Integral Mass Balance (IMB) Method for Measuring Multicomponent Gas Adsorption Equilibria in Nanoporous Materials

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ABSTRACT: To assess the performance of an adsorbent for a particular gas separation, and for process design, it is necessary to determine multicomponent gas adsorption equilibria, either experimentally or from predictions based on models or theory. The experimental techniques commonly used for this purpose, however, are time-consuming and typically require large samples. In this article, we describe a new approach, called the Integral Mass Balance (IMB) method, which combines the controlled flow of a gas mixture with in situ gravimetric measurement and gas composition analysis using quadrupole mass spectrometry. The IMB method allows very rapid equilibrium multicomponent gas adsorption measurements to be performed on samples weighing only a few grams. The method is demonstrated and validated by performing binary O_2/N_2 adsorption measurements on a commercial 5A zeolite, at ambient temperature and a total pressure of 0.915 MPa. Excellent agreement with previously published data was found, using a 3.5 g sample, with a measurement time of only 4 h for a 20 point isotherm. In contrast, other techniques of equivalent accuracy would require around 20 days of experimental effort to collect a comparable amount of data. Selectivities were also calculated and shown to agree with previously published results. In principle, the technique could readily be extended to measure gas adsorption from ternary or higher mixtures.
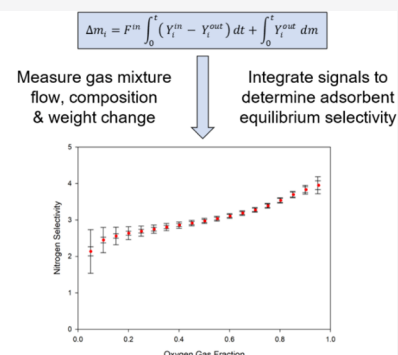
INTRODUCTION

Separating gases using porous adsorbents usually relies on the selective adsorption of one species over another.[1,2] Industrial separations tend to exploit equilibrium selectivity, for which multicomponent (binary or higher) gas adsorption isotherms provide essential information for assessing adsorbents for a given separation and for process design.[3] Obtaining such data, however, is experimentally challenging.[4−9] As a result, usually only binary adsorption data are measured in order to save time and effort on tedious experiments.

Single component (pure gas) isotherms can be measured using a range of techniques, of which the volumetric/manometric[10−12] and gravimetric[10,11,13,14] methods are the most common. Both approaches can be extended to multicomponent adsorption, but the challenge is in determining the adsorbed phase composition—at a specified gas phase composition—in addition to the total amount adsorbed. Gravimetric measurements, for example, provide only the total weight change of a sample, as a result of adsorption, while volumetric/manometric measurements typically involve measuring only the total pressure change in a system of known volume. Neither the total sample weight nor the total system pressure change can determine the amount of each individual component adsorbed by the sample. This information, however, can be obtained in a number of different ways, which we will now briefly review.

Volumetric Methods for Mixture Adsorption Equilibrium. Multicomponent volumetric methods tend to use either open or closed systems, and various approaches have been developed over the past 60 or so years.[4,5,15−21] In the most commonly used closed systems, gases are delivered from different calibrated volumes and are recirculated, using a pump, to mix the components and force them through an adsorbent bed.[20,22−24] Once equilibrium has been achieved, the bed is isolated, and the pressure and temperature are measured. The gas composition in the system is then determined using, for example, a Mass Spectrometer (MS) or, more commonly, a Gas Chromatograph (GC).[19,20,25] The amount of each component adsorbed can then be calculated from material balances between the initial and final contents of the void space of the various calibrated volumes in the system. Care must be taken to ensure equilibrium has been achieved, which may require hours, and although the final gas pressures—both partial and total—can be measured to high accuracy, they
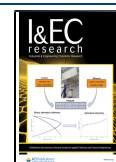
cannot be controlled. This lack of control over the final state of the system can make presentation of phase diagrams challenging due to the additional degree of freedom. Nevertheless, providing a large enough sample is used, high accuracy results can be obtained using this approach.

Open system multicomponent volumetric measurements, meanwhile, involve passing a gas mixture through an adsorbent bed using Mass Flow Controllers (MFCs), while measuring the outlet flow rate and determining the downstream gas composition using a GC[4,23] or MS.[21,26,27] Measurements made at total pressures other than ambient require a back pressure regulator, or a flow controller, to be mounted downstream of the bed. A material balance expression is then used to calculate the amount of each component adsorbed, by integrating the inlet and outlet flow rates and gas compositions. As equilibration is quicker in open systems, these measurements are less time-consuming than their closed system counterparts. An additional advantage is the control over the final partial and total gas pressures, which helps in determining phase diagrams. High accuracy, however, is difficult to achieve, because of the relatively low accuracy of gas flow control and measurement, particularly with mixtures of varying composition and pressure.[21,26]

A third multicomponent volumetric option involves isolating an open system, following equilibration, and then desorbing or transferring the entire contents of the column into a separate volume for analysis. Measuring pressure and temperature, and determining the gas composition in the desorption chamber, then allows calculation of the amount of each component adsorbed, prior to desorption.[28−33] This approach, sometimes called the *total desorption method*,[3,6,27] has been used for many years.[17,18] It is the most accurate way of measuring multicomponent gas adsorption equilibria, at any desired partial or total pressure and temperature, but it is very laborious.[5,6] For every isotherm point, the adsorbent bed must be heated to fully desorb the gas, while the desorption chamber is usually cooled, to collect the contents of the bed. This process, including subsequent analysis of the gas composition, requires hours of additional time and effort.

Gravimetric Methods for Mixture Adsorption Equilibrium. Gravimetric multicomponent methods, meanwhile, tend to take one of two forms.[11] The first involves a similar measurement to the closed volumetric systems described above. A gas mixture is circulated through a gravimetric system, while the sample weight is monitored using the microbalance. Once equilibrium has been achieved—in terms of sample temperature, total pressure, and sample weight—the gas composition is analyzed using a GC or MS. The amount of each component adsorbed can then be calculated by combining the total weight measurement with the final gas composition.[25,34−37] Sample size, in this case, is limited by the microbalance capacity, but the dead volume of the system must also be low enough to make a reliable measurement. Using a small sample in a large volume will prevent detection of sufficient differences in the gas phase, to allow calculation of the amount of each component adsorbed, although an auxiliary adsorbent bed can be used to increase sensitivity, if required.[36] Equilibration times are also lengthy,[35,36] and similar to closed volumetric systems, the final partial and total pressures cannot be controlled.

The second option avoids the need for gas composition analysis, using a GC or MS, by combining the gravimetric and volumetric techniques.[34,38] In this case, gases are delivered from calibrated volumes and circulated through a gravimetric system. Following equilibration, the total pressure and system volume are combined with the sample weight measurement and an equation of state for the gas mixture, in order to calculate the amount of each component adsorbed. This method is limited to binary mixtures and only works for adsorbate pairs with sufficiently different molar masses. Accuracy also depends on the difference between the molecular weights. Further drawbacks include long equilibration times[38] and a lack of control over the final partial and total gas pressures.[3,6]

Other Methods To Approximate Mixture Adsorption Equilibrium. The main approaches described above—both volumetric and gravimetric—provide full adsorption equilibrium characterization data. That is, all variables in the functionalities $n_{1,2} = f_{1,2}(T, P, y_1)$ are measured or set. The intensive variables, n_1, n_2, T, P, and y_1, however, are not independent of one another, due to the Gibbs−Duhem relation,[39] and so thermodynamic relations can be used to calculate the value of one from all the others, at the expense of thermodynamic consistency checks, which in this case then become redundant. Mathematically, these are differential equations, and some of the partial derivatives can be measured directly. Other multicomponent measurement methods, mostly based on gas chromatography,[40−47] therefore exploit this approach.

