Opening the Toolbox: 18 Experimental Techniques for Measurement of Mixed Gas Adsorption

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ABSTRACT: Adsorption separation systems offer the possibility to replace or augment legacy separation systems with more efficient processes, resulting in enormous savings in energy. However, adsorption systems are not as easily evaluated as possible unit operations in process simulation software compared to distillation or absorption columns. The lack of ability to predict adsorption of gas mixtures represents a persistent barrier holding back implementation of adsorption separations. This shortcoming is the result of an equally persistent deficiency in the ability to measure adsorption of gas mixtures, despite the huge variety of existing methods to measure mixture adsorption. This work presents a comprehensive overview of 18 techniques used to measure mixture adsorption, including the equipment and principles used in each method as well as the strengths and shortcomings of each technique. This work also provides recommendations for which methods may best suit the individual needs of experimentalists interested in measuring mixture adsorption and includes an outlook on the future of mixture adsorption measurement.

1. INTRODUCTION

Adsorption separations are among the most energy-efficient classes of chemical separations for gaseous mixtures. Research on adsorption separations spans a variety of end-use applications including air separation,1,2 gas sweetening,3,4 and carbon capture from various sources.5−7 Process conditions for each application differ, and many occur in harsh, complex environments. All gas adsorption separations involve exposing an adsorbent to a mixture of gases. The success of an adsorption process design in any given separation depends strongly on the ability to predict the adsorption behavior of the adsorbent−mixture system under process conditions. This prediction is essential not only for selecting an adsorbent material for use in a separation but also for choosing the process conditions under which to perform the separation.

For decades, adsorption researchers have worked to improve mathematical models for predicting mixture adsorption. While the prediction of mixture adsorption behavior from pure-component adsorption data has seen some success, nonideal behavior remains difficult to predict without mixture adsorption experiments. The need for greater availability of experimental mixture adsorption data has been reiterated for nearly as long as the study of mixture adsorption has existed.8−12 Many problems identified in a 1998 paper by Talu on the status of binary gas mixture adsorption experiments persist.10 This report noted that direct measurement of binary mixture equilibria is complicated and time consuming, while the advent of commercial systems has made measurement of pure-component adsorption much simpler and faster. The report also states that the Ideal Adsorbed Solution Theory (IAST) is widely used to predict mixture adsorption but that it cannot give information on deviations from ideal behavior. Both of these problems persist today. Many methods for measuring mixture adsorption have been reported, each with their own pros and cons.13 A summary and comparison of some methods for measuring mixture adsorption was published in 1999,14 and another work describing traditional measurements of pure and mixed gas adsorption was published in 2007.15 However, the landscape of the field has since changed.

In this work, we consider “mixed gas adsorption” to describe simultaneous adsorption of at least two species from any mixture of gaseous or vapor species. We consider methods which gather complete mixture adsorption data, defined by Cai et al. as data sets which specify the temperature, total pressure, gas-phase mole fractions, and adsorbed amounts for all components or total adsorbed amount and adsorbed fractions for all components.16 Although the Van Ness method is an...
exception to this criterion, its popularity merits inclusion in this work. We consider thermodynamic consistency criteria to be outside the scope of this work but refer readers to Talu and Myers\textsuperscript{17} as well as Rao and Sircar\textsuperscript{18} for discussions of thermodynamic consistency tests which may be applied to mixed gas adsorption data sets.

A small group of commercially available instruments for measurement of mixture adsorption have begun to see limited use in academic research. Perhaps the most widely used are the Belsorp VC\textsuperscript{19} (MicrotracBEL Corp., Japan) and the ISOSORP 2000\textsuperscript{20,21} (Rubotherm GmbH, Germany). These instruments take very different approaches to measuring mixture adsorption, using the closed volumetric and gravimetric-densimetric methods, respectively. Other instruments using breakthrough methods have also been introduced, including the Automated Breakthrough Analyzer\textsuperscript{22} (Hiden Isochema Ltd., UK), Selective Adsorption Analyzer 8100 (Micromeritics Instrument Corp., USA), and MixSorb (3P Instruments GmbH & Co. KG, Germany). Hiden Isochema Ltd. has also recently introduced the integral mass balance method using a specially designed adsorption cell.\textsuperscript{23} However, these instruments are relatively recent developments, and their use is limited compared to that of home-built experimental systems in laboratories around the world.

This work is a natural extension of our recent study of binary gas adsorption measurements compiled from the open literature.\textsuperscript{18} Using systematic search methods, that work found more than 900 examples of mixture adsorption isotherms for gases, a much larger number than had been recognized in previous data compilations. An interesting outcome of this large data set is that 18 methods of mixture adsorption measurement were identified. The aim of this review is to discuss and compare these 18 methods. Figure 1 shows the groupings we used to define different families of methods according to shared principles of operation. We provide a summary of the principles and history relating to each method and also briefly analyze the strengths and weaknesses. Finally, we offer recommendations for which methods may be most useful for measuring mixed gas adsorption for different types of adsorbent–adsorbate systems.

Each of the five groups discussed in this work contain methods lending themselves to different applications. The individual methods and popularity thereof as compiled in the BISON-20 database by Cai et al.\textsuperscript{16} are listed in Table 1. The most widely used techniques are the simple breakthrough and closed volumetric methods. Together, these methods are represented in 70% of references in the database and account for approximately 75% of all mixture adsorption data (isotherms and individual data points) in the database. However, there are some interesting differences in how these methods are used. While more papers in this database use breakthrough methods than any other group of methods, the number of individual data points from closed volumetric instruments is triple that from breakthrough systems (5362 vs 1779). Indeed, over half of all mixture adsorption data points collected in BISON-20 were measured using closed volumetric instruments.

It is important to note that in the data compiled by Cai et al. only entries for which “complete” data including pressure, temperature, gas phase mole fractions, adsorbent loading, and adsorbed phase mole fractions are available. For several of the methods discussed in this work (zero-length column, differential column technique, and isosteric method), no entries are present in the BISON-20 database because authors using these methods did not report all of these quantities, but in theory, it is possible to obtain so-called complete data from these methods. Furthermore, BISON-20 includes only purely experimental data, which explains the omission of any Van Ness data.\textsuperscript{24}

By examining only BISON-20 entries published since 2010, several trends become clear. First, the breakthrough methods have greatly increased in popularity relative to all other methods. Before 2010, only 21% of BISON-20 references used breakthrough methods. Since 2010, this jumps to 55% reflecting a huge rise in popularity of breakthrough methods. This is reflective of the current materials-driven nature of the study of mixture adsorption. Breakthrough measurements are a convenient way to evaluate a specific separation by measuring a small number of data points and thus have been used extensively as a way to show a few experimental measurements of selectivity for adsorption of a mixture on a novel adsorbent. Breakthrough experiments have typically not been used for collection of larger data sets. Accordingly, references using breakthrough measurements tend to report fewer mixture adsorption data points than do references using closed volumetric instruments (17 vs 54 points per reference). As breakthrough methods become more popular, a related trend in the database becomes clear: recent references report fewer mixture adsorption data points than older sources. References reporting mixture adsorption before 2010 contain on average 50 mixture adsorption data points. This number decreased to 21 data points per reference among all references in the database published since 2010. This suggests that as research has become more materials focused the drive to quickly evaluate mixture adsorption on a large number of adsorbents has led to an overall decrease in the number of measurements per material.

A third finding is that many techniques have seen only sparing use in the past decade. Half of the techniques described in this work were not used to collect any of the data points in BISON-20 since 2010. Desorption and specialty methods, in particular, were used much less since 2010 than were the other groups of methods, falling almost entirely out of favor. This trend is a healthy sign that the mixture adsorption community is innovating and moving toward faster or less costly methods as they become available. One obvious example of such innovation is the infrared (IR) spectroscopy method, which

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was introduced shortly before 2010 but has become the fourth-most widely used method since.

Many of the methods in Table 1 could potentially fit into more than one group. Perhaps the most obvious example is the volumetric–gravimetric method, which fits into both the volumetric and gravimetric groups. For the sake of simplicity, we have chosen to include each method in only one group.

