches to understanding mixture adsorption using predictive theories based on pure component adsorption experiments often fail to capture the behavior of more complex, non-ideal systems. In this work, we present an automated volumetric instrument for the measurement of mixed gas adsorption isotherms. This instrument was validated by comparison to other in-house instruments and data available in the literature, and the binary adsorption measurements were found to be thermodynamically consistent. The automation of this instrument allows for rapid collection of high-quality mixture adsorption data.

Introduction

All adsorption separations processes involve the adsorption of a mixture of gases, including CO₂ capture,¹⁻³ gas sweetening,⁴⁻⁶ oxygen concentration,⁷⁻⁹ C₂ hydrocarbon separation,^{10, 11} among others. However, adsorption of mixtures is poorly understood. A recent report on separations science from the National Academies of Sciences, Engineering, and Medicine identifies understanding behavior of complex systems as the biggest challenge in separation science.¹² For adsorption separations, this challenge is apparent as adsorbent materials rarely perform as desired in the presence of multicomponent mixtures, especially when components span a wide range of compositions, or highly dilute or highly concentrated species. Though great advances have been made in increasing the adsorption capacity for a target species, the ability to predict adsorption behavior in complex systems remains an outstanding requirement to implement robust adsorption separations processes. This sentiment has been echoed for decades by researchers across the field of adsorption science.¹³⁻¹⁵

Currently the study of adsorbents for gas separations is dominated by the use of pure component adsorption data to predict how a mixture might be adsorbed by an adsorbent. A number of theories and predictive methods have been developed to predict adsorption equilibrium of mixtures from single component adsorption data, most notably the Ideal Adsorbed Solution Theory (IAST). IAST is becoming more widely used every year, as evidenced by the rapidly increasing number of citations of Myers and Prausnitz's 1965 work.¹⁶ In spite of its utility, IAST is not a perfect predictor of how gas mixtures will be adsorbed. A compilation of several dozen works using mixture adsorption experiments to assess IAST predictions showed that IAST is not always accurate, and in many cases results in errors greater than 100% in predicting selectivity for adsorption of one component from a mixture.¹⁵ This is consistent with findings by other authors that IAST tends to provide poor predictions of mixture adsorption for adsorbents with heterogeneous surfaces and for mixtures of molecules whose sizes, polarities, and polarizabilities vary greatly.^{17, 18}

Increased experimental capacity for multicomponent adsorption measurements will allow for faster identification of adsorbents which are selective for desired components even in mixtures whose composition varies widely. Furthermore, greater experimental capacity brings with it the opportunity to improve understanding of the fundamental phenomena that drive behaviors of multicomponent adsorbent systems. An obvious benefit of a better fundamental understanding of multicomponent adsorption is the opportunity to validate new predictive models for multicomponent adsorption, especially for systems which have not yet been well studied.¹²

The current state of the art in the study of gas adsorption is strong in development of novel materials with high capacities for target adsorbates, but weaker in the study of mixture adsorption and especially lacking in high-quality experimental measurement of mixture adsorption. Experimental measurement of mixture adsorption is nontrivial, and has represented a challenge for decades in the study of adsorption separations.¹⁹ Myriad measurement techniques using different principles have been used by groups spread throughout the world, with no consensus method emerging. Most methods of measurement are labor-intensive and difficult to automate. Moreover, no commercially available instrument has gained widespread popularity. The vast majority of measurements are made using home-built instrumentation, which can be costly as well as time-consuming to build and validate.

There are two broad categories of experimental systems: open systems and closed systems.¹³ Open systems generally involve flowing a gas mixture through a bed of adsorbent while monitoring the composition and flow rate of the feed and effluent streams. The system is considered "open" because gas moves in and out of the system during the measurement. The breakthrough method is the most popular open system used to study mixture adsorption.²⁰⁻²⁶ Open systems also include concentration pulse

chromatography,²⁷⁻³² zero-length column,³³⁻³⁵ differential column method,³⁶ and others.³⁷⁻³⁹ Open systems require careful determination of dead volume or holdup time, and at times require more involved analysis of experimental data to determine equilibrium loadings during an adsorption experiment.

Closed systems do not allow gas to enter or leave the system during adsorption experiments. Gas is discretely dosed into this closed system and allowed to contact the adsorbent. There are many types of closed systems. The most popular is the volumetric-chromatographic system, which evolved from volumetric systems introduced as early as 1917.⁴⁰⁻⁴⁸ Other closed systems make use of the gravimetric method,⁴⁹⁻⁵³ densimetric method,⁵⁴⁻⁵⁷ isotope exchange technique,^{58,59} and more.⁶⁰⁻⁶² Closed systems present a different set of challenges from open systems, but a perhaps underappreciated challenge is slow measurement equilibration in the absence of a pump to circulate gas through the adsorption loop. Adsorption equilibration can take days or weeks in the absence of a circulation pump like the one included in the system described in this work. In addition, slow and labor-intensive operation of most closed systems mean that this group of techniques can be extremely time-consuming to operate manually. One of the principal advantages of the system described in this work is that it is automated in full; after the adsorbent is activated, LabVIEW code allows the measurement to run completely automatically.

The variety of techniques that exist to study mixture adsorption reflects the fact that this measurement is inherently difficult. Many approaches have been tried without any one emerging as the clear favorite of the adsorption community. This is in large part because automation of any of these methods tends to be difficult, limiting each to slow, manual collection of data. A key opportunity for innovation in mixture adsorption measurement is the development and adoption of truly automated experimental systems. Much of the lack of existing experimental mixture adsorption data may be attributed to the labor-intensive nature of data collection for most existing instruments. Public availability of technical detail and validation processes for original mixture adsorption instruments is limited at best, and this lack of information in the literature contributes to a high barrier to entry in measuring adsorption of mixed gases. In this work, we aim to describe, in detail sufficient to facilitate replication, an automated instrument designed to measure adsorption of gas mixtures. We anticipate that this will reduce barriers to the construction and use of similar instruments to gather mixture adsorption data to address a decades-old deficit in the study of adsorption.

Experimental

Instrument Setup

1. Manifold

A schematic of the Multi-Component Gas Adsorption System (MC GAS) instrument developed in this work is illustrated in Figure 1. The bulk of this instrument consists of a stainless steel manifold composed of Swagelok tubing, valves, and fittings. The operation of this manifold and other parts of this system are automated through LabVIEW. The manifold is centered on a reference cell and adsorption loop, which are separated by a needle valve (Swagelok SS-ORS2) and ball valve (Swagelok SS-41GS1). The needle valve is left only slightly open so as to restrict the rate of flow between the reference cell and adsorption loop when the ball valve is open. The reference cell is an empty stainless steel cell (Swagelok 316L-HDF4-150). The adsorption loop contains an identical empty cell for the purpose of increasing the free volume of the adsorption loop. In addition to the empty cell, the adsorption loop also contains a smaller stainless steel sample cell (Swagelok 304L-HDF2-40) which can be filled with adsorbent pellets. This sample cell is connected to the adsorption loop on either end by VCR fittings, which contain 20 μm fritted gaskets (Swagelok SS-4-VCR-2-20M) to ensure the solid adsorbent material does not leave the sample cell during the adsorption measurement. All three of these steel cells (reference cell, empty cell, and sample

cell) are submerged in a water bath. The total internal volume of the reference cell is 154.48 cm³, while that of the adsorption loop devoid of adsorbent is 200.48 cm³. Where possible, all tubing outside of the thermostatic bath is of 1/16" (1.588 mm) outer diameter to minimize the volume of the reference cell and adsorption loop which is outside of this bath. The flexibility of this tubing allows the sample cell to be shifted from the water bath to the activation stage without disconnecting the sample cell from the adsorption loop.