In gas chromatography, the response at the outlet of a column is monitored while a change in the inlet concentration is made. *Frontal chromatography*, for measuring breakthrough curves, for example, is a common approach to studying mixture adsorption.[19,48−51] This is similar to open system multicomponent volumetric measurement, except the outlet flow rate is not usually determined in chromatographic systems, as only the outlet gas composition is required to measure a breakthrough curve. Binary gas adsorption, however, can also be studied using other types of gas chromatography.[43] At low concentrations, for example, a pulse of the gas mixture can be injected into an inert (nonadsorbing) carrier gas, or a pulse of one component injected into an adsorbing carrier.[40] Measured retention times—the time taken for each component to appear in the effluent—are usually related to some form of the partial derivatives of the adsorbed phase, with respect to partial pressure, and can therefore be used to determine Henry's law coefficients for each component. Alternatively, isosteric enthalpies or heats of adsorption can be determined from the temperature derivatives. In *concentration pulse chromatography*, meanwhile, a pulse of one component is injected into a carrier gas consisting of the binary mixture.[42,44,45,52−56] This allows binary gas adsorption to be studied at higher partial pressures. Concentration steps can also be applied.[41]

In contrast to other multicomponent techniques, gas chromatography measurements tend to be quick. A bed must first be prepared for adsorption and equilibrated with the carrier gas, but a single data point can be determined in the time taken for a pulse or concentration change to pass through the column, which may only be a matter of minutes. Measurement conditions are also well controlled. However, the required data analysis is complex. Only differential adsorbed quantities can be determined, so a mathematical isotherm equation must be assumed in order to relate retention time to the amount of each component adsorbed.[42,43,45,46,53,55]

Finally, one very different approach to measuring binary adsorption equilibrium is *isotope exchange*, which uses isotopic

tracers.[57,58] Rynders et al.,[57] for example, described a closed loop cycle method, in which a gas mixture is circulated through an adsorbent bed, before an isotope is switched into the flow. The response of the system is then determined using an MS. Adsorption kinetics can be studied using this method, but multicomponent equilibria can also be determined by monitoring the mole fractions of the isotopic species of different components in the system.[57] The basic premise of this approach is the fact that there cannot be any equilibrium adsorption selectivity between isotopes of the same component. An obvious disadvantage of isotope exchange, however, together with the related technique of *tracer gas chromatography*,[59] is the need to use isotopes, which can be expensive and may not be readily available. A large amount of sample—at least 10 g, for example—is also required to obtain accurate data.

The Ongoing Need for New Methods. Measurements made using the above techniques are therefore mostly time-consuming and typically require large samples. Some early volumetric studies,[22,28] for instance, used tens of grams of material, and a more recent report[26] of an open volumetric system used sample sizes of ~26 g and ~29 g. In closed volumetric or gravimetric systems, several hours are often required to ensure equilibrium has been achieved, solely for a single data point,[4–6,20,36] and the adsorbent must be regenerated each time. Open system measurements, meanwhile, although rapid, tend to be inaccurate due to the difficulty, as noted above, of measuring flow rates of gas streams with changing composition and sometimes pressure.[4,5,26] Errors and uncertainties can also accumulate, particularly when individual readings—of temperature, pressure, or flow—are being summed or integrated over time to calculate adsorbed quantities. Such problems can be reduced, to some extent, by increasing sample size,[36] but this is a significant practical disadvantage. No existing technique therefore provides a widely applicable and convenient way of measuring multicomponent gas adsorption isotherms.[9] The most accurate are laborious, while quicker methods tend to be less accurate and require large samples, which causes a problem when characterizing new materials that are often only available in small quantities.

The number of new nanoporous materials, meanwhile, has increased dramatically in recent years.[7,60–65] There is significant interest in using them to separate gases,[7,19,48,60,61,66] but the lack of convenient methods for practically assessing their performance for specific separations is problematic. To simply estimate their separation performance, single-component isotherms are often combined to predict multicomponent gas adsorption using methods such as Ideal Adsorbed Solution Theory (IAST);[8,67] however, IAST, in particular, has limitations—it applies mainly, for example, to ideal mixtures of adsorbates of similar size and interaction strength.[8] Computer simulations—using, for example, Grand Canonical Monte Carlo (GCMC) methods—are very useful for estimating competitive adsorption. But they rely on idealized computational models of materials and on the accuracy of the description of the intermolecular interactions in any given adsorbate–adsorbent system. The only way to determine the adsorption properties of a real adsorbent to sufficient accuracy, particularly for developing practical separations, is therefore to measure them.[19,20] Despite decades of research, however—and the unquestionable success of industrial separation processes—convenient and accurate

experimental techniques for measuring multicomponent gas adsorption have remained elusive. Advances in this area would therefore still be very valuable.[9]

In light of the above, we now describe a new approach, called the Integral Mass Balance (IMB) method, which combines an open flowing system with in situ gravimetric measurement and gas analysis using quadrupole mass spectrometry. It allows very rapid determination of multicomponent gas adsorption isotherms at near ambient temperature, up to total pressures of at least 1.0 MPa, using only a few grams of sample, and therefore offers the promise of improving the speed, accuracy, and convenience of multicomponent measurement. A complete data set can be collected in a matter of hours, compared to several days of experimental effort using other techniques of comparable accuracy. To the best of our knowledge, it has not been reported before.

We begin by introducing the necessary background, before describing the experimental setup and procedure. We then present O_2/N_2 binary adsorption measurements on a commercial 5A zeolite. These measurements validate the technique because similar, thermodynamically consistent,[68] results have been obtained previously for the same sample, using two different volumetric techniques in two different laboratories,[23] and excellent agreement has been found. We conclude by discussing possible limitations of the technique, and its potential future use for measuring kinetics and adsorption from ternary or higher gas mixtures.

■ BACKGROUND

A conventional open volumetric system uses an adsorption column and operates with a constant inlet flow of known composition, preferably at constant temperature and pressure. The sample mass is determined following activation of the adsorbent at high temperature, under vacuum or helium flow, and the total outlet flow rate and outlet gas composition are measured during an experiment. The material balance for this system enables the partial molar quantities of each component adsorbed to be calculated from the difference between the inlet and outlet molar flow rates of each component and the gas retained in the column void space.

As shown in Figure 1, the system consists of a known internal volume, V^{tot}, containing adsorbent of dry mass, m^{solid}, and containing n_i moles of component i,

$$n_i = n_i^{gas} + n_i^{ads} \tag{1}$$

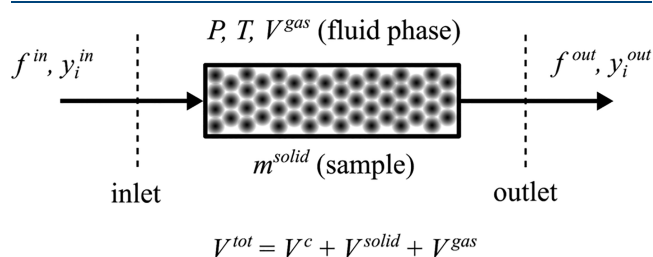$$V^{tot} = V^c + V^{solid} + V^{gas}$$

Figure 1. A schematic diagram of a conventional open volumetric system column, indicating the parameters and variables required to calculate the adsorbed quantities. The inlet quantities (f^{in}, y_i^{in}) are held constant, while the outlet quantities (f^{out}, y_i^{out}) are measured as a function of time, at constant P and T. The control volume, V^{tot}, is a sum of the volumes of the sample, V^{solid}, the gas phase, V^{gas}, and any containment material—a holder, for example, or filters, V^c.

where n_i^{gas} and n_i^{ads} are the molar quantities in the gas and adsorbed phases, respectively. There is also a solid phase of volume, V^{solid}, that component i cannot enter, and a sample container volume, V^c, that is also impenetrable to gas. The total system volume—the control volume—is therefore given by

$$V^{tot} = V^c + V^{solid} + V^{gas} \qquad (2)$$

where V^{gas} is the volume of the gas phase. Note that the adsorbed phase does not occupy any space as per the Gibbs definition of adsorption,[4,69] regardless of where the dividing surface is located between solid and fluid. The actual location of the dividing surface determines which framework is used to describe n_i^{ads} in eq 1, as absolute, excess, or net adsorption.[70]

For a conventional open system volumetric experiment, the molar material balance between the inlet and outlet for the system, assuming no chemical reactions, can be written with respect to chemical component i as

$$f^{in} y_i^{in} - f^{out} y_i^{out} = \frac{dn_i}{dt} \qquad (3)$$

where f is the total molar flow rate and y_i is the molar fraction in the inlet and outlet flows. Open volumetric systems, with all their inherent advantages with respect to experiment time, determine the adsorbed amount of a given component, Δn_i^{ads}, by integration of eq 3 as

$$\Delta n_i^{ads} = \int_0^t (f^{in} y_i^{in} - f^{out} y_i^{out}) \, dt - \Delta n_i^{gas} \qquad (4)$$

where Δn_i^{gas} is the molar quantity of component i accumulated in the gas phase of the column in V^{gas}. This approach, however, has practical limitations with regard to accuracy, as noted in the Introduction, due to the uncertainty in determining the total outlet flow rate.[4,26]

The IMB method overcomes this limitation by combining gravimetric analysis with the open system measurement. As shown in Figure 2, the system still consists of the control volume as above, but with the adsorbent freely suspended in a gas permeable container, or bucket, within the vessel in order that it can be weighed continuously. The gas mixture enters via a diffuser in the base of the vessel and flows past the sample. The exhaust mixture passes through a chimney and is evacuated by the gravimetric system exhaust control valve. The composition of the exhaust gas is then sampled within the chimney to an online MS. Compared to traditional open volumetric systems, the most significant difference is that the outlet flow rate is <u>not</u> measured, because it is not needed, as we show next.