Table 2 lists the elementary parts of the most popular methods and illustrates connections between different methods. A full table listing all methods is available in the Supporting Information (Table S1). For example, Table 2 shows that the open volumetric method and the closed volumetric method both make use of gas composition analysis, but the open volumetric method uses an effluent flow rate measurement rather than static manometry as does the closed volumetric method. The relationships between methods shown in this table illustrate the inherent ambiguity in delineating these methods into discrete groups.

2. BREAKTHROUGH METHODS

The first group of methods discussed in this work contains only two techniques: simple breakthrough and open volumetric methods. These methods are distinguished only by direct measurement of effluent flow rate through an adsorbent column in the open volumetric method or lack thereof in simple breakthrough. Simple breakthrough is extremely commonly used and makes up the majority of breakthrough measurements. This increasingly popular measurement technique already appears in over one-third of the 263 references reporting mixture adsorption data collected by Cai et al. The breakthrough group comprises chromatographic methods in which a flow of mixed gas is introduced to a clean adsorbent bed. The concentration of each component in the effluent is monitored over time until each component "breaks through" the fixed bed. The flow rate of each component in to and out of the bed are integrated until the flow rate out is equal to the flow rate in. In simple breakthrough, the volumetric flow rate of the effluent is assumed to be equal to the feed, while the

Table 1. Methods Constituting Each Group in This Work, Along with Popularity of Each Method in the BISON-20 Database

| Group        | Method                          | Papers  | Isotherms | Points |
|--------------|---------------------------------|---------|-----------|--------|
| Breakthrough | Simple Breakthrough             | 89 (65) | 296 (193) | 1515 (689) |
|              | Open Volumetric                 | 15 (13) | 50 (41)  | 264 (171)  |
|              | Closed Volumetric               | 99 (40) | 393 (131) | 5362 (1182) |
| Volumetric   | Volumetric-Densimetric          | 1 (0)   | 4 (0)     | 34 (0)   |
|              | Volumetric-Gravimetric          | 7 (4)   | 17 (8)   | 231 (116)  |
|              | Closed Gravimetric              | 8 (3)   | 14 (4)   | 391 (143)  |
| Gravimetric  | Gravimetric-Densimetric         | 2 (1)   | 4 (3)    | 25 (15)   |
|              | Integral Mass Balance           | 0 (0)   | 0 (0)    | 0 (0)     |
|              | Gravimetric-van Ness            | 0 (0)   | 0 (0)    | 0 (0)     |
| Desorption   | Desorption-Gravimetric          | 1 (0)   | 1 (0)    | 7 (0)     |
|              | Desorption-Volumetric           | 14 (1)  | 50 (1)   | 345 (2)   |
|              | Zero-Length Column              | 0 (0)   | 0 (0)    | 0 (0)     |
|              | Differential Column Technique   | 1 (1)   | 2 (2)    | 48 (48)   |
| Specialty    | Isotope Exchange Technique      | 2 (1)   | 6 (3)    | 43 (27)   |
|              | Tracer Pulse Chromatography     | 5 (0)   | 5 (0)    | 46 (0)    |
|              | IR Spectroscopy                 | 5 (4)   | 16 (15)  | 159 (155) |
|              | Concentration Pulse Chromatography | 10 (3) | 31 (14)  | 348 (154) |
|              | Isosteric                       | 0 (0)   | 0 (0)    | 0 (0)     |

Numbers in parentheses include only work published since 2010. The IMB method was introduced concurrently with BISON-20 and was not included therein.

Table 2. Elements of the Seven Most Widely Used Methods Discussed in This Work

| Abbreviation         | SB | OV | CV | V-G | CG | IR | CPC |
|----------------------|----|----|----|-----|----|----|-----|
| Section              | 2.1| 2.2| 3.1| 3.3 | 4.1| 6.3| 6.4 |
| Gas Composition Measurement | ✓ | ✓ | ✓ | ✓ | ✓ |
| Effluent Flow Rate Measurement | ✓ |
| Manometry            | ✓ | ✓ |
| Adsorbate Composition Measurement | ✓ |
| Gravimetry           | ✓ | ✓ |
| Chromatography       | ✓ | ✓ |

"Chromatography refers to the analysis of the response of a packed column to determine adsorbent loading inside the column rather than the use of chromatography as a method to measure gas composition."
open volumetric method requires measurement of the volumetric flow rate of the effluent stream. A simple integral of the difference in inlet and outlet molar flow rates of each component as a function of time is used to determine the adsorption of each component.

Breakthrough methods are extremely flexible. Often, a nonadsorbing inert carrier gas is included in the flow of mixed gas. Inclusion of a carrier gas can allow for use with vapors at very low partial pressures. The use of a back-pressure regulator enables measurements at high pressures. This method can be used with less than a gram of adsorbent and is easily adapted for mixtures of different compositions or single component adsorption measurements.

The simplicity and ease of use of breakthrough methods, especially simple breakthrough, set them apart from the other methods presented here. The equipment required for both breakthrough techniques can be assembled quite easily, and several automated instruments for measurement of breakthrough curves are available. While some kinetic information can be gleaned from the shape of the breakthrough curves, this work is focused on measurement of equilibria and will not delve into details of kinetic measurements.

The largest critique of breakthrough methods is that, in the vast majority of publications using a breakthrough method, each breakthrough curve gives one equilibrium data point before the sample must be reactivated, making breakthrough measurements relatively tedious and unsuitable for the collection of large data sets. This is consistent with the low number of data points per reference observed in the BISON-20 database for references using breakthrough methods.

Since the study of adsorption is currently driven by advances in porous materials, often the ability to make just a few measurements is valuable to understanding the performance of a new material in “benchmark” testing conditions. Often, large data sets are not required to understand whether an adsorbent shows some promise for a given separation. Breakthrough measurements are frequently used to make just a few measurements to establish a single-point selectivity measurement for novel adsorbents.

### 2.1. Simple Breakthrough (SB)

Simple breakthrough (SB) for mixed gas adsorption saw early use by Kenney and Eshaya in 1960. However, this method was used for liquid mixtures before it was applied to gases. The name “inverse gas chromatography” has also been used to describe SB experiments, and commonly the name “breakthrough” is applied to this method, although the open volumetric method is also a breakthrough method. SB may be paired with gravimetric measurement, although this combination is not common. A typical SB setup is shown in Figure 2.

The breakthrough group is the most popular for mixture adsorption measurements, appearing in nearly twice as many papers as any other method since 2010. Over 80% of these papers use SB. Each SB measurement begins with a fixed bed of adsorbent that has been activated by heating in a flow of inert, nonadsorbing gas. A feed flow of mixed gas is introduced at a known composition and flow rate. Commonly, the composition of this gas is controlled using a different mass flow controller (MFC) for each adsorbing component and typically one MFC for a nonadsorbing carrier gas. As this feed flows through the bed and adsorption occurs, the composition of the effluent is monitored until the effluent and feed are identical in composition. The difference in the inlet and outlet molar flow rates of each component is integrated over time to find the amount of each component that has been adsorbed in the bed, where the outlet molar flow rate is estimated from indirect measurement or the inlet, and outlet volumetric flow rates are assumed to be identical when adsorbing components are present in low concentrations. This simple mole balance to determine how much of each component is “missing” from the gas phase is shared by many other measurement techniques. A back-pressure regulator is often used to control the total pressure during adsorption. Furthermore, measurements can be made using vapors introduced by a carrier gas, and a tracer gas may be included to facilitate indirect measurement of the effluent flow rate as described by Wilkins et al. However, the inclusion of carrier gases in SB measurements can affect the adsorption of components of interest.

SB measurements are heavily dependent on accurate dead volume measurements, which may be done with sand or glass beads prior to adsorption measurements. Further, as with other fixed-bed methods, care must be taken to ensure uniform temperature distribution in the adsorbent bed. Attention should be paid to repeatable packing of fixed beds and ensuring that wall channeling is mitigated with appropriate particle size and bed diameter. Furthermore, users should be aware of the roll-up phenomenon and take care to handle this appropriately when making measurements. Finally, experiments must be run until every component breaks through to avoid mistakes related to the “order of addition” phenomenon in which a strongly adsorbing component is sequestered to the entrance of the packed bed while another component passes by and adsorbs along the rest of the bed. Many detectors can be used to measure the composition of the effluent gas including the common mass spectrometer (MS) and gas chromatograph (GC). High time resolution for composition measurement is desirable, especially for mixtures containing strongly adsorbing species with sharp breakthrough profiles. This makes the MS the most popular choice, although other sensors like infrared or H2 analyzers have also been used.