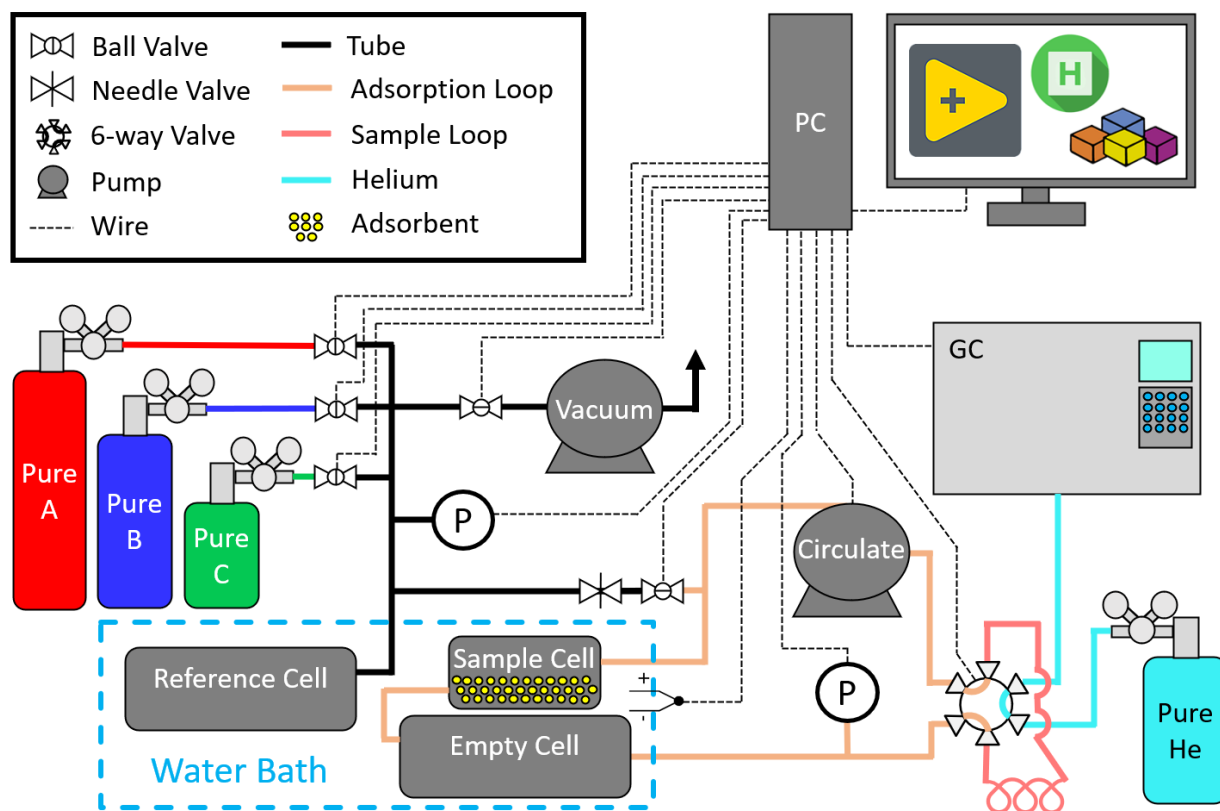


Figure 1: Schematic of the Multi-Component Gas Adsorption System (MC GAS) built in this work.

2. Pressure transducers and thermocouples

Connected to the reference cell is a pressure transducer (Omega PX01K1-1KGI) capable of measuring 0 to 1,000 psig (1 to 70 bar) accurate to $\pm 0.05\%$. The adsorption loop also contains a pressure transducer (Omega PX 409-USBH) capable of measuring 0 to 750 psia (0 to 52 bar) accurate to $\pm 0.08\%$. The temperature in the water bath is monitored by two type J thermocouples (Omega and PolyScience). The PolyScience thermocouple provides feedback to the water bath controller, while the Omega thermocouple provides data to LabVIEW which will later be used in equation of state calculations.

3. Temperature control

During adsorption measurements, all three steel cells are submerged in a water bath whose temperature is controlled by a heated/refrigerated recirculator (PolyScience AD07R-40-A11B) and varies less than ± 0.1 K during a 24 hour period. During adsorbent activation, the sample cell holding the adsorbent pellets is removed from the water bath and clamped in place on an activation stage. This cell, along with a third type J thermocouple, is then wrapped in heating tape (Omega) and an insulation jacket. The cell is heated with heating tape, while the thermocouple provides feedback to a virtual PID controller in

LabVIEW. The temperature varied less than ± 0.5 K from the set point during the 12 hour activation periods at 473 K used in this work.

4. Pneumatic actuators

All ball valves in the system are driven by pneumatic actuators (Whitey Co. 151SR), which are controlled through LabVIEW using solenoid valves (SMC SQ1131NY-5-C4-Q). This is conducive to automation of the system.

5. Circulation pump

A circulation pump (Eldex Optos 3HM) is included to recirculate gas through the adsorption loop and reduce time necessary to reach equilibration in mixture adsorption experiments. This pump can be turned on and off through LabVIEW. Typical mixture adsorption experiments use a flow rate of 10 mL/min and an equilibration time in excess of two hours. The pump operates on a positive displacement, reciprocating piston principle. The seal around the reciprocating piston is a possible source of leaks, and this concern could be avoided by using a welded metal bellows pump instead, though this may reduce the operating pressure of the instrument as the bellows can be limiting. If a reciprocating piston pump is chosen by future investigators, care should be taken to check this seal regularly for leaks and the user should be prepared to replace the seal as a consumable item. While the volume of displacement by the piston is small relative to the volume of the adsorption loop (0.41 cm^3 vs $\sim 200 \text{ cm}^3$), this reciprocation gives rise to small but measurable pressure fluctuations in the system. These fluctuations must be addressed in order to ensure collected data are of the highest accuracy for use in equation of state calculations. To address this problem, pressure data are averaged over two minutes (many cycles of piston reciprocation) before use in equation of state calculations so as to ensure this 0.41 cm^3 piston displacement change in volume does not impact calculations.

6. Vacuum pump

An Edwards RV3 rotary vane pump is used to evacuate the system. This pump is capable of evacuating the system down to approximately 0.1 mbar total pressure.

7. Gas chromatograph

Built into the adsorption loop is a small sample loop with volume approximately 20 μL . The contents of this sample loop can be injected to a gas chromatograph (GC), model Shimadzu GC-2014 for composition analysis. The detector is a TCD (Shimadzu TCD-2014). The chromatograph is equipped with a 6-port sampling valve (Valco 14N-0179V) controlled with electronic actuator (Valco) which allows for automation of composition sampling. For the experiments in this work, the chromatography column used was 2 m in length with 2 mm inner diameter and packed with carbon molecular sieve (Restek ShinCarbon ST 80/100 2m 2mmid). During the experiments in this work, the column was kept at 408 K while the TCD was kept at 418 K.

8. Automation

Automation of the instrument is done primarily using LabVIEW code and National Instruments hardware as shown in Figure 2. LabVIEW is used to record temperature data (through National Instruments NI-9211) and pressure data (National Instruments NI-9203), control valve positions (National Instruments NI-9375), operate virtual PID controller for heat tape, and trigger Windows scripts to operate Shimadzu software. LabVIEW also monitors pressure to determine when equilibration has been reached in the adsorption loop after gas has been dosed to the adsorbent.

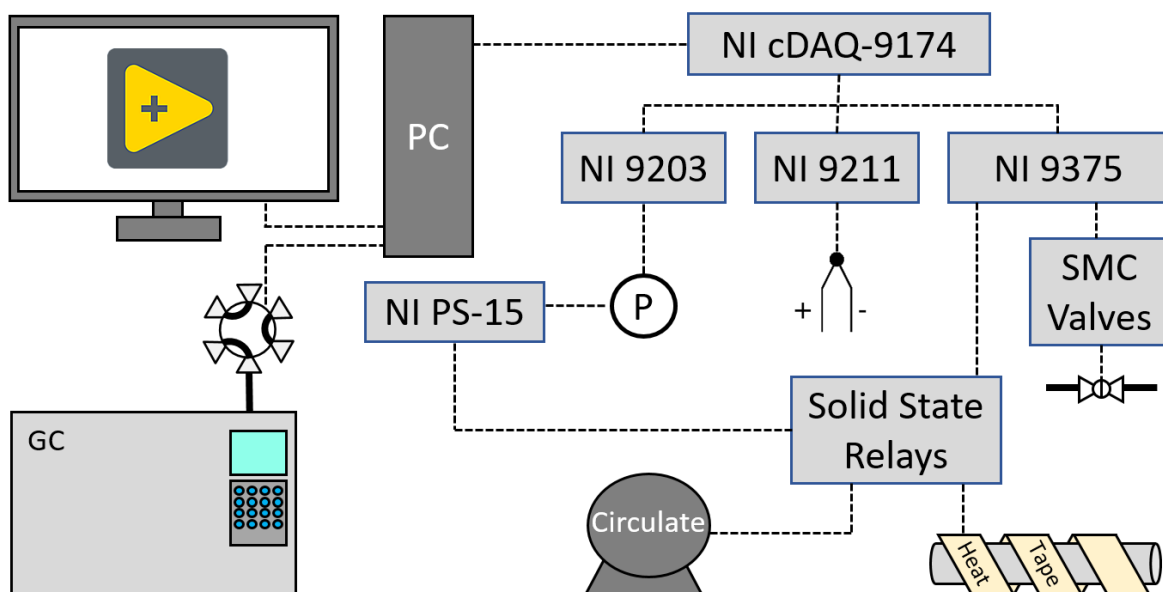


Figure 2: Schematic of how input and output are measured and controlled through LabVIEW.

Windows scripting is done through AutoHotKey, and functions to operate the Shimadzu LabSolutions software which controls the GC. When equilibrium is reached in the adsorption loop, LabVIEW calls a simple Windows script which opens LabSolutions and runs a pre-set injection program which allows for automated checking of the composition of gas in the adsorption loop.

The LabVIEW software operating MC GAS steps through a list of instructions during each experiment. Instructions controlling valve positions, temperature, and GC sampling are among those included in this list. A typical experiment can include thousands to tens of thousands of instructions. The list of instructions dictating the steps in each experiment is generated using Visual Basic for Applications (VBA) code based on a simple list of input variables like activation time and temperature, minimum equilibration time, and others. VBA code is used again after temperature, pressure, and composition data have been collected to iteratively solve the Peng-Robinson equation of state for mixtures to solve the molar volume of the gas mixture in the adsorption loop to determine the number of moles of each component in the gas phase and in the adsorbed phase.