It is easier to work with mass rather than molar balances for the IMB system, and so we begin by defining the mass confined between the inlet and the outlet in Figure 2 as

$$m = m^c + m^{solid} + m^{gas} + m^{ads} \qquad (5)$$

where m^c is the mass of the sample container, and m^{gas} and m^{ads} are the masses of the gas and adsorbed phases, respectively. The mass balance is written with respect to component i as

$$F^{in} Y_i^{in} - F^{out} Y_i^{out} = \frac{dm_i}{dt} \qquad (6)$$

where F is total mass flow rate and Y_i is the mass fraction in the inlet and outlet flows. Mass fraction is defined as
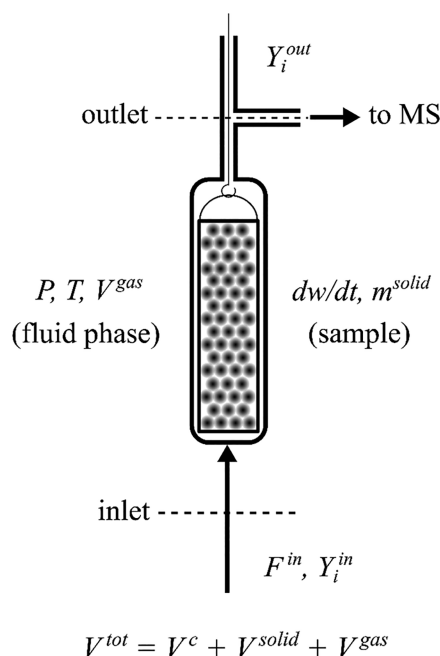

Figure 2. A schematic diagram of the IMB method column, indicating the parameters and variables required to calculate the adsorbed quantities. The inlet quantities (F^{in}, Y_i^{in}) are held constant, while the outlet composition (Y_i^{out}) and weight change of the sample (dw/dt) are measured as a function of time, at constant P and T. The control volume is a sum of the volumes of the sample, the gas phase, and the sample container or bucket.

$$F_i = M_i f ; \quad Y_i = \frac{M_i y_i}{\bar{M}} \qquad (7)$$

where M_i is the molar mass of component i and $\bar{M}$ is the mean molar mass of the gas mixture. The component mass balance in eq 6 can be summed for all components to give

$$F^{out} = F^{in} - \frac{dm}{dt} \qquad (8)$$

The total outlet flow rate, F^{out}, can then be substituted into eq 6, and the equation is integrated to give the change in mass of component i, Δm_i, as

$$\Delta m_i = \int_0^t \left(F^{in} Y_i^{in} - \left(F^{in} - \frac{dm}{dt} \right) Y_i^{out} \right) dt \qquad (9)$$

Here, mass refers to the total accumulation of component i in the system, in both the gas and adsorbed phases. Some simplification then gives

$$\Delta m_i = F^{in} \int_0^t (Y_i^{in} - Y_i^{out}) \, dt + \int_0^t Y_i^{out} \, dm \qquad (10)$$

This is the main equation required to analyze IMB data. Note that the term involving mass only includes a differential quantity, dm, which can be measured more accurately in long experiments.

A typical measurement comprises an isothermal step change to a new fixed gas inlet composition at time $t = 0$. The mass change is calculated in the long-time limit after equilibration ($Y_i^{in} = Y_i^{out}$, $dm/dt = 0$), where both integrals tend to zero; hence, there should be no accumulation of uncertainty. It is essentially a point-to-point measurement of mixture adsorption
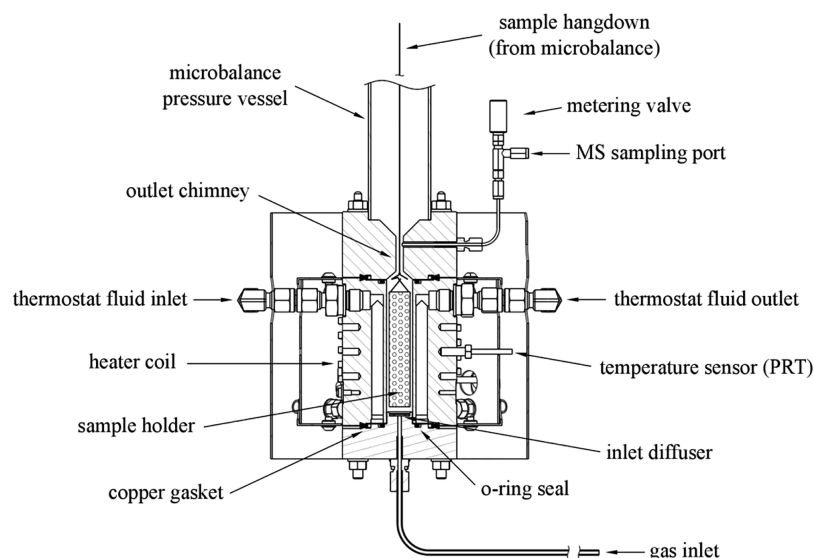
Figure 3. Specially designed IMB method reactor for the Hiden Isochema Intelligent Gravimetric Analyzer (IGA), with key components labeled (MS, mass spectrometer; PRT, platinum resistance thermometer).

with a time response similar to chromatographic experiments. From a practical viewpoint, this also means a dynamic calibration, usually a linear interpolation, can be applied between the gas analyzer and inlet flow composition at the end of each adsorption step. There should therefore also be no disadvantage in using a multipoint method to determine equilibrium isotherms of the partial adsorbed amount, with the concomitant saving in experiment time. Proper time lags, of course, must be applied to different signals in the experiment, in order to bring all to a common time basis before integrating the raw data. Details of the dynamic MS calibration and time-lag measurements are provided in the Supporting Information (SI).

To convert eq 10 to the partial amount of each component adsorbed, two further contributions must be considered:

1. The internal balance measurement, w, must be corrected for buoyancy to calculate the system mass change term, dm.

2. The accumulation in the fluid phase in the column must be subtracted from Δm_i, according to the chosen reference state, whether net, excess, or absolute adsorption.

Details of these contributions are provided in the SI, but the final equation for calculating the partial amount of component i adsorbed using the IMB method is

$$M_i \Delta n_i^{\text{ads}} = F^{\text{in}} \int_0^t (Y_i^{\text{in}} - Y_i^{out}) \, dt + \int_0^t Y_i^{out} \, dw$$
$$+ \frac{PV^{\text{tot}}}{ZRT} \int_0^t Y_i^{out} \, d\bar{M} - M_i \Delta y_i \frac{PV^{\text{gas}}}{ZRT} \qquad (11)$$

The first term on the right-hand side of eq 11 is the flow integration common to all open system measurements, but notice it only involves the inlet flow. The second integral term is with respect to dw, or the direct balance reading, while the last term is the usual correction for gas phase accumulation. The third term is the buoyancy correction applied to the balance measurement. It includes the spatially averaged molecular weight, $\bar{M}$, of the gas mixture in the column. Interestingly, as explained in the SI, it involves the total column

volume, V^{tot}, rather than just the sample container and sample volumes, $V^{\text{c}} + V^{\text{solid}}$. V^{tot} is easier to measure when the column is empty, or to estimate from the dimensions of the column. The split between the gas phase and "impenetrable" volume, however, still needs to be measured, according to the reference state used to define adsorption. The value used for V^{gas} in eq 11 determines if results correspond to net, excess, or absolute adsorption.[69,70] Excess is used in this work where prior data are used for confirmation, but this can be converted to net adsorption using the helium density of the solid matrix.