SB is presently the most popular method of mixture adsorption measurement because it is inexpensive, flexible, and relatively simple. SB experiments offer the ability to control the composition and pressure of the gas phase at equilibrium. Small quantities of adsorbent may be used; SB

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**Figure 2.** SB measurement apparatus. This setup is shown using a mass spectrometer, although other detectors may replace this for gas composition measurement.
A simple OV instrument is illustrated in Figure 3. The OV method was used at least as early as 1974 by Reich.40 The OV method for mixed gas adsorption is similar to the simpler SB, and the two measurements share similar instrumental setups and procedures. The name “dynamic column breakthrough” has been applied to describe open volumetric systems, which reflects the fact that similar open-system methods have gone by different names. Readers are referred to Wilkins et al. for an excellent overview of open-system adsorption measurement methods.26 A simple OV instrument is illustrated in Figure 3. The addition of direct measurement of effluent flow rate adds complexity and distinguishes this method from SB. While some users have neglected to account for composition change in the effluent gas while measuring its flow rate,36,41,42 others have done so.35,44 The need to account for composition variation while measuring effluent flow rate is discussed in greater detail by Hofman et al.45 OV is more complex than the closed volumetric method but holds notable advantages in control over gas composition and pressure as discussed by Talu et al., who used both methods in the same work.2

Each OV measurement is identical to an SB measurement except that the effluent flow rate is monitored and accounted for in the mass balance on the fixed bed. As the composition of the effluent stream changes during each adsorption measurement, the effluent flow rate measurement is not trivial. Most mass flow meters respond to changes in composition as well as flow rate, as has been recognized in earlier work.2 Measurement of effluent flow rate allows the experimentalist to account for flow rate differences in the inlet and outlet which occur as adsorption happens in the column, which can lead to an experimental error of 10%−15%,2 especially when adsorbates are in high concentrations in the feed stream.

The most important quantities to measure precisely in the OV technique are the effluent composition and the effluent flow rate. Maintaining the inlet composition and flow rate throughout the measurement is essential as well. This can be done by using a premixed gas cylinder with a single flow controller, but the use of pure gases with individual flow controllers for each offers extra flexibility. As in SB, again a back-pressure regulator can be used to control the pressure at which measurements are made.

The extra precision that comes from measuring the outlet flow rate means that measuring adsorption loadings of different mixture compositions or pressures without reactivating the adsorbent are possible with the OV method. Thus, the OV method provides increased throughput compared to SB, which requires a clean adsorbent sample for each equilibrium measurement. OV may be the more appropriate breakthrough method when high precision or high throughput measurements are required. The precision required for measuring the outlet flow rate adds difficulty to the OV method that limits its use compared to the more easily operated SB. As discussed by Talu et al.,47 a common hot wire flow meter may not be sufficient as a method of flow rate measurement, and other methods may be costly (e.g., Coriolis flow meter) or labor intensive (e.g., bubble flow meter).

2.2. Open Volumetric (OV) Method. The OV method is more complicated for mixtures and requires a GC or other analytical method to determine the composition of the gas phase.

In general, methods like the desorption—volumetric and volumetric—gravimetric methods could be grouped into more...
than one category discussed in this work. We have made these somewhat arbitrary grouping decisions based on the greatest similarity in experimental procedure. For example, a desorption–volumetric measurement is more similar in experimental setup and procedure to a desorption experiment than a volumetric experiment because of the need for a cryogenically cooled desorption cell and nonisothermal desorption steps in the procedure. The principles of volumetric measurement may be paired with a number of techniques to assess mixture adsorption. Volumetric measurements of mixture adsorption work well for many systems, including mixtures with more than two components. Volumetric methods have even been used to study mixture adsorption in slurries and fluidized beds. Generally, volumetric methods rely on an equation of state to predict the compressibility factor of the gas mixture being studied. Volumetric methods also use large adsorbent samples compared to breakthrough and gravimetric methods. A persistent difficulty of the volumetric methods is lack of control over the pressure and composition of the gas phase at equilibrium, although the use of a manostat or electronic dosing control can grant control over equilibrium pressure. Three important variations of this method are described in the following subsections.

3.1. Closed Volumetric (CV) Method. First in the volumetric group of measurement techniques is the commonly used closed volumetric method. Figure 4 depicts a CV instrument using a GC for gas composition measurement. The first measurement of mixed gas adsorption using what was essentially the CV method was made in 1931 using chemical analysis to measure gas composition. Several other examples using an Orsat apparatus for composition analysis preceded the invention of gas chromatography in 1952. Perhaps the most useful modification of the instrumentation used here is the addition of a manostat or electronic dosing control that can grant control over equilibrium pressure. Three important variations of this method are described in the following subsections.

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Second only to SB in popularity among mixture adsorption techniques, the CV method is powerful and versatile and can be used for nearly any adsorbent–mixture system. This method and the others in the volumetric group are distinguished from the OV method in that they employ closed loop recycle systems rather than open flow systems. The CV method uses a closed system with two volumes: an empty reference cell and an adsorption loop containing adsorbent. The system starts under vacuum after the adsorbent has been activated. The process consists of dosing gas of known composition to the reference cell, where pressure and temperature measurements, in conjunction with the known volume of this cell and an equation of state (EOS), allow for calculation of the molar quantity of each component in the gas phase in this cell. Then, gas is dosed from the reference cell to the adsorption loop. The inclusion of a circulation pump to mix gas in the adsorption loop is best practice and may be essential for some systems to reach equilibrium on the time scale of hours rather than weeks. This pump also ensures that the gas in the head space is well mixed throughout the adsorption loop. This gas is allowed to equilibrate with the adsorbent. After equilibrium is reached, the molar quantity of each component remaining in the gas phase is calculated from pressure readings and gas composition measurements. Most commonly, the gas composition is measured by taking a sample of 10–200 μL from the head space for analysis with a GC. A material balance on the difference between the amount of each component dosed to the adsorption loop and the

![Figure 4. CV adsorption measurement apparatus. This setup is shown using a GC, although other methods of gas composition measurement are possible.](image1)

![Figure 5. V-Den adsorption measurement apparatus. This apparatus is shown using a magnetic suspension balance, although, in principle, other microbalances may be used for this method.](image2)
Figure 6. V-G adsorption measurement apparatus. This apparatus is shown using a magnetic suspension balance, although, in principle, other microbalances may be used for this method.

The main weakness of the closed volumetric method is that control of the final equilibrium state is difficult to achieve. Although the pressure at equilibrium may be controlled using a manostat, the composition of the gas phase is still outside the control of the experimentalist. Furthermore, automation of a manostat presents a challenge. The strength and longevity of the CV method are due to its adaptability to many different systems. Adsorption of nearly any mixture on any kind of adsorbent can be measured with the CV method. It is one of the few techniques that has achieved some commercial success.

### 3.2. Volumetric–Densimetric (V-Den) Method

The V-Den method is the first of two methods using densimetry to replace the need to measure the composition of the gas with a separate analytical instrument. The apparatus is shown in Figure 5. The one-to-one relationship between density and composition of a gas mixture is the key to this method, which is therefore restricted to measurement of adsorption of binary mixtures only and further restricted to pairs of gases with different molecular weights. The first to combine volumetric measurements with densimetry were Keller et al. in 2005, who used this method in conjunction with determination of the density of the adsorbate to determine not only the Gibbs surface excess of each component but also the absolute amounts adsorbed of each component from several binary mixtures. These authors note that the use of the magnetic suspension balance allows, in principle, for measurement of coadsorption of corrosive gas mixtures as it removes the delicate parts of the microbalance from the corrosive environment by virtue of magnetic coupling. The same densitometer used in this work has been used in other volumetric methods, allowing calculation of the composition of the gas phase.