9. Range of Operation

The operating ranges and conditions for MC GAS are summarized in Table 1. This instrument has been optimized for use with adsorbent samples approximately 5 g in mass, though larger sample masses may be required for testing adsorption of weakly adsorbing components, especially at low partial pressures. The volume of the 40 cm³ sample cell limits the maximum amount of sample that can be used, while the minimum sample mass is limited by the sensitivity of the GC and the adsorption affinity for each species as discussed in Calculation S3.

Table 1: Range of operating conditions available on MC GAS

Condition	Operating Range
Pressure during activation	< 0.0001 bar
Pressure during adsorption	0.1 – 20 bar

Temperature during activation	Tested up to 523 K
Temperature stability during activation	±0.5 K
Temperature during adsorption	253-333 K
Temperature stability during activation	±0.1 K
Adsorption loading of each component	≥ 0.01 mmol/g
Adsorbent mass	~5 g

Calibration

Calibration measurements must be made to ensure that the internal volume of the system is well known and the GC is properly calibrated to measure the composition of the mixture to be used in adsorption experiments.

1. Free volume measurement

The free volume of the reference cell and the adsorption loop must be known very precisely so as to be able to calculate the number of moles of gas present in each of these volumes during adsorption experiments. This can be done by evacuating both the reference cell and the adsorption loop, then filling the reference cell to a known pressure with a non-adsorbing gas, such as helium. Both volumes are held at 298 K in the water bath during this measurement, and no adsorbent is loaded into the adsorption loop. It is reasonable to assume that helium does not adsorb on the internal surfaces in the instrument at 298 K.^{43, 45} Once the reference cell has been filled and the adsorption loop remains evacuated, the pressure in the reference cell is recorded. Then the reference cell is opened to the adsorption loop and the pressure is recorded again. This measurement gives the ratio of the volume of the reference cell to that of the reference cell plus the adsorption loop. This measurement is repeated several times.

Assuming ideal gas behavior, we find that charging the reference cell with helium to P_0 and then opening the reference cell to the adsorption loop will result in final pressure P_1 . With the additional assumption that the number of moles of helium gas does not change, we can write equation 1. This equation can be rearranged to equation 2, which gives the ratio of the volume of the reference cell to that of the reference cell plus the adsorption loop. All variables are defined in Table S1 in the Supporting Information.

$$P_0 V_{RC} = n_0 RT = P_1 (V_{RC} + V_{AL}) \quad [1]$$

$$\frac{V_{RC}}{V_{RC} + V_{AL}} = \frac{P_1}{P_0} \quad [2]$$

After expanding helium from the reference cell into the empty and evacuated adsorption loop, the adsorption loop is packed with glass beads of known volume, and the helium expansion is repeated. This measurement gives the ratio of the volume of the reference cell to that of the adsorption loop filled with a known volume of glass beads. This gives two equations (2 and 4) with two unknowns (V_{RC} and V_{AL}) which can be solved simultaneously to determine the volume of both the reference cell and the adsorption loop.

$$P_2 V_{RC} = n_1 RT = P_3 (V_{RC} + V_{AL} - V_{beads}) \quad [3]$$

$$\frac{V_{RC}}{V_{RC} + V_{AL} - V_{beads}} = \frac{P_3}{P_2} \quad [4]$$

Once the volume of the reference cell is known, this experiment can be repeated with adsorbent loaded into the adsorption loop to give the free volume in the adsorption loop.

$$P_4 V_{RC} = n_2 RT = P_5 (V_{RC} + V_{AL} - V_{adsorbent}) \quad [5]$$

$$\frac{V_{RC}}{V_{RC}+V_{AL}-V_{adsorbent}} = \frac{P_5}{P_4} \quad [6]$$

2. GC calibration

Before this system can be used to measure the adsorption of gas mixtures, it must be capable of determining the composition of gas in the head space of the adsorption loop. This is done using a GC. This GC is calibrated using mass flow controllers (MKS PFC-50 μ MFC) to generate mixed streams of gases which are collected in a tube and then injected into the GC. The stated accuracy of these mass flow controllers is $\pm 0.2\%$ of full scale for the flow rates used in calibration ($< 20\%$ full scale). The GC peaks associated with each species are integrated for a variety of gas compositions, and the ratio of these GC peak areas is plotted against the molar composition of the gas from the mass flow controllers to form a calibration curve. The mass flow controllers used to generate the calibration mixtures are checked for accuracy by sampling their output with a mass spectrometer (Hiden DSMS HAL 201) and comparing main MS peak intensities for each species ($m/z = 16$ for methane and $m/z = 28$ for ethane).

Single component adsorption measurement

A typical single component adsorption measurement includes many of the steps necessary for a mixture adsorption measurement, so it is helpful to start with an understanding of this simpler process before moving on to the procedure for a mixture adsorption measurement. Each experiment can be broken into four steps: sample activation, free volume measurement, isotherm measurement, and finally use of an equation of state to convert pressure, volume, and temperature data (so-called ‘‘PVT’’ data) into excess amounts adsorbed.

1. Activation

Although the sample can be activated in situ, it is not possible to determine the dry mass of the sample in situ. To determine the dry mass of adsorbent used, approximately 1-5 grams of adsorbent pellets are first activated by heating under vacuum in a vacuum oven (Fisherbrand Isotemp 280A) for 24 hours and then weighed to determine their dry mass. Once the dry mass has been determined, the adsorbent is loaded into the sample cell of the instrument described in this work. The sample cell is clamped to the activation stage, where the sample cell and a thermocouple are wrapped in heating tape and then covered with an insulating jacket. The sample is then activated in situ under heat and vacuum. A typical activation might run for 12 hours at 473 K.

2. Free volume measurement

After activation, the free volume in the adsorption loop must be measured to ensure collection of high quality PVT data. This is done using the same helium expansion method outlined above. The reference cell is charged with helium, which is then expanded into the adsorption loop. This is repeated ten times to ensure precision.

3. Isotherm measurement

Single component adsorption is measured according to the well-known pressure decay principle.⁶³ First, gas is dosed to pressure P_0 into the reference cell, which has volume V_{RC} . The volume of this cell is well-known, and the pressure and temperature of this gas are recorded. This allows the use of the Peng-Robinson equation to calculate the number of moles of gas in the reference cell. The reference cell is then briefly opened to the adsorption loop before being closed again. As time passes, gas adsorbs on the adsorbent in the adsorption loop, and the pressure is observed to decay from its initial maximum. The system is allowed to equilibrate for a minimum of one hour, and for sufficient time that the pressure has stopped changing (rate of decrease less than 10 mbar/h). At this point, PVT data are recorded for both the reference cell and the adsorption loop. This allows calculation of number of moles of gas in both volumes. The number of moles adsorbed at the pressure in the adsorption loop can be taken to be the number of moles

that is “missing” from the gas phase. This is the first point of the isotherm. Then, the reference cell is charged to a higher pressure and the process is repeated several times to gather points for the rest of the isotherm.

Beginning with the step of filling the reference cell to pressure P_0 , one can use the Peng-Robinson equation in conjunction with a mole balance for each step of dosing gas to the adsorption loop and allowing time for equilibration. First, the Peng-Robinson equation is iteratively solved for V_{m0} , the molar volume of gas in the reference cell.⁶⁴ This equation is chosen for its mathematical simplicity.

$$P_0 = \frac{RT}{V_{m0}-b} - \frac{a}{V_{m0}(V_{m0}+b)+b(V_{m0}-b)} \quad [7]$$

Here, a and b are empirical constants specific to the adsorbate gas and differ in value for each gas used in this work:

$$a = 0.45724(R^2T_c^2/P_c)\alpha \quad [8]$$

$$b = 0.07780(RT_c/P_c) \quad [9]$$

Where

$$\alpha = (1 + m(1 - T_r^{1/2}))^2 \quad [10]$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad [11]$$

Where ω is defined as

$$\omega = -\log_{10}(P_r^*) - 1, \text{ at } T_r = 0.7 \quad [12]$$

Dividing the molar volume by the volume of the reference cell gives the number of moles in the reference cell, n_0 .

$$n_0 = \frac{V_{RC}}{V_{m,RC,0}} \quad [13]$$

This gives the initial number of moles charged into the reference cell. After the reference cell is opened to the adsorption loop and the system is allowed to equilibrate, some moles of gas remain in the reference cell, some move to the adsorption loop, and some are adsorbed onto the adsorbent. This mole balance is as follows:

$$n_1 = \frac{V_{RC}}{V_{m,RC,1}} + \frac{V_{AL}}{V_{m,AL,1}} + n_{ads} \quad [14]$$

There is no reaction in the system, so the number of moles of adsorbate remains constant, and it can be stated that:

$$\frac{V_{RC}}{V_{m,RC,0}} = \frac{V_{RC}}{V_{m,RC,1}} + \frac{V_{AL}}{V_{m,AL,1}} + n_{ads} \quad [15]$$

The Peng-Robinson equation can be solved for V_{m0} , V_{m1} , and V_{m2} using pressure and temperature data. The volumes V_{RC} and V_{AL} are known from the free space measurement. Therefore, equation 15 allows for the solution of the number of moles adsorbed the first time adsorbate is dosed to the adsorbent. For subsequent dosing of more adsorbate to collect more isotherm points, this equation may be modified to include the differential number of moles in each volume:

$$\left(\frac{V_{RC}}{V_{m,RC,0}} - \frac{V_{RC}}{V_{m,RC,1}} \right) = \left(\frac{V_{AL}}{V_{m,AL,1}} - \frac{V_{AL}}{V_{m,AL,0}} \right) + (n_{ads,1} - n_{ads,0}) \quad [16]$$

Equation 16 reduces to equation 15 in the case that $V_{m,AL,0}$ approaches infinity and $n_{ads,0}$ approaches zero, which is true when the adsorption loop is evacuated and the adsorbent is clean. Equation 16 is solved for $n_{ads,1}$ for each point in the isotherm.