There is inherent uncertainty in determining $\bar{M}$—and hence $d\bar{M}$ in the third term of eq 11—because of the adsorption wave traveling through the column. This is a potential limitation of the IMB method, unless there is either an accompanying spatially resolved measurement of the gas distribution in the column or if the system mass is measured externally to directly provide dm in eq 10, to eliminate the need for internal buoyancy corrections. However, spatially resolved measurement of the gas distribution in the column is not feasible, and it would be experimentally challenging to externally weigh an entire flow-through system to sufficient accuracy. To determine $\bar{M}$ in our calculations, we instead assume a simple arithmetic average of the inlet and outlet conditions, at every instant.

Note that the third term of eq 11 vanishes if the components have equal molar masses because, in this case, $d\bar{M} = 0$. Conversely, it will increase as the difference in molar mass increases, because $d\bar{M}$ will then proportionally increase or decrease during each step change in concentration. The magnitude of the uncertainty can be estimated by rewriting this term, using integration by parts, as

$$\int_0^t Y_i^{out} \, d\bar{M} = [Y_i^{out} \bar{M}]_0^t - \int_0^t \bar{M} \, dY_i^{out} \qquad (12)$$

The value of the integral is therefore finite, with the first term on the right-hand side of eq 12 representing the maximum possible value. Later, we show that this contribution is very small, at least for the data presented in this work.

EXPERIMENTAL SECTION

The IMB method is demonstrated here using a Hiden Isochema Intelligent Gravimetric Analyzer (IGA) equipped with a specially designed reactor, consisting of a column holding the sample in a cylindrical sample container, as shown in Figure 3. The sample container, made from 316L stainless steel woven mesh, is suspended from one side of the balance by a gold chain and a fine-tungsten hangdown wire. The maximum height of the sample container, and hence the effective length of the column, is 70 mm, with a diameter of 10 mm in this instance. This provides a volume of 5.5 cm^3, enough to hold approximately 4 g of zeolite. Different size containers to suit sample packing can also be accommodated using a hollow cylindrical spacer.

The weight of the sample and container is measured *in situ* using an electronic compensating beam balance mounted in a thermostated vacuum- and pressure-compatible chamber.[13,71,72] The highest available dynamic weighing range (1 g) with a resolution of 1 μg and a long-term stability of ± 1 μg is used for the present study. A recirculating water bath controls the isotherm temperature of the reactor, in the range 283 to 313 K, with a regulation accuracy of ± 0.025 K, while integral heating elements can be used to increase the sample temperature further, to 523 K for standard Kalrez internal reactor seals or to 623 K with metal internal seals. Temperature is measured and controlled against a platinum resistance thermometer (PRT), as indicated in Figure 3.

During an experiment, a gas mixture of controlled composition is introduced at the base of the column, via a diffuser, with the total pressure regulated using a stepper motor-controlled bellows valve positioned at the outlet of the IGA. Gas flow rates are controlled using Brooks Instruments (Hatfield, PA, USA) 5850E MFCs, with a maximum flow rate of 100 mL min^{-1} and a manufacturer flow measurement accuracy of $\pm 1\%$ full scale. The flow calibration is improved by cubic polynomial expansion of the calculated volume flow rate during free pressurization for a series of command values. Total pressure is measured using a GE Sensing PDCR 4020 strain gauge sensor, with a quoted measurement accuracy of $\pm 0.04\%$ full scale and a typical control regulation accuracy of ± 1 mbar. Gas is initially introduced to the column using a pneumatically actuated 4-way, 2-position VICI (Valco Instruments Corporation Inc., Houston, TX, USA) GC valve, to establish flow prior to switching the mixture to the sample position.

The outlet gas composition is determined by sampling from the chimney at the top of the column (see Figure 3). A capillary connects the sampling port to a Hiden Analytical (Warrington, UK) Dynamic Sampling Mass Spectrometer (DSMS). The capillary, combined with a bypass line on the DSMS, allows reduction of the pressure from ambient down to the high vacuum conditions required in the MS chamber. A manual metering valve is used to control the further pressure drop required when performing measurements at elevated (above ambient) pressures.

The remainder of the instrument is maintained at a constant pressure throughout the experiment using a helium counterflow. Sample degassing is performed in a helium flow at elevated temperature and the dry state determined from the weight of the sample in helium prior to the analysis; the entire instrument can also be evacuated, if required, using a dry turbomolecular pump system, with a base vacuum <10^{-6} mbar.

Total inlet flow rate and pressure, as well as temperature, are maintained constant during each analysis, and only the inlet gas composition is varied.

The material used to demonstrate the method is a commercial 5A zeolite (Tosoh Corporation), as originally studied by Talu et al;[23] the original N$_2$/O$_2$ adsorption data were shown to be thermodynamically consistent and have been used later in other adsorption studies.[73,74] Approximately 3.5 g of sample were used in this work. The sample was degassed *in situ* at a temperature of 523 K for 24 h in vacuum and subsequently in a flow of helium, until the weight stabilized. High purity gases obtained from Air Products were used, with the following purity levels: He (99.999%), N$_2$ (99.999%), and O$_2$ (99.999%). No further purification was applied. The skeletal sample volume, V^{solid}, was determined *in situ* from isothermal helium displacement at a series of gas pressures up to 1.0 MPa. The corresponding skeletal density was 2.57 g cm^{-3}. The sample container volume, V^c, was previously established using helium pycnometry by an independent laboratory, while V^{tot} was determined using digital calipers and the engineering drawings. A value of 11.757 (± 0.115) cm^3 was used for V^{tot} for all measurements.

The aim of the experiments presented here was to replicate multicomponent analyses presented previously.[23] Total pressure was therefore set to 0.915 MPa, and a series of pure component (O$_2$ or N$_2$) and binary mixture (O$_2$/N$_2$) adsorption isotherms were measured at 296.45 K (23.3 °C). The IMB method enables multipoint isotherms to be followed automatically, in a single run, with the equilibration time at each point determined by monitoring the microbalance weight reading and outlet composition until the steady state conditions, $Y_i^{in} = Y_i^{out}$ and dw/d$t = 0$, are met.

A total of 10 experiment cycles were performed; 5 cycles started with determination of pure N$_2$ sorption followed by 20 mixtures of N$_2$/O$_2$ between the extremities and then pure O$_2$ desorption; 5 cycles were the reverse direction. This was to test the repeatability of the measurements and also to investigate reversibility, in particular whether the difference in the flow pattern between directions of measurement was significant in this instance. Individual N$_2$ and O$_2$ vacuum adsorption measurements were also made using an independent gravimetric instrument to test the agreement between the excess uptakes of pure N$_2$ and O$_2$ up to a total pressure of 1.0 MPa.

RESULTS AND DISCUSSION

The total uptake measurements reported by Talu et al.,[23] and replicated in this study, are shown in Figure 4a. All reported adsorbed quantities are expressed as excess adsorption. Using the labeling from the original work, the pure N$_2$ adsorption isotherm is shown as the path A → B, the mixed N$_2$/O$_2$ region as B → D, and the pure O$_2$ adsorption (or desorption) isotherm as D → E. These data were measured using a closed (recirculating) volumetric system at Cleveland State University and an open (flowing) volumetric system at Air Products and Chemicals, Inc., in Allentown, PA. Figure 4b shows the equivalent total adsorption data measured in this work.