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### 3.3. Volumetric–Gravimetric (V-G) Method

The volumetric–gravimetric method depicted in Figure 6 can be categorized into either the volumetric group or the gravimetric group. Like the V-Den method, the V-G method avoids the need to directly measure the composition of the gas phase at the cost of restricting use to binary mixtures only. In this method, manometry is used together with gravimetry to determine partial loadings of each component on the adsorbent. Perhaps less obviously than the V-Den method, this technique also relies on the difference in molar masses of the adsorbates. In the V-G method, the usual volumetric adsorption technique is used to determine the total molar quantity adsorbed on the adsorbent at a given temperature and pressure. The adsorbent sits on a microbalance monitoring the sum of the gravitational and buoyant forces acting on the sample during adsorption. As in other volumetric methods, the total molar quantity adsorbed on the sample can be determined from the volumetric measurement. Gravimetric measurement determines the mass of the adsorbed phase after corrections for the buoyant force.
4. GRAVIMETRIC METHODS

The most popular group of methods after breakthrough and volumetric measurements is the family of gravimetric measurements. Already enormously popular for measurement of pure component adsorption, gravimetric methods are generally considered more reliable at higher pressures than volumetric methods, and they often allow for comparable precision with much lower adsorbent mass. While the volumetric family of methods seeks to measure the molar quantity adsorbed by determining the moles that are “missing” from the gas phase, gravimetric methods measure the change in the weight of the sample as gas molecules adsorb on it.

In a gravimetric experiment, a small quantity of the adsorbent is loaded on a sensitive microbalance. As little as 1 mg may be required for single component adsorption measurements. The cell containing this sample is pressurized with adsorbing gas, and the weight of the sample increases as gas adsorbs. Some complexity is introduced by the need to correct for the buoyant forces acting on the adsorbent, the adsorbed phase, and the microbalance itself. The weight change in the sample is attributed to adsorption; this change determines the total mass adsorbed on the sample.

For a single component system, the weight change is sufficient to determine the quantity of a pure gas adsorbed on the sample. For mixtures, another method must be paired with the gravimetric system to determine the composition of the adsorbed phase and/or the composition of the gas phase. The pure component gravimetric method can be paired with a measurement of gas composition to form the closed method. Other gravimetric methods include the gravimetric–densimetric method and the gravimetric–Van Ness method. Although the Van Ness method is not a true experimental measurement of the equilibrium conditions of mixture adsorption, its widespread use merits its consideration in this work.

An exciting recent development is the introduction of the newest technique discussed in this work: the integral mass balance method. This method can be thought of as the addition of gravimetry to SB. The use of gravimetry allows for measurement of “stepwise” breakthrough curves without reactivation of the sample between step changes in partial pressures of adsorbates in the feed.

The need to correct for the buoyant effects in pure component adsorption measurements with gravimetry is well known. This correction is relatively simple for adsorption of pure gases but more complex in the case of mixtures as the density of the gas phase depends not only on pressure and temperature but also on gas composition. An equation of state can be used to determine the density of the gas phase, or this density can be measured directly as in the gravimetric–densimetric method. Further precision may be gained by accounting for the density of the adsorbed phase, which is not easily measurable. The potential theory developed by Polányi and the pore-filling model ofDubinin have been adapted to suit this application for mixture adsorption.

Broadly, the gravimetric measurement techniques discussed here allow for the use of a smaller sample mass than volumetric techniques. The experimental apparatus required for these techniques are centered on the microbalance required for measurement of adsorbent weight. The most proven of the methods discussed here is the closed gravimetric method. The gravimetric–densimetric method can be used only with binary mixtures whose molecular weights differ, and the gravimetric–Van Ness method is not a true experimental measure of mixture adsorption, although it is useful in predicting adsorption for mixtures whose adsorbed phase is known to be ideal. Presently, the most widely used gravimetric method is the gravimetric–densimetric method. This popularity is due to the relatively widespread use of the ISOSORP instrument from Rubotherm GmbH. The high throughput of the integral mass balance technique makes this a method of interest moving forward.

4.1. Closed Gravimetric (CG) Method. The gravimetric group of methods contains several techniques which overlap in some regard with one from the volumetric group. The CG method is similar to the closed volumetric method, and as shown in Figure 7, the required apparatus for the CG method
is similar to that for the closed volumetric method. Keller et al. were the first to introduce a CG apparatus, which they termed a “gravimetric—chromatographic” apparatus, in 1999. Since the inception of this measurement technique, the CG method has been used to test adsorption of mixtures on a variety of adsorbents including porous glass, coal, activated carbon, mesoporous silica, and metal–organic frameworks.

In a CG experiment, the adsorbent sits in a crucible coupled to a microbalance. Before the adsorbent is loaded into the instrument, the tare weight of the crucible must be measured. For a single beam balance, taring of the empty crucible should be done in vacuum and also with the system pressurized with the sorptive mixture across the pressure range to be used in the experiment. Then, the adsorbent is loaded into the crucible. The volume of the adsorbent must be estimated, commonly with helium expansion measurements. From this point, gas of known composition is dosed to the adsorption cell and mixed via circulation pump. The pressure and composition of the gas are measured after reaching equilibrium. The total mass of the gas supplied to the adsorption cell can be determined from gas density and microbalance measurements of the adsorbate weight. Gas density is determined through an EOS using the composition of the gas and the pressure and temperature of the adsorption cell. Readers are referred to Keller et al. for a mathematical description of the mass balance used to determine adsorbent loadings through this process.

Like CV measurements, CG experiments place prime importance on measurement of gas composition to ensure high-quality data are collected. Unlike CV measurements, knowledge of the internal volumes of the system is not essential. The CG method shares many strengths and weaknesses with the closed volumetric method. It is robust and usable for a wide variety of adsorbent–adsorbate systems. The use of a magnetic suspension balance can allow use with corrosive gases that may otherwise damage the microbalance in this setup. If the volume of the adsorbent is known, this technique can also be used to calculate absolute adsorption in addition to the usual Gibbs surface excess. Finally, the CG method may be used with a smaller adsorbent mass than the CV method; this advantage may be attractive for groups studying materials which may be synthesized only in quantities less than one gram.

### 4.2. Gravimetric–Densimetric (G-Den) Method

The G-Den method is similar in principle to the V-Den method and is likewise restricted to use with binary mixtures of components with different molecular weights. Dreisbach et al. introduced the G-Den method in 2002. The ISOSORP instrument by Rubotherm operates on these principles and has seen some use for the measurement of binary mixture adsorption. The key to this instrument is the simultaneous measurement of density and sample mass using the same balance, achieved by lifting the magnet in the adsorption cell to different heights using magnetic suspension. When the magnet is lowered, the sample and sinker rest on supports. When it is raised, the adsorbent is lifted by the wire and weighed. Raising this magnet further as in Figure 8 also picks up the sinker, allowing density measurement.

One key advantage of this method over the V-Den method is the elimination of the need for careful measurement of the internal volumes of the instrument with each new sample. The mass of each component of the mixture fed to the adsorption cell can be determined from gravimetric and densimetric data alone with no further assumption. This process begins with one calibration measurement that must be made only once per instrument: the inner volume of the adsorption cell must be measured. Furthermore, if the system is to be used with a gas mixture for which an equation of state is not known, the compressibility of the gas mixture can be measured experimentally. Each binary adsorption measurement begins with activation of the sample under heating and vacuum. Then, the gas mixture is fed to the adsorption cell to the desired pressure. The equilibrium values for temperature, pressure, sample mass, and gas density are recorded. Subsequent measurements can be made by dosing the adsorption cell with the gas mixture at an increased pressure. After data collection, a buoyancy correction must be applied. Since density of the gas is being measured throughout the experiment, calculation of the buoyant force is relatively straightforward. The loadings of each component are determined from a mass balance on each component using the mass of the adsorbent and the density of the gas phase.