Binary adsorption measurement

The procedure for measurement of binary mixture adsorption is very similar to that for single component adsorption. However, additional complexity arises from the needs to circulate gas over the adsorbent to achieve equilibration, sample the composition of the gas in the adsorption loop, and use a mixture equation of state for PVT calculations rather than a pure component equation of state.

The same sample activation and free volume measurement procedure are used for single component and binary adsorption measurements. Following the free volume measurement, the reference cell is charged with pure gas A. The PVT data for pure A in the reference cell are recorded, and then the reference cell is briefly opened to the adsorption loop. The number of moles of A adsorbed is calculated according to the same methodology used for single component adsorption. Then, the reference cell is evacuated and charged with pure gas B. Again, the reference cell is briefly opened to the adsorption loop. It is assumed that no gas flows back from the adsorption loop into the reference cell. This is reasonable as the pressure in the reference cell is always at least one bar higher than the adsorption loop when the two are connected, and the connection is made for a period of less than five seconds through a narrowly open needle valve in line with 1/16" (1.588 mm) OD tubing. The system is left to equilibrate while the circulation pump circulates gas through the adsorption loop. After at least three hours, or such time that the pressure in the adsorption loop is no longer decreasing, the composition of the gas in the adsorption loop is checked using the GC.

In addition to the temperature, pressure, and volume of the adsorption loop, the composition of the gas completes all of the data that are needed to use the Peng-Robinson equation of state for mixtures to calculate the number of moles each of A and B that are present in the gas phase in the adsorption loop. The difference between the number of moles of A and B dosed into the adsorption loop and the number of moles of each component remaining in the gas phase after equilibration is the quantity of each component that remains in the adsorbed phase. This is the first equilibrium mixture adsorption data point. It is assumed that this 20 μ L sample of gas is sufficiently small so as not to affect the adsorption measurement (See Calculation S1 in supplementary information). Thus, more points can be collected without re-activating the sample by simply charging more component B into the reference cell and then repeating the process of opening the reference cell to the adsorption loop and sampling the gas composition after equilibration has been reached.

After all pressure, temperature, volume, and gas composition data ("PVTy" data) have been collected, they are used to calculate the number of moles of A and B in the reference cell and in the adsorption loop during each measurement step. The same process used to track the moles of gas in each volume for single component adsorption measurements is applied to each gas for the binary adsorption measurement.

The experiment begins with a clean adsorbent and evacuated adsorption loop. The reference cell is charged to pressure P_0 with pure component A, so that the number of moles of A in the reference cell can be solved using the molar volume of A in the reference cell using the following expressions:

$$n_{A,0} = \frac{V_{RC}}{V_{m,A,RC,0}} \quad [17]$$

Notice this is equation 13 rewritten for component A alone. When opening the reference cell to the adsorption loop to allow component A to adsorb, this same approach follows with modifying equation 14 for component A:

$$n_{A,1} = \frac{V_{RC}}{V_{m,A,RC,1}} + \frac{V_{AL}}{V_{m,A,AL,1}} + n_{A,ads} \quad [18]$$

After allowing the system to equilibrate, the reference cell is evacuated and charged to P_2 with component B.

$$n_{B,2} = \frac{V_{RC}}{V_{m,B,RC,2}} \quad [19]$$

The reference cell is then opened to the adsorption loop again to allow component B to mix with the gas in the head space of the adsorption loop. This creates a gas mixture of A and B. After allowing sufficient time for equilibration, we can write independent mole balances for each A and B in the style of equation 15:

$$\left(\frac{V_{RC}}{V_{m,A,RC,0}} - \frac{V_{RC}}{V_{m,A,RC,1}} \right) = \left(\frac{V_{AL}}{V_{m,A,AL,1}} - \frac{V_{AL}}{V_{m,S,SL,0}} \right) + (n_{A,ads,1} - n_{A,ads,0}) \quad [20]$$

$$\left(\frac{V_{RC}}{V_{m,B,RC,0}} - \frac{V_{RC}}{V_{m,B,RC,1}} \right) = \left(\frac{V_{AL}}{V_{m,B,AL,1}} - \frac{V_{AL}}{V_{m,B,AL,0}} \right) + (n_{B,ads,1} - n_{B,ads,0}) \quad [21]$$

These equations can be used to solve the number of moles of A and B in the adsorbed phase at each step of a mixture adsorption measurement. However, some additional complexity arises in calculating the molar volume of the mixed gas. In this case, the van der Waals mixing rules are applied to the Peng-Robinson equation for each pair of species i and j in the gas phase:

$$a = \sum_i \sum_j y_i y_j (1 - \delta_{ij}) (a_i a_j)^{1/2} \quad [22]$$

$$b = \sum_i y_i b_i \quad [23]$$

The binary interaction parameter δ_{ij} in this work was taken from Fateen et al,⁶⁵ and used in calculating mole balances for each component (eq. 20-21) which give the adsorption loading at all equilibrium points in mixture adsorption experiments.

Validation experiments and results

Construction of a new instrument requires some validation of the measurement capabilities thereof. Though the measurement of gas mixture adsorption is frequently done using home-built apparatuses, this step is often omitted. In this work, validation is done twofold: once for measurement of pure component isotherms and separately for validation of binary mixture adsorption measurement. The strategy chosen was to compare single component isotherm measurements on the instrument constructed in this work both to measurements reported in the literature, and to measurements made on other trusted instruments in the lab. For multicomponent measurements, comparison was made to published results.

Choosing a system for validation was not trivial. Many systems use adsorbents synthesized in-house, and this adds a level of difficulty in first reproducing the adsorbent material. Many metal-organic frameworks are either subject to this difficulty, or to added difficulty from instability under humid conditions.^{66,67} Zeolites are a class of materials less subject to these challenges, but bring challenges of their own- activation conditions can require very high temperatures to remove adsorbed water molecules, which can have strong effects on adsorption properties.⁶⁸ For this work, BPL carbon was chosen as the adsorbent

for validation. This material has been available from Calgon for decades, is stable under humid conditions, and easily activated. The system chosen for this work was the adsorption of a methane/ethane mixture on BPL carbon. We have chosen to validate our instrument against the measurements made by He et al.²¹ This work was chosen for several reasons beyond simply the fact that these authors studied BPL carbon. These authors applied a number of thermodynamic consistency tests to their data. Moreover, they were successful in validating the single-component measurement capability of their instrument. We are confident that the data reported in this study are of the highest quality, and are suitable for use in the validation of the instrument constructed in this work.

Materials

BPL carbon, 4x6 mesh, was generously supplied by Calgon corporation. All gases used were purchased from AirGas in the following purities: nitrogen- 99.999%, helium- 99.999%, methane- 99.99%, ethane- 99.99%.

Pure component adsorption

The BPL carbon used in this work had BET surface area of 1135 m²/g and average pore size of 10.9 Å, measured by nitrogen physisorption at 77 K on a Quadrasorb by Quantachrome. BET area was calculated using adsorption in the linear range of the BET plot where 0.01 < P/P₀ < 0.2. Pore size distribution was calculated using the density functional theory (DFT) method. These values are very similar to those reported by He et al, which were 1061 m²/g BET surface area and 10.2 Å average pore size.²¹ The BPL carbon used in this work is, by initial inspection, similar to that used by He et al.

The first step in validating the instrument built in this work was measurement of pure component isotherms for methane and ethane for comparison with in-house instruments (Hiden Isochema IGA-003 and Micromeritics 3Flex) and measurements by He et al also using BPL carbon from Calgon.²¹ These measurements are shown in Figure 3. The measurements shown from MC GAS correspond to the first of the three replicates in Tables S2 and S5.