To compare the total adsorption data, Figure 5 shows each individual path, A → B, B → D, and D → E, for the Talu et al.[23] study and our replication. Excellent agreement was found, apart from a small discrepancy in the amount of N$_2$ adsorption obtained at the highest pressure. There is no obvious reason
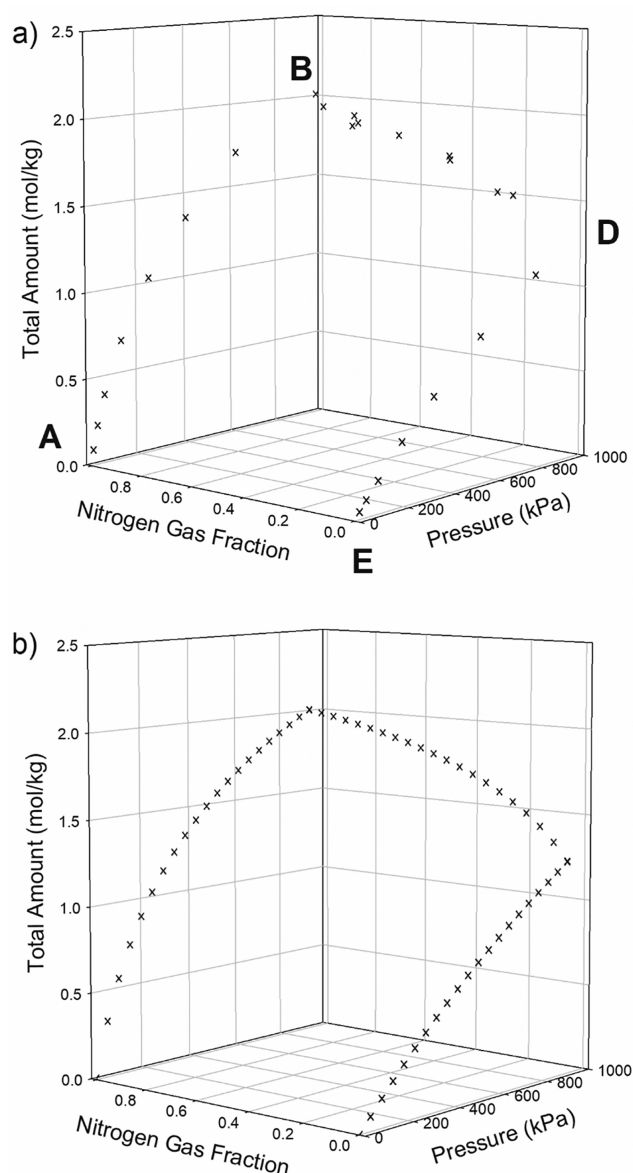
Figure 4. 3D plots of the original total adsorbed quantity for O_2/N_2 adsorption by Tosoh 5A zeolite at 296.45 K. Constant pressure path (B → D) is at 0.915 MPa, (a) as reported by Talu et al.,[23] illustrating the path A → B→D → E, and (b) as measured in this study.

Figure 5. Plots of each branch of the full path for Tosoh 5A zeolite at 296.45 K, showing (a) the pure N_2 adsorption isotherm (path A → B), (b) binary N_2/O_2 mixture (path B → D) at 0.915 MPa, and (c) the pure O_2 adsorption isotherm (path D → E).

for this discrepancy, but good agreement was found between the pure N_2 adsorption isotherm measured in the flowing system (Figure 4a) and an independent measurement performed on another gravimetric instrument. A period of nearly 25 years separates the measurements made by Talu et al.[23] and those reported here. Furthermore, good agreement between gas adsorption measurements made at elevated pressures in different laboratories is difficult to achieve.[75] So it is perhaps unsurprising to find a small difference (approximately 2% to 3%) in the uptakes measured using different techniques in different laboratories, separated by such a long period of time.

Figure 6 shows the real time raw data obtained for the binary N_2/O_2 adsorption isotherm measurement shown in Figure 5b (path B → D). It can be seen that the weight change measured by the microbalance at each partial pressure step rapidly follows the change in inlet gas composition, as determined
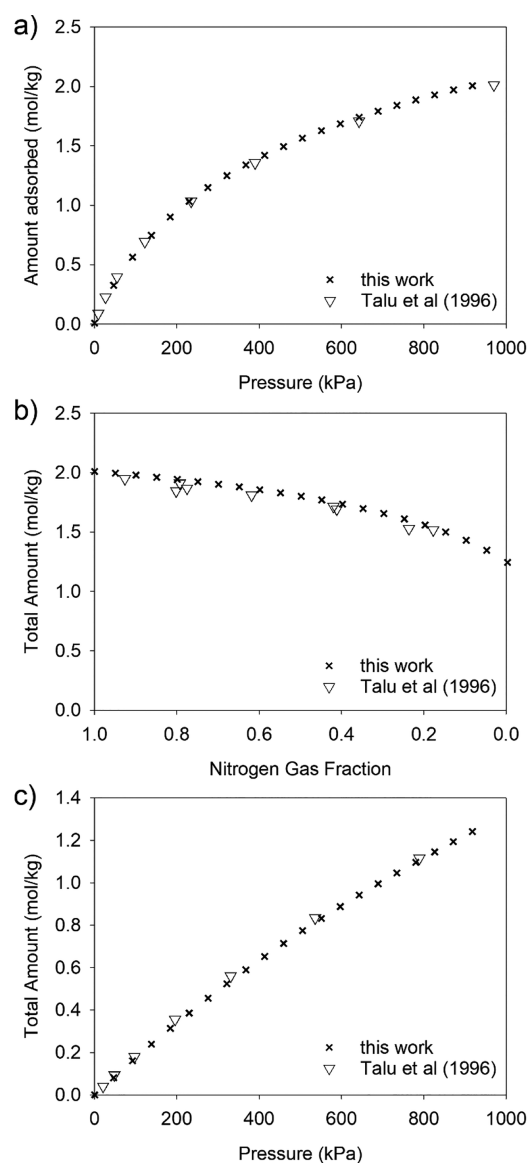
from the MFC signal. Adsorption occurs over the course of a few minutes, before the system reaches a steady state.

Figure 7 shows the integrals in the mass balance expression (eq 11) through the course of the binary N_2/O_2 adsorption isotherms (path B → D), for the data presented in Figure 6. This demonstrates the relative contributions from each term under the reported conditions. The flow term dominates among the three integrals in eq 11. The quantity of N_2 and O_2 adsorbed at each equilibrium point is given by the difference between the total amount of each gas in the column (the sum of the three integrals) and the amount of each species remaining in the gas phase, as indicated by the diamond symbols (◆) in Figure 7. Note that the MS signal expressed as partial pressure in Torr, as shown in Figure 6, must be converted to Y_i^{out} in eq 11 using calibration measurements described in the SI. Notice that the approximated term involving the average molecular mass, $\bar{M}$, is small compared to the other terms, particularly for O_2.
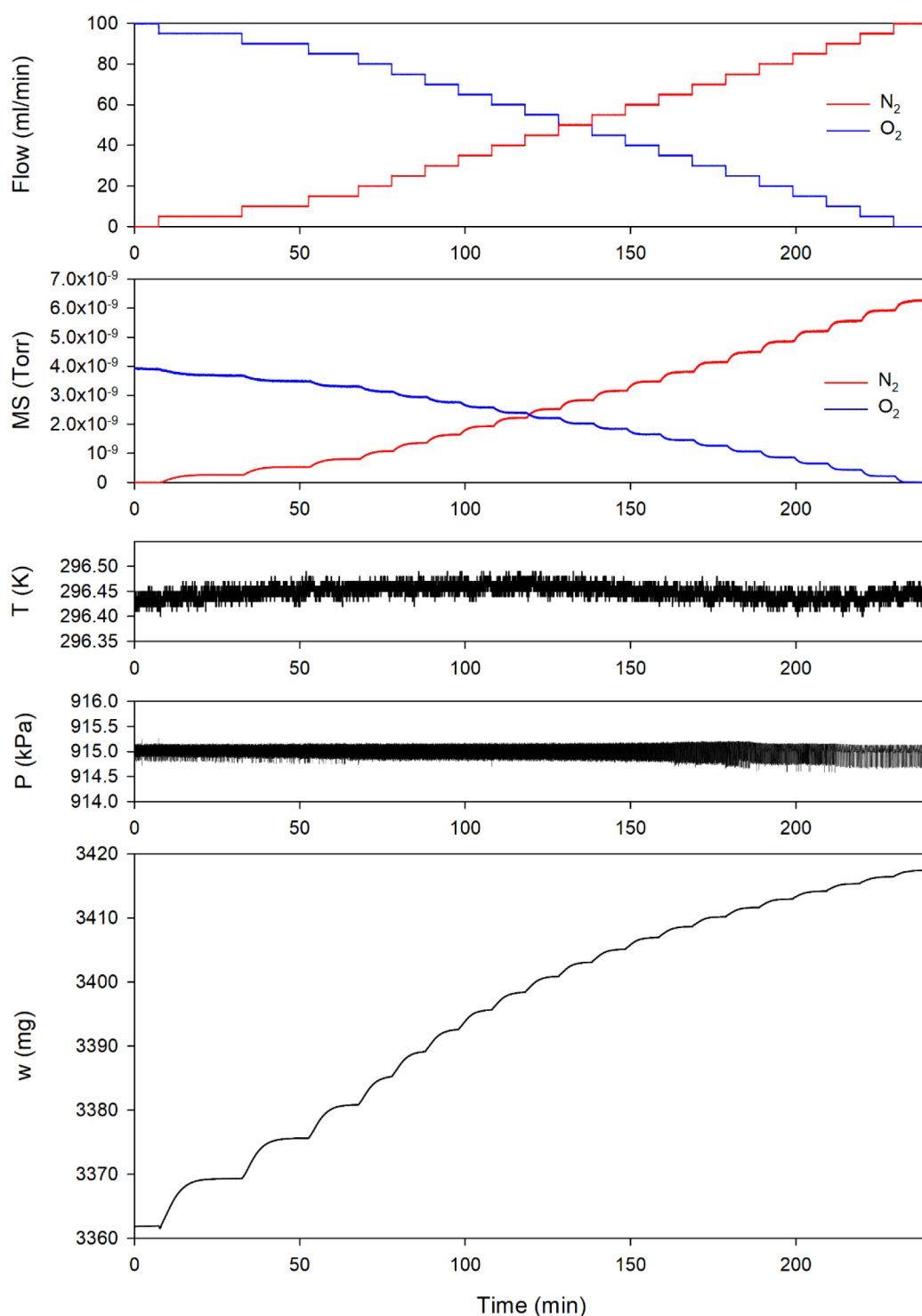
Figure 6. Raw data for a binary N_2/O_2 adsorption isotherm, shown in Figure 5b (path B → D), measured at 0.915 MPa and 296.45 K.