The G-Den method is designed specifically for measurement of adsorption from binary mixtures of components with different molecular weights but can be sensitive enough to measure coadsorption of N$_2$/O$_2$ mixtures. The elimination of the need for an analytical instrument to measure gas composition makes this method relatively simple and helps explain its commercial success.

### 4.3. Integral Mass Balance (IMB) Method

The IMB method combines gravimetry with principles from breakthrough techniques. It was introduced in 2020 by Broom et al. and has more recently been used by Bell et al. as well. Like the breakthrough methods, each experiment begins with a clean adsorbent activated under heating and flow of inert purge gas. The adsorption measurement begins when the purge stream is switched to a flow of mixed gas. The effluent composition is monitored by MS until it is equal to the inlet composition. However, unlike the OV method, the IMB method does not measure the outlet flow rate to complete a mole balance on the system. Instead, the weight of the sample is monitored using a microbalance as shown in Figure 9, and the weight of the adsorbent throughout the measurement is used to calculate the total mass adsorbed. This weight measurement eliminates the need to carefully measure and integrate the molar flow rates of each species in the outlet. Measurement of outlet composition combined with weight of the adsorbent is sufficient to determine the quantity adsorbed of each component. Measurement of effluent flow rate in the
OV method is considered difficult, so the IMB method compares favorably to the OV method in ease of use.

Broom et al. are one of two groups who have reported data with the IMB method to date, and readers are referred to their work for an in-depth analysis of the principles of the IMB method. An analysis of the strengths and weaknesses of the IMB method after one example of use would be premature.

The custom IMB pressure vessel built for the experimental setup in the first instance of this method appears to be somewhat more complex than those used in other home-built setups cited in this work. Independent fabrication of the setup used for IMB measurements might pose a technical challenge.

4.4. Gravimetric–Van Ness (Van Ness) Method. The method introduced in 1969 by Van Ness for calculation of partial loadings from multicomponent mixtures differs in crucial ways from the other methods discussed in this work. The Van Ness method does not experimentally determine the adsorption of each component from a mixture. However, it is popular as a method to determine pseudoexperimental binary adsorption data, and therefore, we have decided to include it here. The experimental procedure involves monitoring the mass of an activated adsorbent in contact with a mixed gas of known composition using an apparatus like that in Figure 10. The feed flows over the adsorbent until equilibrium is reached. The pressure, temperature, and adsorbent mass are the only experimental data recorded, and then, the excess mass adsorbed at the equilibrium pressure and temperature for a mixture of known composition is determined.

The quantity missing from this measurement is the composition of the adsorbed phase. While the total mass adsorbed is known, the mass adsorbed of each component is not determined experimentally. Instead, the partial loadings of each component are determined through the use of thermodynamic relationships described by Van Ness. This method requires assumptions similar to the Ideal Adsorbed Solution Theory (IAST). An ideal adsorbed phase is assumed, but as Van Ness notes, it is not necessary to assume an ideal gas phase. Readers are referred to the work of Möllmer et al. for a detailed stepwise example of a Van Ness method calculation. It should be emphasized that the assumption of an ideal adsorbed phase behavior is rarely justified, and experiments often show that this assumption does not reflect reality.

Since its introduction in 1969, this method has been modified several times to achieve better agreement with experimentally determined mixture adsorption data. The most recent use of the Van Ness method appears alongside a separate entirely experimental method of measuring mixture adsorption and uses the Van Ness method as a point of comparison only. The incremental gravimetry method introduced by Tondeur et al. uses a similar approach to the Van Ness method, measuring adsorbed mass as gas composition changes while total pressure is held constant. However, Tondeur’s work used nonideal thermodynamic relations to calculate partial loadings of each component. While nonideal relations can better capture adsorbed phase behavior than the assumption of an ideal adsorbed phase, the incremental gravimetry method requires models for the composition dependence of activity coefficients to estimate binary adsorption isotherms. Activity coefficients are not generally well known for adsorbed phases and thus the requirement of known activity coefficients is a significant obstacle.

5. DESORPTION METHODS

Including both static and dynamic methods, desorption techniques offer diverse options for measurement of mixture adsorption equilibria. The hallmark of these methods is desorption of the adsorbed phase for direct composition analysis. Such analysis offers the highest accuracy of any methods in this work in determining the composition of the
adsorbed phase. While all other methods discussed to this point calculate the composition of the adsorbate by material balances to determine the amount of each component removed from the gas phase, desorption methods work differently. In general, the amount of each component in the adsorbed phase in equilibrium with a mixed gas phase is determined by desorbing the adsorbed molecules for analysis.

The first and perhaps simplest methods in this group are the desorption—gravimetric and desorption—volumetric methods. Like the CG and CV methods, these desorption methods use a mass or mole balance in conjunction with a composition measurement to determine the equilibrium conditions. The key difference is that here the composition is that of the adsorbed phase. These static desorption methods heat the adsorption cell while cryogenically cooling an empty “desorption” cell connected to the adsorption cell. In theory, all of the adsorbed molecules desorb from the heated adsorbent and condense in the desorption cell. The desorption cell is then isolated and allowed to warm to room temperature. The composition of the gas in this cell can then be measured with a GC or similar instrument.

Dynamic desorption methods are slightly more complex. The most used among these is the zero-length column (ZLC) method, although the differential column technique has some advantages for measurements at higher pressures. In both cases, the adsorbent is packed in a fixed bed, and an inert purge stream is introduced after the adsorbent has been equilibrated in a flow of mixed gas. The ZLC method involves a sudden, complete replacement of the mixed gas feed with the purge stream, while the differential column technique introduces the purge stepwise while simultaneously stepping down the flow rate of the mixed gas stream. Both of these dynamic methods allow the collection of multiple equilibrium data points during one complete desorption step. Collecting multiple data points per desorption step is an enormous advantage over the static desorption methods, which are very slow due to their collection of only one point per desorption. Thus, labor-intensive collection of desorbate with the aid of liquid nitrogen or another cooling agent hinders data collection for static desorption methods.

This section highlights four desorption-based experimental techniques for measuring mixture adsorption. While the gravimetric methods require correction for the buoyant forces on the sample, the desorption methods require a head space correction for the gas phase molecules remaining in the adsorption cell at the time desorption begins. Both dynamic methods and static methods require head space correction, as the lag time and dead volume, respectively, determine the magnitude of this correction in either case. Despite the need for this kind of correction, these methods can be powerful because they analyze the composition of the adsorbate through desorption rather than by a mass balance on the gas phase during adsorption. Desorption methods can be coupled with other adsorption methods to reveal when hysteresis exists and can give unparalleled accuracy when the adsorbed amount of one or both components is very small.

5.1. Desorption—Gravimetric (Des-G) Method. In the Des-G method, the adsorbed phase is desorbed for direct analysis with GC or an MS as shown in Figure 11. This pairing of gravimetry with the desorption technique was first used in 2002 by Fletcher et al.107

There are two subgroups of desorption systems: static systems that seek to capture the desorbate in a condensing vessel and dynamic systems that use an inert purge gas to dilute the desorbate in flow whose composition is continuously measured. Either method of desorption may be paired with either static or dynamic adsorption procedure. Gravimetric analysis has been paired with the desorption method using both static108 and dynamic107 methods for desorption. Different experimental apparatus are required for each method. Figure 11 shows the setup required for dynamic adsorption and desorption steps. The clean adsorbent is loaded on a microbalance and then contacted with a mixed gas. After reaching equilibrium indicated by constant mass, the mass of the adsorbent–adsorbate system is recorded and corrected for buoyancy as in other methods using gravimetry. This mass determines the total excess mass adsorbed on the sample. To determine the composition of the adsorbate with a dynamic system, the mixed gas contacting the adsorbent is replaced with an inert gas purge stream, and the composition of the effluent gas is recorded. This approach is incompatible with weakly adsorbing gases that begin to desorb immediately when the purge is introduced and should be restricted to mixtures of vapors only. Strongly adsorbing species can be desorbed into the purge stream using temperature-programmed desorption, which allows for easier quantification of these species.107 For a static system, desorption is performed using a desorption cell connected to the adsorption cell. After equilibrium is reached between the mixed gas and the adsorbent, the adsorption cell is connected to the evacuated desorption cell, and these cells are isolated from the rest of the system. The adsorption cell is heated while the desorption cell is cooled using liquid nitrogen or similar. Finally, the composition of the desorbed phase is measured.