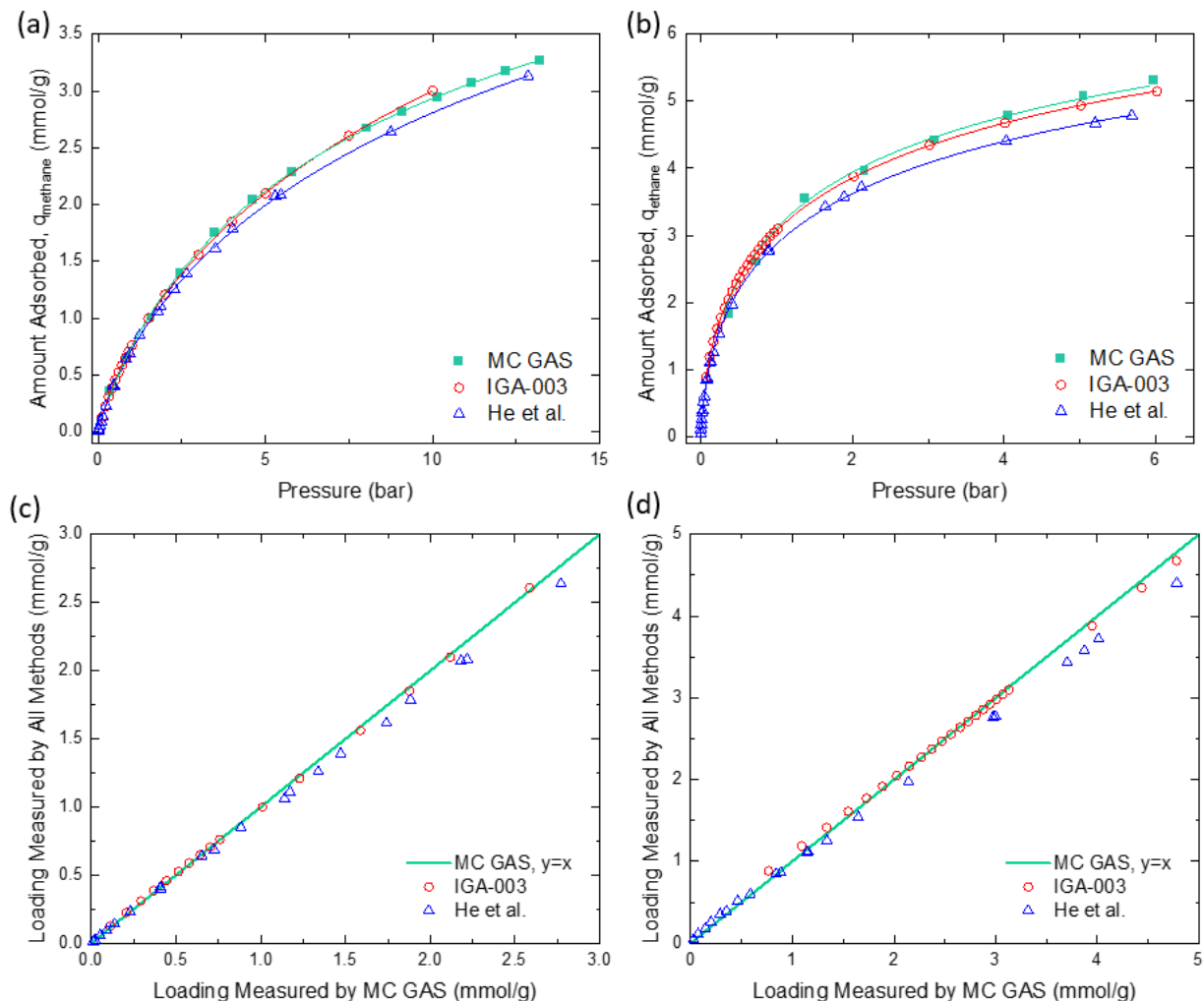


Figure 3. Single component adsorption of methane and ethane compared to measurements on IGA-003 and by He et al. 2004. (a) Methane adsorption isotherms on BPL carbon at 301.4 K. (b) Ethane adsorption isotherms on BPL carbon at 301.4 K. (c) Difference in methane loading of three measurements compared to loading measured by MC GAS. (d) Difference in ethane loading of three measurements compared to loading measured by MC GAS.

Measurements from the instrument built in this work agree with measurements made on IGA-003. Loadings are slightly higher in both instruments compared to that reported by He et al., but the difference is not large. This difference could be attributed in part to the higher surface area of the BPL carbon used in this work ($1124 \text{ m}^2/\text{g}$) compared to that used by He et al. ($1061 \text{ m}^2/\text{g}$). These results validate the capability of the instrument built in this work to measure single component adsorption.

Binary mixture adsorption

The problem of validating mixture adsorption capabilities offers several challenges beyond those of validating single component adsorption capabilities. The nature of the volumetric apparatus for mixture adsorption means that it is impossible to directly control the pressure and composition of the gas phase at equilibrium. Thus, it is difficult to precisely replicate mixture adsorption points reported in other works. However, because the volume of the adsorption loop in this work and the loading of the adsorbent in the reference work are known, it should be possible to replicate points to some extent. Knowledge of the volume

of the adsorption loop allows calculation of the number of moles of each component that should be in the gas phase at equilibrium to match the partial pressure of each component at equilibrium in the reference work. If we assume that the loadings of each component are likely to be similar to the reference work, we can also estimate the number of moles of each component that will be present in the adsorbed phase. By precisely dosing the number of moles of each component that sums to satisfy both the partial pressure of that component in the gas phase and the loading of that component in the adsorbed phase at equilibrium, we can ensure that the system can reach an equilibrium very close to any data point reported in another work.

This of course does not ensure the same equilibrium will be reached, merely that those conditions could be reached. Efforts to replicate measurements of binary mixture adsorption reported by He et al. for adsorption of methane and ethane on BPL carbon have been successful considering this inherent difficulty. These results of He et al. are presented in Table 2, while the replication of these results using MC GAS is shown in Table 3. Adsorption loadings are shown in Figure 4(a) and 4(b) while selectivity values are shown in Figure 4(c) and 4(d).

Table 2: Mixture adsorption loadings and compositions for adsorption of methane and ethane on BPL carbon at 301.4 K, measured by He et al.

P (bar)	y ethane ^a	x ethane ^b	q ethane ^c (mmol/g)	q methane ^c (mmol/g)	ethane/methane Selectivity
1.96	0.97	0.996	3.61	0.01	8.4
1.97	0.73	0.972	3.25	0.09	12.7
1.96	0.51	0.930	2.78	0.21	12.7
1.97	0.28	0.861	2.15	0.35	15.6
6.84	0.97	0.996	4.97	0.02	7.4
6.83	0.73	0.965	4.53	0.17	9.9
6.84	0.51	0.918	4.04	0.36	10.8
6.83	0.28	0.826	3.19	0.67	12.0
6.84	0.09	0.571	1.75	1.32	12.8
6.85	0.03	0.308	0.81	1.82	14.4

y = gas phase mole fraction x = adsorbed phase mole fraction q = adsorption loading

Table 3: Mixture adsorption loadings and compositions for adsorption of methane and ethane on BPL carbon at 301.4 K, measured in this work

P (bar)	y ethane ^a	x ethane ^b	q ethane ^c (mmol/g)	q methane ^c (mmol/g)	ethane/methane Selectivity
1.93	0.94	0.992	3.68	0.03	7.8
1.94	0.72	0.963	3.38	0.13	10.1
1.97	0.59	0.947	3.01	0.17	12.4
2.04	0.35	0.906	2.40	0.25	17.7
1.98	0.04	0.412	0.57	0.81	16.8
7.02	0.72	0.960	5.10	0.21	9.6
6.92	0.49	0.915	4.56	0.42	11.2
6.77	0.14	0.698	2.63	1.14	14.0
6.74	0.11	0.669	2.33	1.15	15.5

y = gas phase mole fraction x = adsorbed phase mole fraction q = adsorption loading

Efforts to replicate mixture adsorption reported by He et al. show a relatively small difficulty in replicating equilibrium pressure, and a larger difficulty in replicating gas phase composition. This is

reflective of the nature of closed volumetric adsorption instruments. However, despite this difficulty there is good agreement in amounts adsorbed for each species at similar pressures and gas phase compositions. Furthermore, in rows 1 and 5 of Table 3, it is apparent that the amounts adsorbed of each species approaches the pure component loading as the gas phase composition approaches its endpoints. As can be seen in Figure 4, the experimental data cross the thermodynamically consistent IAST model at least once across measurements at both pressures.