The equilibrium binary N_2/O_2 adsorption isotherms calculated from the data in Figure 7, indicating both the total uptake and the partial adsorbed quantities of N_2 and O_2, are shown in Figure 8. Both the IMB method data and those determined by Talu et al.[23] are presented for comparison. Excellent agreement was found, particularly given the scatter in the original data and the time period of nearly 25 years between the measurements. The repeatability of the IMB method data, meanwhile, is demonstrated in Figure 9, which shows the results of ten binary N_2/O_2 adsorption isotherms,

including the original run and nine repeats. No significant differences in the data displayed in Figure 9 were observed.

Adsorbent selectivity is important for process design and theory, but it is difficult to measure accurately in experiments. Figure 10 shows the equilibrium selectivity, S_{eq}, calculated using the following expression,
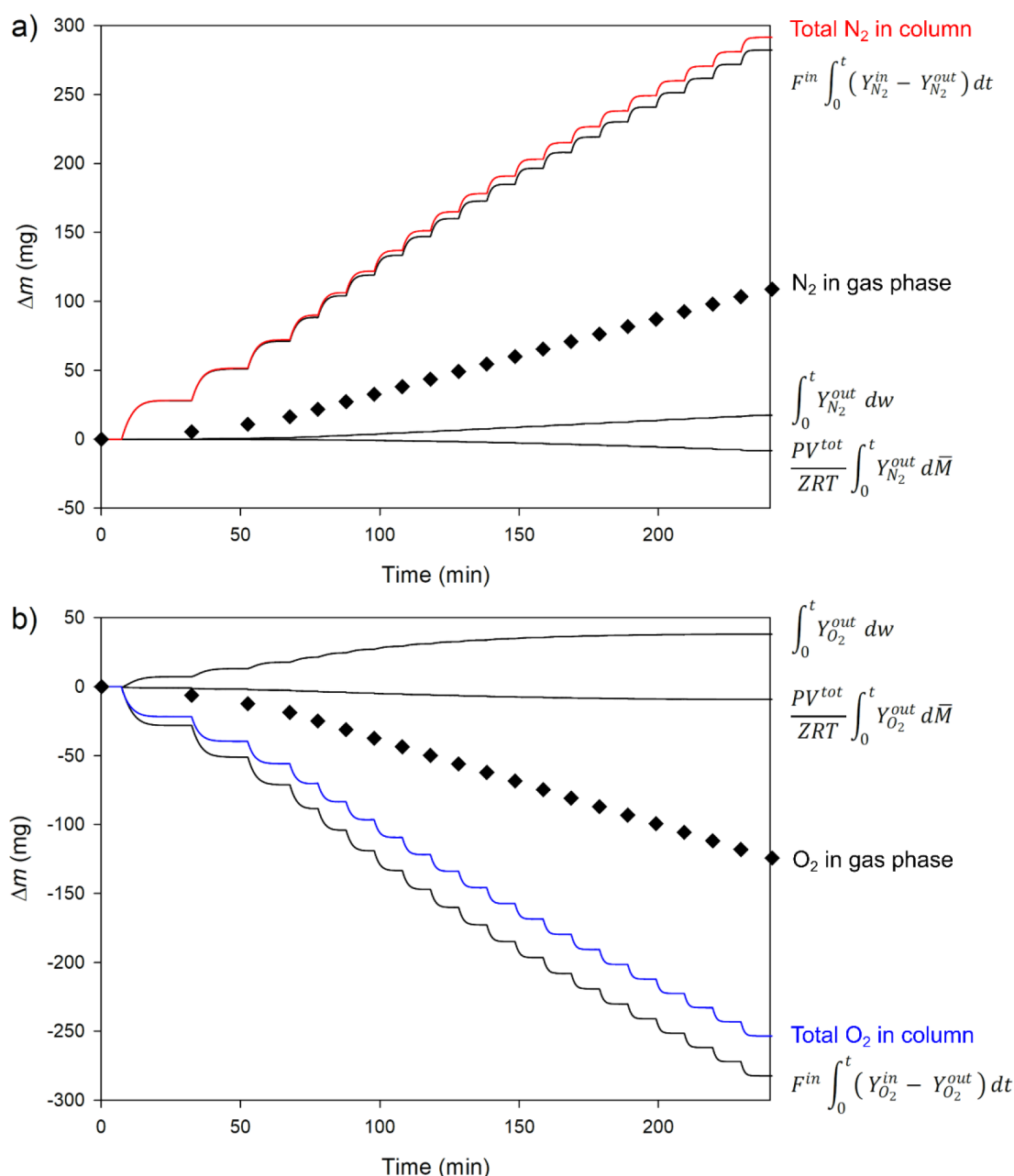
$$S_{eq} = \frac{n_1/y_1}{n_2/y_2}$$

(13)

Figure 7. A plot of the integrals in the mass balance expression (eq 11) for a binary N_2/O_2 adsorption isotherm (path B → D).

where n_1 and n_2 are the partial molar adsorbed quantities of N_2 and O_2, respectively, and y_1 and y_2 are their gas phase mole fractions. The experimental data of Talu et al.[23] and the IMB method are shown and compared to the IAST calculations reported by Talu et al.[23] The variation in the selectivities calculated using the IMB method reflect the sensitivity of S_{eq} to the precise values of n_1 and n_2 used for each calculation. The data presented here are, in general, within the uncertainty band reported by Talu et al.[23] for their data.

To summarize the results obtained using the IMB method, Table 1 shows the averaged values of the phase equilibrium data using all the binary adsorption data measured in this study. The full data set, including the standard deviations calculated from each individual measurement, is presented in Tables S1 and S2. The standard deviations shown in Tables S1 and S2, apart from those for the selectivity, are essentially random, so we have presented the averages in Table 1, to

indicate their order of magnitude. In Table S2, we have presented both the standard deviations of the calculated selectivities—representing the spread in the values across all ten measurements—and the standard deviations obtained from estimates of the uncertainties in each of the various measured parameters. The final average values of the selectivities, together with both the experimental and calculated standard deviations, are plotted in Figure 11. Note that these standard deviations are not directly comparable to the uncertainty bounds reported by Talu et al.[23] and plotted in Figure 10, because Talu et al.[23] obtained their uncertainties from a propagation of error analysis. The standard deviations presented in Figure 11 indicate the precision of the IMB method data, but not their accuracy.