The principal strength of the Des-G technique is that it measures the total mass adsorbed independently from the composition of the adsorbed phase, which means that the uncertainties in composition measurement are not as
detrimental here to the adsorption calculations as in the CV or CG techniques. The main difficulty in using the Des-V method arises from geometric constraints on the adsorption cell. Desorption methods require minimization of the head space in the adsorption cell and the need to include a microbalance complicates this.

5.2. Desorption–Volumetric (Des-V) Method. The Des-V method eliminates the need for the microbalance used in the Des-G method. This method is most commonly used with a static method of desorption, although the option for dynamic desorption exists if a noncondensing carrier gas is used. Both dynamic and static methods of adsorption may be used, but dynamic adsorption is usually paired with the Des-V method. The term “flow desorption” is commonly used to describe this pairing. The use of dynamic adsorption allows control of the pressure and composition of the gas phase at equilibrium. When using the Des-V technique with a dynamic adsorption method as shown in Figure 12, the clean adsorbent in the adsorption cell is first introduced into a flow of mixed gas. The composition of this stream is monitored until equilibrium has been reached. The adsorption cell is then isolated from the flow and connected to the previously evacuated desorption cell. The adsorption cell is heated while the desorption cell is cryogenically cooled to condense the desorbate in the desorption cell. After full desorption, the desorption cell is isolated and allowed to warm back to room temperature. The final pressure and composition of gas in the desorption cell are recorded. Care should be taken to ensure the pressure does not exceed safe limits while the sealed desorption cell is allowed to warm back to room temperature. Along with the volume of the desorption cell, an EOS can be used to determine the molar quantity of each component in the desorption cell. This quantity corresponds to the adsorbed quantity of each component at equilibrium plus the quantity of each species in the head space of the adsorption cell, which is subtracted as a free space correction.

The volumes of both the adsorption cell and desorption cell must be known for this method to give accurate results. The need for a free space correction means that the geometry of the adsorption cell and the valves which isolate it should be designed carefully to minimize the free volume of the adsorption cell. Both dynamic and static adsorption methods have been used with the Des-V method. Dynamic adsorption is more widely used, but static adsorption requires less gas. Static adsorption has been in used the Des-V method to study separation of costly isotopically labeled gases. The Des-V method has gone by the names of the “pore probe” method and the “differential adsorber bed” method.

Slow operation is the principal weakness of the Des-V method. The first equilibrium data point requires three time-intensive steps: activation of the adsorbent, full equilibration of the adsorbent in mixed-gas flow, and full desorption of the adsorbent under heating. For subsequent points, however, the desorption step in the last measurement also serves as the activation step for the next measurement. The need for cryogenic cooling also makes this process difficult to automate. Nonetheless, this technique measures the composition of the adsorbed phase in a more direct way than the more popular SB and CV techniques. Desorption methods are the most accurate methods available for measurement of adsorbed amounts of very weakly adsorbing species.

5.3. Zero-Length Column (ZLC) Method. The ZLC method was introduced by Eic and Ruthven in 1988 as a method to study single component gas diffusion in zeolites, exploiting the high sensitivity of FIDs available at the time. Use of ZLC has expanded since those early diffusion measurements to measurements of binary mixture adsorption and adapted to include temperature-programmed desorption (TPD) for desorption of strongly bound species. An MS is used instead of an FID for mixture adsorption measurement as the MS allows simultaneous monitoring of the concentration of more than one adsorbing component at once. It is also, in principle, possible that an IR gas analyzer could be used to measure effluent composition of mixtures of IR-active components at low cost.

The ZLC technique uses a fixed bed of adsorbent of nearly zero length, as illustrated in Figure 13. The thin layer of adsorbent is activated by heating in a purge stream, then equilibrated in a mixed-gas stream in an inert carrier. After reaching equilibrium, as determined by the effluent gas stabilizing in composition, the mixed gas feed is switched to a purge stream of inert purge gas. The adsorbed components immediately start to desorb into this stream. The effluent composition and flow rate are monitored.
Adorption calculations using ZLC are performed under the assumption that the flow rate of purge gas is sufficiently low that the adsorbent–adsorbate system is essentially in constant equilibrium with the purge gas stream. To ensure such a condition is met, experimental replicates using different purge flow rates under otherwise identical conditions can be performed, which should give the same equilibrium curves independent of purge flow rate. Integration of the difference in the inlet and effluent flow rates of each component until full desorption yields the amount of each component adsorbed at the initial equilibrium between the mixed gas feed and the adsorbent. Since the effluent gas is always in equilibrium with the adsorbed phase, each ZLC desorption yields a curve of partial pressure vs loading of each component on the adsorbent. The constant equilibrium between gas and adsorbate allows for collection of much more information than one equilibrium data point per desorption and obviates the primary weakness with the Des-G and Des-V methods, which is their slow and labor-intensive nature.

A key strength of ZLC is that one desorption measurement provides many mixture adsorption equilibrium data points. Only a few milligrams of adsorbent are required to operate ZLC equipment with acceptable sensitivity. While initial measurements were hampered by the requirement that the adsorbing components should adsorb with roughly equal affinity, the use of TPD later addressed this weakness.\textsuperscript{123} It has been noted\textsuperscript{121} that ZLC measurements of diffusivity are usually restricted to the Henry’s constant region, although this restriction is not essential for equilibrium measurements. Readers are referred to Brandani and Ruthven\textsuperscript{122} for a detailed mathematical explanation of this process.

### 5.4. Differential Column Technique (DCT)

Rather than a single desorption step as seen in the other desorption methods mentioned to this point, the DCT makes use of multistep desorption. Like the ZLC method, DCT measurements allow for more than one equilibrium point per desorption. However, this method uses a larger adsorbent sample and does not rely on the assumption that the fixed bed is always in equilibrium with the desorbing purge stream. The DCT was introduced by Shirani and Eic in 2017.\textsuperscript{124} It has not yet seen widespread use in the literature but offers a key advantage over older Des-V and Des-G techniques in its capacity for much higher throughput. It is similar to the widely used SB method, and we anticipate that this technique could see growing use in the coming years.

A typical setup for DCT is shown in Figure 14. To begin each measurement, a fixed bed of adsorbent is activated then equilibrated in flow of mixed gas. A step change is then made in composition of the feed of this mixed gas. The flow rate of the mixed gas is reduced, and helium is added to the feed to keep the total flow rate constant. During this step change, the composition of the mixed gas stream is held constant. The switch to lower partial pressures of each adsorbing component results in desorption of adsorbed species from the column until a new equilibrium is reached. Monitoring of the effluent flow rate and composition allows for integration of the desorbed amount of each component. The principle is the same as that of the OV method, except here the measurement is concerned with the desorbing molecules that are “added” to the effluent rather than the species that are “missing” from the gas phase by adsorption in a breakthrough measurement.

This technique requires simultaneous switching of flow rates of the adsorbate mixture feed and helium streams, which means that using a separate MFC for each adsorbing component adds some experimental complexity. This problem can be avoided by using a mixed gas cylinder whose flow rate can be adjusted using only one MFC but at the cost of decreased flexibility for which mixtures can be studied. Additionally, like the OV method, the flow rate of the effluent must be measured to enable precise integration of the amount of each component exiting the column.

The principal weakness of the DCT is that it requires a large sample mass for operation. The authors who introduced this technique used about 7 g of adsorbent to achieve good measurement sensitivity. This quantity is $10^2$–$10^3$ times more sample than is required for ZLC measurements and may limit the application of this technique to adsorbents which may be easily synthesized in gram scale quantities. In conjunction with more traditional methods of increasing loadings, DCT measurements have the potential to reveal hysteretic behavior in adsorption processes at high pressure because equilibrium is approached from higher toward lower loadings rather than from lower loadings moving to higher loadings. The equipment required for this method is relatively easy to set up and may be used to conduct both DCT measurements and OV measurements.