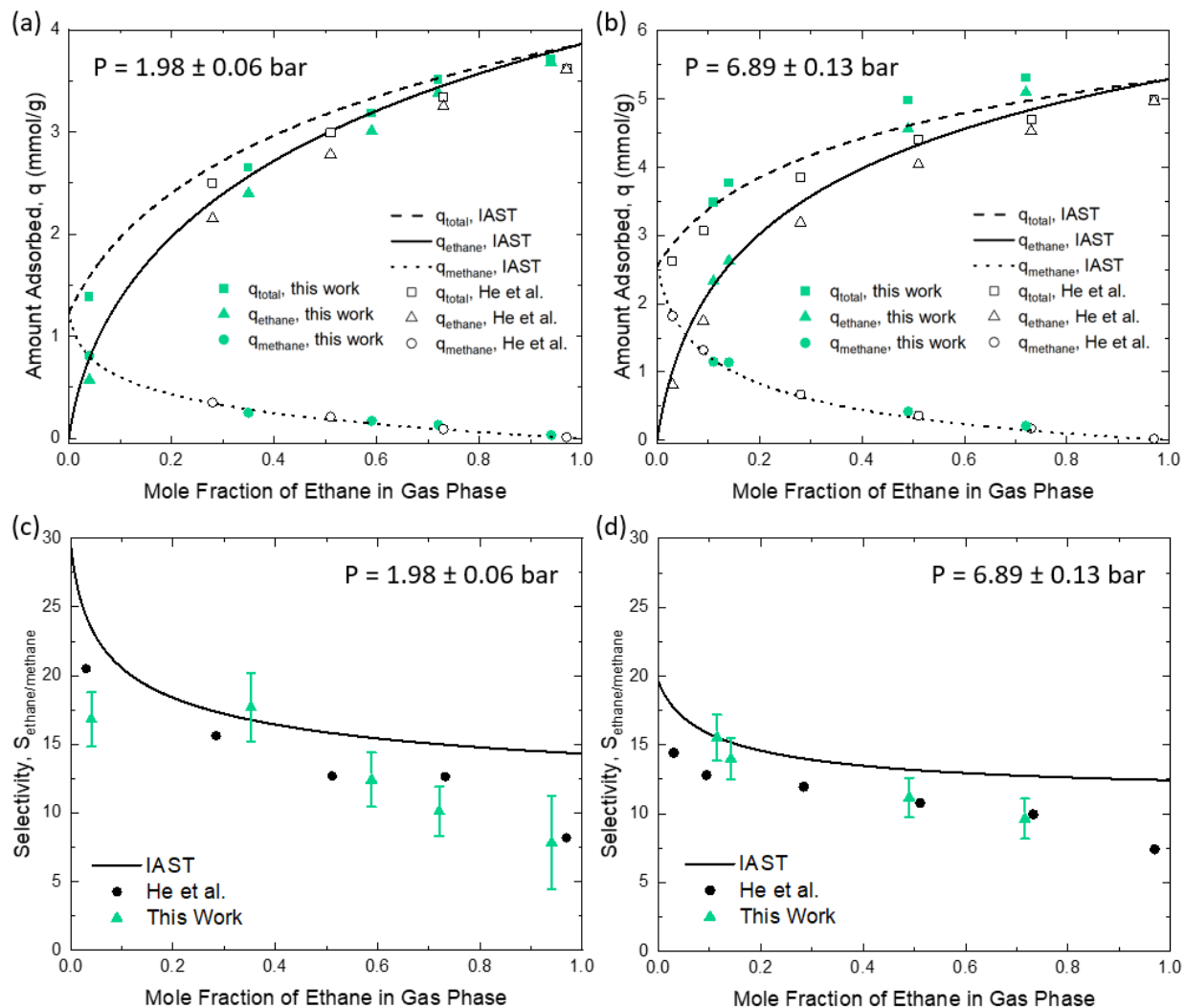


Figure 4: Binary adsorption measurements of methane/ethane mixtures on BPL carbon at 301.4 K. (a) Amounts adsorbed at 1.98 ± 0.06 bar. (b) Amounts adsorbed at 6.89 ± 0.13 bar. (c) Selectivity for ethane at 1.98 ± 0.06 bar. (d) Selectivity for ethane at 6.89 ± 0.13 bar.

There is generally good agreement between IAST and experiment for loading of each component, as shown in Figure 4 (a-b). This is consistent with the findings of He et al. However, small differences between IAST and experiment are amplified in the calculation for selectivity. It has been noted by other authors that small uncertainties in amounts adsorbed lead to large uncertainties in selectivity.¹⁴ Error bars in selectivity are calculated by propagation of experimental uncertainty as shown in Calculation S2.⁶⁹ Nearly all of this uncertainty comes from uncertainty in the loading of methane, the more weakly adsorbed component. Uncertainty in selectivity is most noticeable when the amount of methane adsorbed is very low.

This is especially evident in Figure 4 (c) where the rightmost data point measured in this work has large uncertainty as the adsorbed phase for this measurement contains very little methane. Furthermore, measurement at lower pressures is generally more difficult than at higher pressures because amounts adsorbed are lower at lower pressures. This can likely explain the relatively larger scatter of the selectivities measured in this work and those measured by He et al shown in Figure 4 (c). The problem of high fractional uncertainty in loading of the more weakly adsorbed component is not unique to the instrument used in this work. This problem is not easily solved in other mixture adsorption measurement techniques, and can be especially evident when calculating selectivity for very selective adsorption, as can be the case in carbon dioxide capture applications.⁷⁰

Mixture adsorption equilibrium measurements are extremely difficult and prone to many more sources of error than single component adsorption measurements. Thermodynamic consistency tests for binary mixture adsorption have been developed by Talu et al.^{9,71} to ensure internal consistency among a set of single component and mixture adsorption data. While these tests do not assure the accuracy of the data collected, consistency within a data set increases confidence that the data are accurate. There are numerous ways to assess the consistency of mixture adsorption equilibrium data, and we have employed the following tests:

1. At fixed temperature and pressure, the total amount adsorbed must equal the single component values at the composition end points. (Tables 2 and 3).
2. At fixed temperature and pressure, the x-y and selectivity curves of all thermodynamically consistent models must cross the experimental curves at least once (Figure 4).

These binary adsorption data meet these thermodynamic consistency criteria. While this does not in itself prove that these data are correct, the combination of agreement with the high quality data of He et al. and the satisfaction of these two thermodynamic consistency criteria validate this instrument as capable of measuring binary adsorption equilibria for light gases. Further validation measurements could be necessary for experiments with heavier components like water vapor. The instrument MC GAS developed in this work is fully automated and capable of repeatable, high-throughput measurements of binary mixture adsorption. The full automation of this instrument vastly increases the speed of data collection and available operating time relative to comparable manually operated systems.

While the strength of this instrument lies in its automation, the process of automation is not totally without drawbacks. By its nature, the closed volumetric system in this work does not give the user control over the equilibrium pressure at each adsorption measurement point. This problem has been solved by others who have used manostats, or carefully calibrated pistons, to adjust the internal volume of the instrument during measurements to allow equilibration at a pre-determined pressure.^{72, 73} Automation of a manostat is certainly possible and could be implemented as a future improvement to this instrument or others like it. In addition, the circulation pump used in this work could be replaced with a bellows pump to reduce potential for leaks during experiments. This instrument could also benefit from a single temperature control device. While the use of heating tape during sample activation and a water bath during adsorption measurements was sufficient to reach high activation temperatures and also hold temperature very stable during adsorption measurements, a single temperature control mechanism like an oil bath could achieve both of these goals and eliminate the need for two temperature controllers.

Conclusion

We have developed and validated an automated volumetric instrument for the measurement of binary gas mixture adsorption. The validation of this instrument has been completed by comparison of single component and binary adsorption measurements with data available in the literature, as well as single

component adsorption measurements made in-house on commercially available instruments. We expect that the level of technical description here will allow for replication of this type of instrument, which will more widely enable the study of binary mixture adsorption and thereby address a major weakness in the study of adsorption separations.

Supplementary material

Definitions for all variables used in the equations presented in this paper are listed in Table S1 of the supplementary material. Tables of methane, ethane, and nitrogen adsorption isotherm data are presented in Tables S2-S8. Figures of methane and ethane adsorption isotherms are also included (Figures S1 and S2). Sample calculations outlining the choice of the volume of gas samples and the mass of adsorbent samples and for determining the propagation of uncertainty in mixture adsorption measurements are also included (Calculation S1 — S3).

Acknowledgements

This material is based upon work supported by the U.S. Department of Energy, under RAPID Subaward DE-EE0007888-9.6 (DS) and by the National Science Foundation under grant no. IIP-1701025 (BM).