Finally, an independent instrument was used to directly measure pure component isotherms in a traditional gravimetric experiment, without any need for composition measurements.
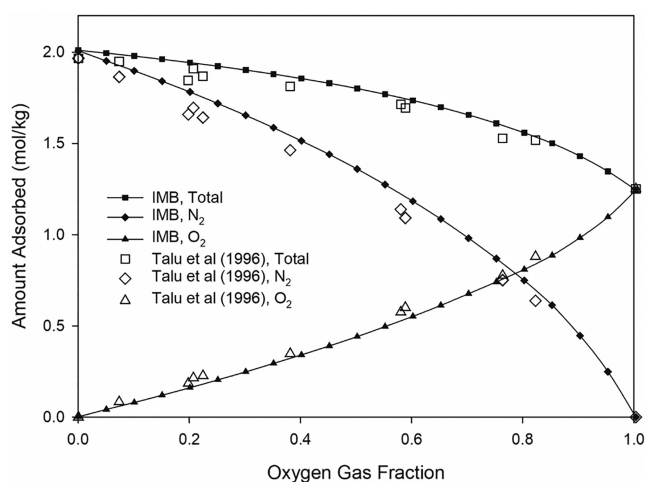
Figure 8. Equilibrium binary N_2/O_2 adsorption isotherms, calculated from the data shown in Figure 7, measured at 0.915 MPa and 296.45 K.
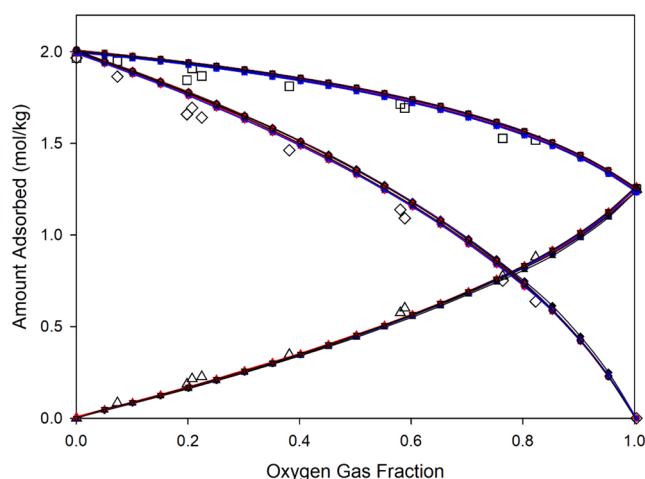

Figure 9. Binary N_2/O_2 adsorption isotherms for Tosoh 5A at 0.915 MPa and 296.45 K, showing the original data set and nine repeats. The Talu et al.[23] data are shown by the open symbols, as in Figure 8.

We call this *vacuum mode*. In addition, the IMB flow-through approach introduced here can also be used with helium as a second component to determine pure component isotherms. The results of these two types of experiments are compared to the Talu et al.[23] pure component data in Figure 12. It can be seen that there is good agreement between the three data sets, with O_2 adsorption measured in vacuum mode being slightly higher than the other two.

The data presented here demonstrate the practical application of the IMB method to measuring binary gas adsorption by nanoporous materials. Both the adsorbent and adsorbates were chosen due to the availability of the original sample and prior data for validation purposes. It is likely that the method can be applied widely to a variety of different gases and materials, although there may be limits to the experimental conditions under which it works to sufficient accuracy. Such limits may include sample size, total pressure, and potentially the range and number of different adsorbate species.

With regard to species, the adsorption of binary mixtures of N_2 and O_2 is not particularly challenging to measure, compared to some other gas pairs. N_2 and O_2 are relatively similar in

molar mass, and hence density. As noted in the Background section, there is inherent uncertainty in determining the third integral term on the right-hand side of eq 11, because it depends on the mean molar mass, $\bar{M}$, which will be subject to perturbation from fluctuations in gas density due to adsorption. Such fluctuations are likely to be greater when the properties of each adsorbate differ, in terms of both density and interaction strength. A larger change in the mean molar mass, for example, during a step change in concentration, due to differences in the molar masses of each component, will increase the magnitude of $\bar{M}$. On the other hand, if the components have equal molar masses, then the third term will vanish because $d\bar{M}$ will be zero. Errors or uncertainties associated with this issue will therefore be greater when the components are more disparate in molar mass and density. Examples include mixtures of H_2 with CO_2 or heavier hydrocarbons. The range of applicability of the IMB method, in terms of combinations of different species, will therefore have to be tested in the future, to determine if there are limits due to differing gas properties. It may be possible, however, to minimize the difficulties associated with such differences by adjusting the experimental parameters, for example, by reducing the concentration step size during isotherm determination.

The above issue is also related to the maximum total pressure used for a measurement. As for single-component (pure gas) gravimetric gas adsorption experiments, buoyancy effects increase with gas pressure and density. We have demonstrated that the technique, as implemented in this study, can produce physically reasonable and thermodynamically consistent data at total pressures of up to 1.0 MPa using N_2 and O_2. Accurate measurements are likely to be achievable at yet higher pressures with these species. In the case of combinations of gases of significantly different molar masses, however, the upper pressure limit may be lower.

A further limitation may be the kinetics of adsorption. In the case of very slow kinetics, long equilibration and hence experiment times may be required. This will lead to integrations being performed over extended periods, and this may increase accumulative error or uncertainty. Again, such cases will need to be tested, bearing in mind that the kinetics of adsorption for some species may depend significantly on the properties of the adsorbent, specifically its pore size, morphology, and the adsorbate−adsorbent interaction strength in each case.

Related to this, the IMB method may be useful, in the future, for studying adsorption kinetics. Each measurement, following a step change in inlet concentration, as shown in Figures 6 and 7, is effectively a breakthrough curve, although note that the adsorbent column is not a fixed bed, so the determined values of Y_i^{out}, as a function of time, may be affected by bypass flow. Furthermore, the calculated values of Δn_i^{ads} depend on knowledge of the density profile of the gas in the column. In this work, we have used an approximation, in which we assume a simple arithmetic average of the inlet and outlet conditions, at every instant, to calculate $d\bar{M}$ in the third term of eq 11. This assumption may be inadequate to extract sufficient kinetic information from the data, but this will have to be investigated further before any firm conclusions can be drawn on the usefulness of the IMB method for kinetic studies. Temperature effects are another important consideration.
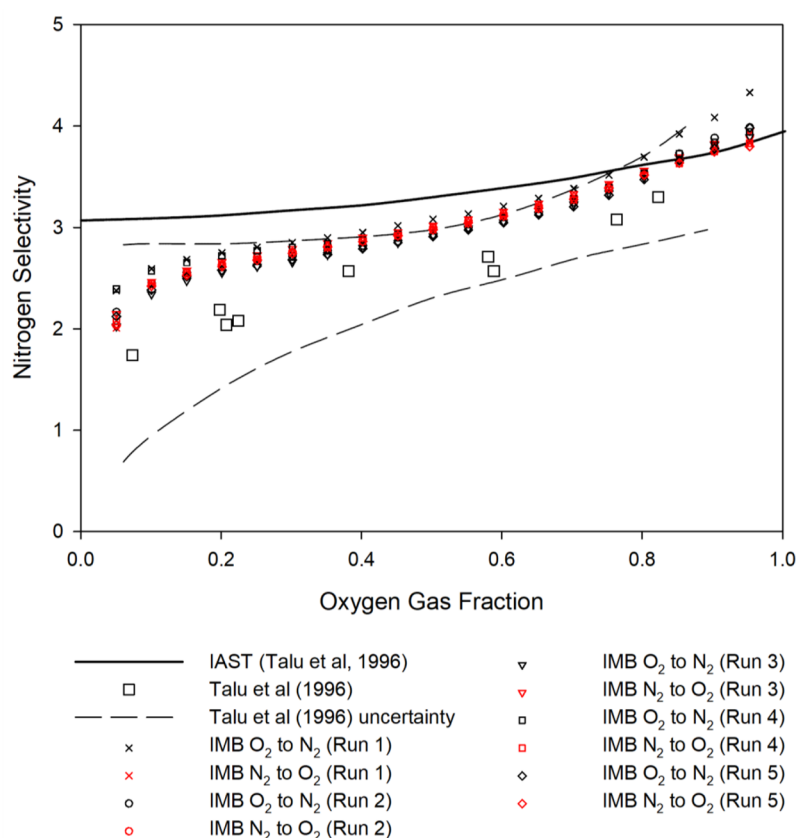
Figure 10. Equilibrium selectivities for the O_2/N_2/Tosoh 5A system at 0.915 MPa and 296.45 K, comparing the IMB method and Talu et al.[23] data with IAST calculations.