### 6. SPECIALTY METHODS

This final section will highlight several nonstandard methods for mixture adsorption. These methods range from isotopic techniques to using flow experiments and IR spectroscopy in creative ways. They all offer conceptually distinct and powerful ways to measure mixture adsorption and are highlighted here for completeness. We do not expect any of these methods to become the easy, high-throughput, low-cost method of the future for measuring mixed-gas adsorption, but they might find niche use for certain adsorbent–adsorbate pairs.
Concentration pulse chromatography is the most flexible of this group. Although this method was originally restricted in use to dilute systems where components were adsorbed in similar amounts, subsequent work has expanded the use to more selective systems and more highly concentrated mixtures. This technique requires a relatively simple experimental setup and allows for relatively high throughput.

The specialty group is rounded out with the isosteric method, which offers the ability to measure changes in temperature, pressure, and gas composition as the loading of all components on the adsorbent is held constant. The isosteric method is useful for applications where the loading of the adsorbent is more important than the selectivity. However, the isosteric technique is usually restricted to measurement at low temperatures and pressures, which eliminates isosteric experiments from consideration for study of many high temperature applications of mixture adsorption. Finally, three methods which might be added to this group are described in the Supporting Information for completeness, although their use is not common.

6.1. Isotope Exchange Technique (IET). A number of techniques make use of isotopic labeling to measure adsorption of mixed gases. The use of labeled species allows for some powerful measurement techniques which are otherwise impossible. The IET is a method for measuring mixture adsorption in a static experimental setup as Figure 15 illustrates. The IET was initially developed for study of self-diffusion of gases in zeolites. This technique was applied for measurement of mixed gas adsorption in 1997 by Ryinders et al. and used to measure both kinetics and equilibria of mixed gas adsorption. Others have since used this method to measure kinetics and equilibria of mixture adsorption for both binary and ternary systems on zeolites and metal–organic frameworks (MOFs).

In an IET measurement, mixed gas containing unlabeled species only flows over a fixed bed of adsorbent until the effluent composition is steady, indicating equilibrium has been reached. At this time, the dosing loop, whose volume is also known, is filled with a gas mixture of the same chemical composition as the adsorption loop. However, the mixture in the dosing loop contains only isotopically labeled species. Both loops are connected to form a closed loop with mixing facilitated by a circulation pump, and the gas mixture–adsorbent system is again allowed to equilibrate. Equilibration results in net adsorption of the labeled species and corresponding desorption of the unlabeled species without changing the molar quantity adsorbed of any component. The composition of the gas in the head space of the adsorption loop is constantly monitored with an MS fed through a leak valve. A mass balance on the labeled species dosed into the sample loop with those remaining in the gas phase at equilibrium gives the quantity of each component adsorbed. This mass balance can be calculated equivalently for the bulk isotopes, and the same values for loading of each component should result.

The IET allows complete control over the pressure and composition of the gas phase at equilibrium due to its combination of dynamic adsorption of unlabeled species and static adsorption of labeled species. Static adsorption of labeled species dramatically reduces the required amount of labeled species because performing an open flow adsorption measurement with labeled species would require much more of the labeled species. Measurements can be repeated easily to check reproducibility without reactivating the adsorbent. This technique can be used with sample sizes on the order of one gram. One advantage the IET has over other methods is that it does not disturb the concentration of each component in the adsorbed phase. Hence, measurement is completely isothermal, making experiments simpler than for nonisothermal methods. However, use of this technique is limited due to the high cost of isotopically labeled species.

6.2. Tracer Pulse Chromatography (TPC). TPC is a dynamic method making use of a small pulse of trace isotope flowing over a fixed bed of adsorbent. TPC was initially proposed by Helfferich and Peterson in 1963. The first experiments using TPC were performed in 1965 for very dilute gas mixtures, then in 1966 for pure components at high pressures. In 1980, Danner et al. were the first to use TPC
to study mixture adsorption over the full composition range for adsorption of a binary mixture.133 Early methods used ionization chambers to monitor radioisotope concentrations, but the MS has surpassed this as the detector of choice. TPC has since been paired with positron emission profiling to measure diffusion of mixtures in silicalite.134

The procedure for this method begins with activation of the fixed bed in an inert purge flow. This stream is then switched to a mixed gas stream containing unlabeled gases. The effluent concentration of each species is continuously monitored by MS as shown in Figure 16. Once the concentration of each species in the effluent has reached steady state, a “tracer pulse” of labeled species of one component is introduced to the inlet stream. The retention volume of the molecules in the tracer pulse can be calculated easily by monitoring the effluent concentration of the labeled species after the tracer pulse is introduced. The retention volume for the labeled species of a given component is used to calculate the partition coefficient for that component. In this context, the partition coefficient is equivalent to the adsorption equilibrium constant for that component under the equilibrium conditions in the fixed bed. Readers are referred to Hyun and Danner135 for details.

Introducing one pulse of labeled species for each component in the gas mixture allows determination of the slope of the relationship between the gas molecule fraction and adsorbed phase mole fraction for each component in the mixture under the equilibrium conditions at which the tracer pulses are introduced. Introducing tracer pulses at different compositions allows determination of the mixture isotherm slope across a range of compositions at fixed temperature and pressure.

One important consideration in the design of equipment for TPC is the need to carefully measure the lag time, the time for a tracer pulse to reach the detector in a fixed bed packed with a nonadsorbing material. Without correcting for the lag time TPC overestimates the loading of each component. The magnitude of this overestimation can be minimized by minimizing the dead volume of the ionization cell used with the detector.

TPC is fast, reliable, and requires less adsorbent (typically less than one gram) than more conventional volumetric techniques. It can provide better precision than the comparable concentration pulse method.136 Although separate pulses of trace isotopes must be introduced to measure the loading of each different component at equilibrium, TPC still allows faster throughput than most other methods. Like the IET, TPC is limited in use due to the cost of isotopically labeled species.

6.3. IR Spectroscopy (IR). IR spectroscopy has a myriad of uses.137 In addition to uses in investigating liquid- or gas-phase samples, this method can be used to assess the transmittance or reflectance of incident light on a solid sample. The amount of light absorbed can be related to the amount of a species adsorbed by integrating absorbance bands in the IR spectrum corresponding to each adsorbed species. Although IR spectroscopy has long been used to study adsorbed molecules,138 the first use of this technique to study loadings of species adsorbed from a gas mixture was in 2008 by Cai et al., who used near-IR (NIR) spectroscopy rather than IR.139 Either IR or NIR spectroscopy have been applied to the study of adsorption of mixtures including light gases,140 hydrocarbons,141 organic vapors,139 and water vapor.142

In the context of adsorption, the absorption spectrum for adsorbents can change with the loading of adsorbate molecules. The intensity of bands associated with absorption of infrared light by an adsorbate can be calibrated to the loading of that adsorbate on the sample.143 Moreover, if multiple adsorbates have spectra with nonoverlapping absorbance bands, IR spectroscopy can be used to simultaneously measure the concentrations of these multiple components in the adsorbed phase in a setup like that shown in Figure 17. This approach affords the ability to directly measure the concentration of components in the adsorbed phase in situ, a very strong advantage relative to the other methods discussed herein. The experimentalist must additionally measure the temperature, pressure, and composition of the gas phase in equilibrium with the adsorbent; fortunately, these measurements are routine.

The primary assumption made in using this technique is that the absorbance of infrared light can be reproducibly used to calculate the loading of adsorbates on the sample. While some authors have made measurements using only IR or NIR spectra to measure partial loadings of adsorbed components,139–141,144,145 others have used IR spectra to measure only the composition of the adsorbed phase in conjunction with another method to measure total loading.142,143 This method also requires use of an adsorbent whose IR spectrum can be reproducibly background subtracted from the region of the spectrum containing bands corresponding to adsorbed species. This is challenging for adsorbents which absorb strongly in the same regions of the IR spectrum as the adsorbing species of interest, as the background spectrum of the adsorbent may drown out signals from adsorbed species. This requirement has contributed to the restriction of this technique thus far to investigation of mixture adsorption on MFI146–149 or FAU150 zeolites and silica gel.150–152 While the application of IR or NIR spectroscopy to measure mixture adsorption on other adsorbents may be possible, this method might require careful selection of adsorbates which have absorption bands in regions where the adsorbent does not absorb. For example, adsorbates with bands in the region below 1700 cm−1 would be challenging to observe on MOF adsorbents, which themselves tend to absorb strongly below 1700 cm−1. Given these challenges, IR spectroscopy may be
difficult to apply to adsorbents like MOFs or activated carbons and is limited to adsorbates which have IR-active modes.