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

1. Ben-Mansour, R.; Habib, M. A.; Bamidele, O. E.; Basha, M.; Qasem, N. A. A.; Peedikakkal, A.; Laoui, T.; Ali, M., Carbon capture by physical adsorption: Materials, experimental investigations and numerical modeling and simulations – A review. *Applied Energy* **2016**, *161*, 225-255.
2. Yu, C.-H.; Huang, C.-H.; Tan, C.-S., A Review of CO₂ Capture by Absorption and Adsorption. *Aerosol and Air Quality Research* **2012**, *12* (5), 745-769.
3. Chaffee, A. L.; Knowles, G. P.; Liang, Z.; Zhang, J.; Xiao, P.; Webley, P. A., CO₂ capture by adsorption: Materials and process development. *International Journal of Greenhouse Gas Control* **2007**, *1* (1), 11-18.
4. Shah, M. S.; Tsapatsis, M.; Siepmann, J. I., Hydrogen Sulfide Capture: From Absorption in Polar Liquids to Oxide, Zeolite, and Metal–Organic Framework Adsorbents and Membranes. *Chemical Reviews* **2017**, *117* (14), 9755-9803.
5. Shah, M. S.; Tsapatsis, M.; Siepmann, J. I., Identifying Optimal Zeolitic Sorbents for Sweetening of Highly Sour Natural Gas. *Angewandte Chemie International Edition* **2016**, *55* (20), 5938-5942.
6. Tagliabue, M.; Rizzo, C.; Onorati, N. B.; Gambarotta, E. F.; Carati, A.; Bazzano, F., Regenerability of zeolites as adsorbents for natural gas sweetening: A case-study. *Fuel* **2012**, *93*, 238-244.
7. Pan, M.; Omar, H. M.; Rohani, S., Application of Nanosize Zeolite Molecular Sieves for Medical Oxygen Concentration. *Nanomaterials* **2017**, *7* (8), 195.
8. Mathias, P. M.; Kumar, R.; Moyer, J. D.; Schork, J. M.; Srinivasan, S. R.; Auvil, S. R.; Talu, O., Correlation of multicomponent gas adsorption by the dual-site Langmuir model. Application to nitrogen/oxygen adsorption on 5A-zeolite. *Industrial and Engineering Chemistry Research* **1996**, *35* (7), 2477-2483.
9. Talu, O.; Li, J.; Kumar, R.; Mathias, P. M.; Moyer, J. D.; Schork, J. M., Measurement and analysis of oxygen/nitrogen/ 5A-zeolite adsorption equilibria for air separation. *Gas Separation & Purification* **1996**, *10* (3), 149-159.

10. Lin, R.-B.; Li, L.; Zhou, H.-L.; Wu, H.; He, C.; Li, S.; Krishna, R.; Li, J.; Zhou, W.; Chen, B., Molecular sieving of ethylene from ethane using a rigid metal–organic framework. *Nature Materials* **2018**, *17* (12), 1128-1133.
11. Wu, Y.; Chen, H.; Liu, D.; Qian, Y.; Xi, H., Adsorption and separation of ethane/ethylene on ZIFs with various topologies: Combining GCMC simulation with the ideal adsorbed solution theory (IAST). *Chemical Engineering Science* **2015**, *124*, 144-153.
12. National Academies of Sciences, Engineering, and Medicine 2019. A Research Agenda for Transforming Separation Science. Washington, DC: The National Academies Press.
<https://doi.org/10.17226/25421>.
13. Walton, K. S., 110th Anniversary: Commentary: Perspectives on Adsorption of Complex Mixtures. *Industrial & Engineering Chemistry Research* **2019**, *58* (37), 17100-17105.
14. Talu, O., Needs, status, techniques and problems with binary gas adsorption experiments. *Advances in Colloid and Interface Science* **1998**, *76-77*, 227-269.
15. Wu, C.-W.; Sircar, S., Comments on binary and ternary gas adsorption selectivity. *Separation and Purification Technology* **2016**, *170*, 453-461.
16. Myers, A. L.; Prausnitz, J. M., Thermodynamics of mixed-gas adsorption. *AIChE Journal* **1965**.
17. Walton, K.; Sholl, D., Predicting Multicomponent Adsorption: 50 Years of the Ideal Adsorbed Solution Theory. *AIChE Journal* **2015**, *61* (504), 2757-2762.
18. Cessford, N. F.; Seaton, N. A.; Düren, T., Evaluation of Ideal Adsorbed Solution Theory as a Tool for the Design of Metal–Organic Framework Materials. *Industrial & Engineering Chemistry Research* **2012**, *51* (13), 4911-4921.
19. Talu, O., Measurement and Analysis of Mixture Adsorption Equilibrium in Porous Solids. *Chemie Ingenieur Technik* **2011**, *83* (1-2), 67-82.
20. Van Assche, T. R. C.; Duerinck, T.; Van der Perre, S.; Baron, G. V.; Denayer, J. F. M., Prediction of Molecular Separation of Polar–Apolar Mixtures on Heterogeneous Metal–Organic Frameworks: HKUST-1. *Langmuir* **2014**, *30* (26), 7878-7883.

21. He, Y.; Yun, J.-H.; Seaton, N. A., Adsorption Equilibrium of Binary Methane/Ethane Mixtures in BPL Activated Carbon: Isotherms and Calorimetric Heats of Adsorption. *Langmuir* **2004**, *20* (16), 6668-6678.
22. Wu, Y.-J.; Yang, Y.; Kong, X.-M.; Li, P.; Yu, J.-G.; Ribeiro, A. M.; Rodrigues, A. E., Adsorption of Pure and Binary CO₂, CH₄, and N₂ Gas Components on Activated Carbon Beads. *Journal of Chemical & Engineering Data* **2015**, *60* (9), 2684-2693.
23. Habgood, H. W., The kinetics of molecular sieve action. Sorption of nitrogen-methane mixtures by Linde molecular sieve 4A. *Canadian Journal of Chemistry* **1958**, *36* (10), 1384-1397.
24. Zandvoort, I. v.; Ras, E.-J.; Graaf, R. d.; Krishna, R., Using transient breakthrough experiments for screening of adsorbents for separation of C₂H₄/CO₂ mixtures. *Separation and Purification Technology* **2020**, *241*, 116706.
25. Shang, S.; Tao, Z.; Yang, C.; Hanif, A.; Li, L.; Tsang, D. C. W.; Gu, Q.; Shang, J., Facile synthesis of CuBTC and its graphene oxide composites as efficient adsorbents for CO₂ capture. *Chemical Engineering Journal* **2020**, *393*, 124666.
26. Goyal, P.; Purdue, M. J.; Farooq, S., Adsorption and diffusion of moisture and wet flue gas on silica gel. *Chemical Engineering Science* **2020**, *227*, 115890.
27. van der Vlist, E.; van der Meijden, J., Determination of adsorption isotherms of the components of binary gas mixtures by gas chromatography. *Journal of Chromatography A* **1973**, *79*, 1-13.
28. Ruthven, D. M.; Kumar, R., An Experimental Study of Single-Component and Binary Adsorption Equilibria by a Chromatographic Method. *Industrial & Engineering Chemistry Fundamentals* **1980**, *19* (1), 27-32.
29. Triebe, R. W.; Tezel, F. H., Adsorption of nitrogen and carbon monoxide on clinoptilolite: Determination and prediction of pure and binary isotherms. *The Canadian Journal of Chemical Engineering* **1995**, *73* (5), 717-724.
30. Harlick, P. J. E.; Tezel, F. H., A Novel Solution Method for Interpreting Binary Adsorption Isotherms from Concentration Pulse Chromatography Data. *Adsorption* **2000**, *6* (4), 293-309.

31. Han, Q.-J.; Wu, H.-L.; Cai, C.-B.; Tang, L.-J.; Yu, R.-Q., Using near-infrared spectroscopy and differential adsorption bed method to study adsorption kinetics of orthoxylene on silica gel. *Talanta* **2008**, *76* (4), 752-757.
32. Kennedy, D.; Handan Tezel, F., Improved method for determining binary adsorption isotherms by using concentration pulse chromatography: adsorption of CO₂ and N₂ by silicalite at different pressures. *Adsorption* **2014**, *20* (1), 189-199.
33. Brandani, F.; Ruthven, D., Measurement of Adsorption Equilibria by the Zero Length Column (ZLC) Technique Part 2: Binary Systems. *Industrial & Engineering Chemistry Research* **2003**, *42* (7), 1462-1469.
34. Eic, M.; Ruthven, D. M., A new experimental technique for measurement of intracrystalline diffusivity. *Zeolites* **1988**, *8* (1), 40-45.
35. Brandani, F.; Ruthven, D. M., The Effect of Water on the Adsorption of CO₂ and C₃H₈ on Type X Zeolites. *Ind. Eng. Chem. Res.* **2004**, *43* (26), 8339-8344.
36. Shirani, B.; Eic, M., Novel Differential Column Method for Measuring Multicomponent Gas Adsorption Isotherms in NaY Zeolite. *Ind. Eng. Chem. Res.* **2017**, *56* (4), 1008-1018.
37. Danner, R. P.; Nicoletti, M. P.; Al-Ameeri, R. S., Determination of gas mixture adsorption equilibria by the tracer-pulse technique. *Chemical Engineering Science* **1980**, *35* (10), 2129-2133.
38. Ohlin, L.; Grahn, M., Detailed Investigation of the Binary Adsorption of Carbon Dioxide and Methane in Zeolite Na-ZSM-5 Studied Using in Situ ATR-FTIR Spectroscopy. *The Journal of Physical Chemistry C* **2014**, *118* (12), 6207-6213.
39. Bajusz, I.-G.; Goodwin, J. G.; Galloway, D.; Greenlay, N., Isotopic Transient Study of Multicomponent N₂ and O₂ Adsorption on CaX Zeolite. *Langmuir* **1998**, *14* (7), 1846-1852.
40. Mollmer, J.; Lange, M.; Moller, A.; Patzschke, C.; Stein, K.; Lassig, D.; Lincke, J.; Glaser, R.; Krautscheid, H.; Staudt, R., Pure and mixed gas adsorption of CH₄ and N₂ on the metal-organic framework Basolite A100 and a novel copper-based 1,2,4-triazolyl isophthalate MOF. *Journal of Materials Chemistry* **2012**, *22* (20), 10274-10286.