Table 1. Phase Equilibrium Data for the N_2/O_2/Tosoh 5A System, Obtained from the Averaging All the Datasets Shown in Figure 9[a]

	P (kPa)	T (K)	$y_{O_2}^{in}$	$n_{N_2}^{ads}$	$n_{O_2}^{ads}$	N_2 selectivity	σ (selectivity)
1	915.000	296.45	0.00	2.005	−0.006	-	-
2	914.999	296.44	0.05	1.945	0.048	2.14	0.125
3	915.000	296.45	0.10	1.891	0.086	2.45	0.078
4	915.001	296.45	0.15	1.834	0.127	2.56	0.061
5	915.000	296.45	0.20	1.774	0.168	2.64	0.055
6	915.001	296.45	0.25	1.711	0.212	2.69	0.051
7	914.999	296.45	0.30	1.645	0.257	2.75	0.050
8	915.000	296.45	0.35	1.576	0.303	2.80	0.043
9	915.002	296.45	0.40	1.504	0.351	2.86	0.041
10	915.000	296.45	0.45	1.428	0.401	2.91	0.042
11	914.998	296.44	0.50	1.348	0.453	2.97	0.040
12	914.998	296.45	0.55	1.262	0.509	3.04	0.038
13	915.002	296.45	0.60	1.171	0.565	3.11	0.041
14	915.001	296.44	0.65	1.074	0.625	3.19	0.042
15	914.999	296.45	0.70	0.968	0.690	3.28	0.045
16	915.000	296.44	0.75	0.855	0.757	3.39	0.048
17	914.998	296.45	0.80	0.733	0.828	3.54	0.055
18	915.003	296.45	0.85	0.593	0.909	3.70	0.067
19	915.004	296.45	0.90	0.428	1.004	3.83	0.079
20	914.998	296.45	0.95	0.232	1.116	3.95	0.122
21	914.999	296.45	1.00	0.000	1.253	−	−
Ave. σ	0.0035	0.014	−	0.0086	0.0060	−	0.059

[a]Average standard deviations (σ) are shown for the relevant parameters, calculated from the individual values presented in Figures S1 and S2.

In principle, the IMB method can also be applied to ternary or higher mixtures. Equation 11 is general and applies to any number of components i. Practical testing of the reported apparatus for a larger number of components, however, has not
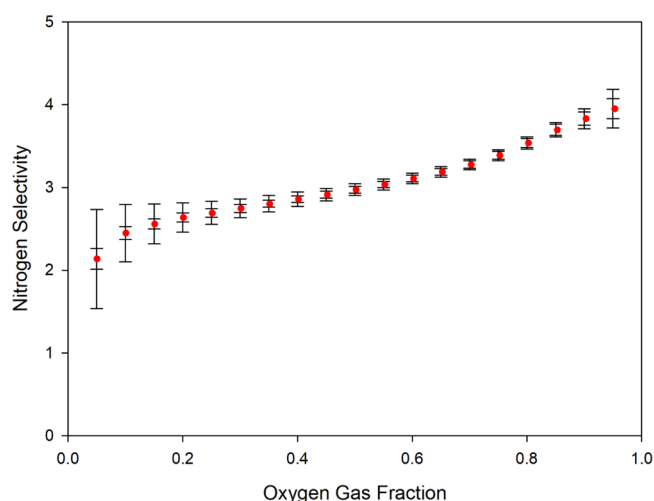
Figure 11. Equilibrium selectivities for the O_2/N_2/Tosoh 5A system at 0.915 MPa and 296.45 K, calculated by averaging all the data measured using the IMB method in this study, as shown in Table 1. The standard deviation of the experimental values and the standard deviations from calculations using estimated uncertainties in each of the measured parameters are shown (see Table S2).
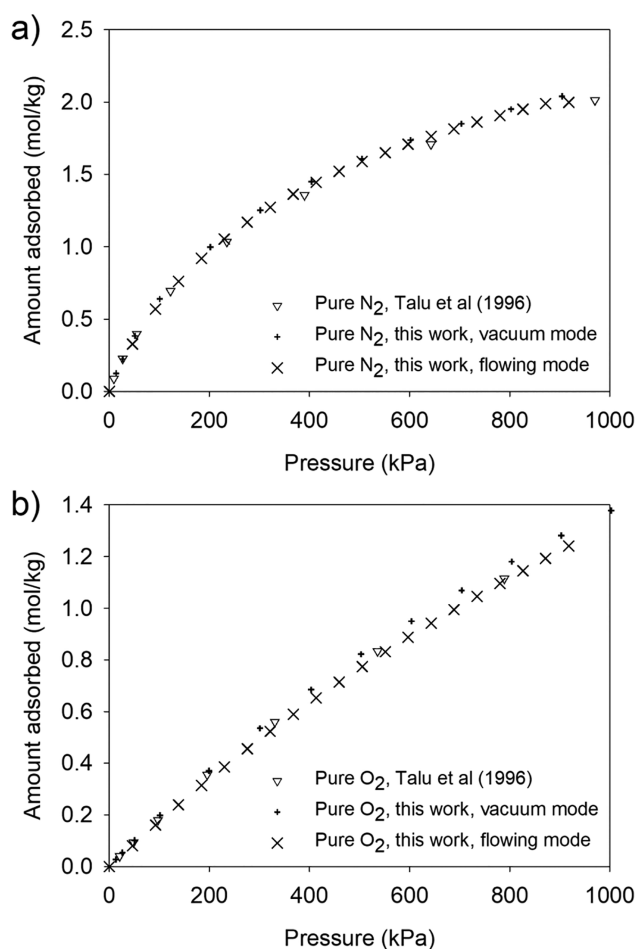

Figure 12. A comparison of the pure component, (a) N_2 and (b) O_2, adsorption isotherms measured up to 1.0 MPa at 296.45 K using a flow of He carrier gas and an independent gravimetric instrument operating from vacuum.

yet been performed, and this will be the subject of future work. There must be limits to the number of components that can be used, even with regard to the accuracy with which Y_i^{in} can be controlled for more complex mixtures. But these are difficult to predict or determine without performing practical experiments.

The apparatus used in this study has not yet been optimized for smaller samples. Using a smaller sample will reduce the overall magnitude of each contribution to eq 11, as shown in Figure 7 for the measurements made in this work. A lower cutoff is likely to exist, below which the quality of the data is too poor to yield accurate values of the equilibrium uptakes of each component in the mixture. As noted in the Experimental Section, however, a hollow cylindrical spacer can be used to accommodate samples of smaller diameter. It may be possible to significantly reduce the sample size, particularly for materials that adsorb relatively large quantities of gas, as this will result in larger relative weight change signals from the microbalance. The sensitivity of the MS to smaller amounts of gas in a system of reduced volume and hence sample size seems unlikely to be a limiting factor. But further tests will need to be performed to determine how far the sample size can be reduced and to investigate ways in which measurements using the IMB method may be performed with even smaller samples than those used in this work.

CONCLUSION

This article describes a new method—combining an open flowing system with in situ gravimetric measurements and quadrupole mass spectrometry—that allows very rapid determination of accurate multicomponent gas adsorption isotherms. Its implementation has been demonstrated and validated by performing binary O_2/N_2 adsorption measurements on a commercial 5A zeolite at ambient temperature and a total pressure of 0.915 MPa. Excellent agreement with previously published data was found, using a 3.5 g sample, with a measurement time of only 4 h for a 20 point isotherm. Selectivities were also in good agreement with previously published results. In addition to being fast and accurate, the final equilibrium conditions in the gas phase, in terms of temperature, pressure, and composition (T, P, and y_i), can be controlled exactly. Furthermore, since it is fast, the method can also provide a more detailed description of 3D phase diagrams, by determining more data points per isotherm in a given experimental time.

The technique should be tested in the future for other gas combinations under different experimental conditions, for different samples, to determine its full range of applicability. Wider use of the technique may allow acquisition of large amounts of equilibrium multicomponent gas adsorption data, enhancing the field of gas adsorption, both in terms of applications and for theoretical studies.

ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.0c04162.

> Further detail on the conversion of mass balance to partial amount adsorbed, flow rate calibration, mass spectrometer signal calibration, and time lag measurement; full phase equilibrium data calculated using all the binary adsorption data measured in this study; and

photographs of the full IMB system (IGA-003-MC) (PDF)

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Notes

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