41. Siperstein, F. R.; Myers, A. L., Mixed-gas adsorption. *AIChE Journal* **2001**, *47* (5), 1141-1159.
42. Siperstein, F.; Gorte, R. J.; Myers, A. L., A New Calorimeter for Simultaneous Measurements of Loading and Heats of Adsorption from Gaseous Mixtures. *Langmuir* **1999**, *15* (4), 1570-1576.
43. Mofarahi, M.; Bakhtyari, A., Experimental Investigation and Thermodynamic Modeling of CH₄/N₂ Adsorption on Zeolite 13X. *Journal of Chemical & Engineering Data* **2015**, *60* (3), 683-696.
44. Bazan, R. E.; Bastos-Neto, M.; Staudt, R.; Papp, H.; Azevedo, D. C. S.; Cavalcante, C. L., Adsorption Equilibria of Natural Gas Components on Activated Carbon: Pure and Mixed Gas Isotherms. *Adsorption Science & Technology* **2008**, *26* (5), 323-332.
45. Rios, R. B.; Stragliotto, F. M.; Peixoto, H. R.; Torres, A. E. B.; Bastos-Neto, M.; Azevedo, D. C. S.; Cavalcante Jr, C. L., Studies on the adsorption behavior of CO₂-CH₄ mixtures using activated carbon. *Brazilian Journal of Chemical Engineering* **2013**, *30*, 939-951.
46. Wang, Y.; LeVan, M. D., Adsorption Equilibrium of Binary Mixtures of Carbon Dioxide and Water Vapor on Zeolites 5A and 13X. *Journal of Chemical & Engineering Data* **2010**, *55* (9), 3189-3195.
47. Liu, J.; Wang, Y.; Benin, A. I.; Jakubczak, P.; Willis, R. R.; LeVan, M. D., CO₂/H₂O Adsorption Equilibrium and Rates on Metal–Organic Frameworks: HKUST-1 and Ni/DOBDC. *Langmuir* **2010**, *26* (17), 14301-14307.
48. Richardson, L. B., The adsorption of carbon dioxide and ammonia by charcoal. *Journal of the American Chemical Society* **1917**, *39* (9), 1828-1848.
49. Keller, J. U.; Staudt, R.; Tomalla, M., Volume-Gravimetric Measurements of Binary Gas Adsorption Equilibria. *Berichte der Bunsengesellschaft für physikalische Chemie* **1992**, *96* (1), 28-32.
50. Cermakova, J. R.; Markovic, A.; Uchytíl, P.; Seidel-Morgenstern, A., Single component and competitive adsorption of propane, carbon dioxide and butane on Vycor glass. *Chemical Engineering Science* **2008**, *63* (6), 1586-1601.
51. Lafortune, S.; Adelise, F.; Bentivegna, G.; Didier, C.; Farret, R.; Gombert, P.; Lagny, C.; Pokryszka, Z.; Toimil, N. C., An experimental approach to adsorption of CO₂ + CH₄ gas mixtures onto

- coal. In *12th International Conference on Greenhouse Gas Control Technologies, Ghgt-12*, Dixon, T.; Herzog, H.; Twinning, S., Eds. Elsevier Science Bv: Amsterdam, 2014; Vol. 63, pp 5870-5878.
52. Schell, J.; Casas, N.; Pini, R.; Mazzotti, M., Pure and binary adsorption of CO₂, H₂, and N₂ on activated carbon. *Adsorption-Journal of the International Adsorption Society* **2012**, *18* (1), 49-65.
53. Pini, R.; Ottiger, S.; Storti, G.; Mazzotti, M., Pure and competitive adsorption of CO₂, CH₄ and N₂ on coal for ECBM. *Energy Procedia* **2009**, *1* (1), 1705-1710.
54. Dreisbach, F.; Seif A. H., R.; Lösch, H. W., Gravimetric Measurement of Adsorption Equilibria of Gas Mixture CO/H₂ with a Magnetic Suspension Balance. *Chemical Engineering & Technology* **2002**, *25* (11), 1060-1065.
55. Dreisbach, F.; Seif, R.; Lösch, H. W., Adsorption equilibria of CO/H₂ with a magnetic suspension balance: Purely gravimetric measurement. *Journal of Thermal Analysis and Calorimetry* **2003**, *71* (1), 73-82.
56. Belmabkhout, Y.; Sayari, A., Adsorption of CO₂ from dry gases on MCM-41 silica at ambient temperature and high pressure. 2: Adsorption of CO₂/N₂, CO₂/CH₄ and CO₂/H₂ binary mixtures. *Chemical Engineering Science* **2009**, *64* (17), 3729-3735.
57. Mittelmeijer-Hazeleger, M. C.; Ferreira, A. F. P.; Blik, A., Influence of Helium and Argon on the Adsorption of Alkanes in Zeolites. *Langmuir* **2002**, *18* (25), 9613-9616.
58. Rynders, R. M.; Rao, M. B.; Sircar, S., Isotope exchange technique for measurement of gas adsorption equilibria and kinetics. *AIChE Journal* **1997**, *43* (10), 2456-2470.
59. Kloutse, F. A.; Hourri, A.; Natarajan, S.; Benard, P.; Chahine, R., Experimental benchmark data of CH₄, CO₂ and N₂ binary and ternary mixtures adsorption on MOF-5. *Separation and Purification Technology* **2018**, *197*, 228-236.
60. Graham, P.; Hughes, A. D.; Rees, L. V. C., Sorption of binary gas mixtures in zeolites. **1989**, *3* (2), 56-64.

61. Hampson, J. A.; Rees, L. V. C., Adsorption of ethane and propane in silicalite-1 and zeolite NaY: determination of single components, mixture and partial adsorption data using an isosteric system. *Journal of the Chemical Society, Faraday Transactions* **1993**, 89 (16), 3169.
62. Rees, L. V. C., Sorption and Separation of Binary Mixtures of CH₄, N₂ and CO₂ in Zeolites. In *Catalysis and Adsorption by Zeolites*, Öhlmann, G.; Pfeifer, H.; Fricke, R., Eds. Elsevier: 1991; Vol. 65, pp 61-74.
63. Koros, W. J.; Paul, D. R., Design considerations for measurement of gas sorption in polymers by pressure decay. *Journal of Polymer Science: Polymer Physics Edition* **1976**, 14 (10), 1903-1907.
64. Peng, D.-Y.; Robinson, D. B., A New Two-Constant Equation of State. *Industrial & Engineering Chemistry Fundamentals* **1976**, 15 (1), 59-64.
65. Fateen, S.-E. K.; Khalil, M. M.; Elnabawy, A. O., Semi-empirical correlation for binary interaction parameters of the Peng–Robinson equation of state with the van der Waals mixing rules for the prediction of high-pressure vapor–liquid equilibrium. *Journal of Advanced Research* **2013**, 4 (2), 137-145.
66. Huang, L., Synthesis, morphology control, and properties of porous metal–organic coordination polymers. *Microporous and Mesoporous Materials* **2003**, 58 (2), 105-114.
67. Schoenecker, P. M.; Carson, C. G.; Jasuja, H.; Flemming, C. J. J.; Walton, K. S., Effect of Water Adsorption on Retention of Structure and Surface Area of Metal–Organic Frameworks. *Industrial & Engineering Chemistry Research* **2012**, 51 (18), 6513-6519.
68. Ohlin, L.; Berezovsky, V.; Öberg, S.; Farzaneh, A.; Holmgren, A.; Grahn, M., Effect of Water on the Adsorption of Methane and Carbon Dioxide in Zeolite Na-ZSM-5 Studied Using in Situ ATR-FTIR Spectroscopy. *The Journal of Physical Chemistry C* **2016**, 120 (51), 29144-29152.
69. Ku, H. H., Notes on the Use of Propagation of Error Formulas. *Journal of Research of the National bureau of Standards - C. Engineering and Instrumentation* **1966**, 70C (4), 263-273.
70. Billemont, P.; Heymans, N.; Normand, P.; De Weireld, G., IAST predictions vs co-adsorption measurements for CO₂ capture and separation on MIL-100 (Fe). *Adsorption* **2017**, 23 (2-3), 225-237.

71. Talu, O.; Myers, A. L., Rigorous thermodynamic treatment of gas adsorption. *AIChE Journal* **1988**, *34* (11), 1887-1893.
72. Wilson, R. J.; Danner, R. P., Adsorption of synthesis gas-mixture components on activated carbon. *Journal of Chemical & Engineering Data* **1983**, *28* (1), 14-18.
73. Zanota, M. L.; Heymans, N.; Gilles, F.; Su, B. L.; Frère, M.; De Weireld, G., Adsorption Isotherms of Pure Gas and Binary Mixtures of Air Compounds on Faujasite Zeolite Adsorbents: Effect of Compensation Cation. *Journal of Chemical & Engineering Data* **2010**, *55* (1), 448-458.