6.4. Concentration Pulse Chromatography (CPC). CPC is perhaps the best-explored chromatographic method other than SB. The first use of CPC occurred in 1973. Other early users measured binary mixture adsorption on zeolites and activated carbons and noted difficulty when the adsorbent had much higher affinity for one component than others. Although an early critique of CPC was the complexity of data analysis, this technique has since seen arguably the most consistent innovation since conception of any method discussed in this work. Tezel and coworkers have expanded the use of CPC to more selective adsorbents and higher pressures. In CPC experiments, a fixed bed of adsorbent like that in Figure 18 is equilibrated in a feed flow of mixed gas of known composition. This mixed gas is called the carrier gas, which is distinct from the “carrier gas” referred to in other methods which is an inert, nonadsorbing gas like helium. The effluent exits the fixed bed and flows over a thermal conductivity detector (TCD) or similar. A small “sample gas” pulse of one component is then injected into the inlet of the column using a sampling valve. This pulse enters the fixed bed, and the response of the column is recorded with the TCD at the exit. The retention time of this pulse in the column can be mathematically related to the slope of the curve relating the gas phase and adsorbed phase compositions, as described elsewhere. Along with a model describing the form of the uptake curve, these data provide sufficient information to describe equilibrium behavior and have compared well with data from the CV method in a comparative study. Pulse injections of each component at different mixture compositions of the feed allow for complete determination of adsorption behavior at fixed temperature and pressure. CPC invites comparison with TPC (see Section 6.2). The difference is that a pulse in the concentration of one component of the feed stream replaces the pulse of trace isotopes in the feed stream used in TPC. The need for a detection method which can distinguish isotopes of the same component is avoided in CPC. Like TPC, this technique requires a dosing loop of carefully calibrated volume as well as careful measurement of the lag time of the experimental system and effluent flow rate. Additionally, a second TCD may be used to ensure the composition ofwe feed stream stays constant throughout the experiment as this method is sensitive to untimely fluctuations in feed composition.

CPC is essentially an analog for TPC which can be used without isotopically labeled gases. CPC relinquishes some sensitivity but decreases the cost of operation and increases the number of gases that can be studied relative to TPC. The equipment required for CPC is among the least costly of all methods discussed here to set up and operate. While an initial critique is that mathematical treatment of data was difficult, application of more flexible models to experimental data have made progress in this area. This method boasts higher throughput than many of the more widely used breakthrough and volumetric methods. CPC has overcome many of the initial limitations at the time of its development and stands as a relatively simple, fast method for mixture adsorption measurement. However, CPC has not become widely used as fitting of experimental equilibrium constant data and conversion to more useful equilibrium loading data remain barriers.

6.5. Isosteric Method. The isosteric method seeks to hold constant the loading of each component throughout the experiment. That is, each experiment seeks to gather data for an isostere where adsorbent loading is held constant and pressure changes as temperature is ramped up. The isosteric method was been used to measure adsorption of pure components long before it was applied to mixtures. The isosteric method for pure components was first conceptualized in 1967 and used in 1969. The method was then applied to binary mixture adsorption and later some ternary mixtures. However, this method has seen sparing use lately with the most recently published case in 2007.

The measurement of isosteres is relatively simple for pure gases, but it is more complicated for mixed gases. In the mixed gas application of the isosteric method, a known amount of each component of the mixture is dosed to the adsorbent. This...
is typically done by first filling reference cells of known volume with each pure component, as shown in Figure 19. The contents of these reference cells are mixed, then opened to the adsorption cell containing the adsorbent. To ensure that essentially all of the gas in the reference cells is transferred to the adsorption cell, cryogenic cooling is applied to the adsorption cell. The adsorption cell is then sealed. The isostere is then measured by stepwise increases of adsorption cell temperature. At each temperature, the pressure and composition of the head space of the adsorption cell are measured. Typically, composition is measured with an MS connected by a leak valve. However, the use of a GC with a small sampling loop is also viable.

A central assumption for this method is that desorption as the temperature increases causes negligible changes in loading. This assumption is generally valid at low temperatures and pressures, but it begins to fail at higher temperatures as indicated by the otherwise linear isosteres becoming curved.\textsuperscript{158} Constant loading is best achieved when the adsorbed phase contains many more moles than the gas phase. Thus, experimental design requires a large mass of adsorbent used with the minimum possible head space.

Isosteric operation allows for calculation of isosteric heats of adsorption for components in a mixture.\textsuperscript{157} However, the use of this technique is largely restricted to low pressures and temperatures; many applications of mixture adsorption do not fit these conditions. The need for a large sample of adsorbent (~20 g) restricts this method further, making it even less useful for materials screening where synthesis of this scale may be costly or impractical. The isosteric method maintains niche strength despite these weaknesses because it is the only method allowing measurement of different conditions in which a given loading can be achieved.

6.6. Other Specialty Methods. Three more specialty methods are described in the Supporting Information. These methods are not currently used for mixture adsorption measurement but are included for completeness. Among these are Steady-State Transient Isotopic Kinetic Analysis (SSITKA), Gas-Phase NMR, and the Oscillometric–Chromatographic method.

7. RECOMMENDATIONS FOR CHOOSING AMONG EXPERIMENTAL METHODS

Now that we have presented a wide spectrum of extant techniques to measure adsorption of mixed gases, it is helpful to consider the goals and constraints commonly faced by experimentalists interested in measuring mixture adsorption. The techniques discussed above have a diverse range of advantages and shortcomings. Choosing a method and developing instrumentation for measurement of mixed gas adsorption require a large investment of time and effort. Additionally, providing guidance as to which systems are best for which applications is complex as many of these setups are home-built using different hardware, making rules of thumb difficult to establish. We hesitate to make blanket comparative statements relating to properties like maintenance or quantitative measures of throughput which may not reflect the diversity of instruments in use. Two broad factors usually determine the method best suited to a given application: the nature of the adsorbent–adsorbate systems of interest and the type of experimental data needed. On the basis of a short list of simple criteria, the 18 measurement techniques in this work can be narrowed to a few that best fit the needs of the experimentalist.

The simplest criterion that can narrow the list of techniques available is the scale at which the adsorbent(s) of interest are available. The isosteric method requires the most adsorbent of any method in this work, roughly 20 g of adsorbent for practical measurements. For materials whose synthesis is difficult or costly, 50 mg is a more practical sample size. Several techniques (gravimetric methods, ZLC, IR) can be employed with less than 50 mg of adsorbent, while others (volumetric methods, static desorption methods, CPC) can require more than one gram. Some adsorbents pose challenges for the IR method, which has not been used with carbon or MOF adsorbents. But essentially all other methods can be used with a wide variety of adsorbents. Methods using flow systems may present some challenge for powder adsorbents due to high pressure drop and attrition, but in many cases, users might find pelletized samples avoid these problems.

The adsorbate mixture of interest can also dictate which methods are available for use. Some of the specialty family of methods requires the use of isotopically labeled gases, which can be costly and, for some gases or vapors, not easily

Figure 20. Flow diagram to narrow selection of available measurement techniques for different applications.
Manostat use is discussed in Section 3.1 as applied to the CV over pressure at equilibrium through the use of a manostat. Measurement methods, this list can be narrowed using the control the composition and quantity of the adsorbed phase. Diagram in Figure 20. This chart seeks to use several heuristics used successfully.45,114,164

Uncertainty. In some cases, much larger samples have been noted that larger samples will usually give less measurement uncertainty. In some cases, much larger samples have been procured. These additional costs may make some specialty methods unattractive for routine measurements. Densimetric measurements (V-Den and G-Den) are restricted to use with mixtures of only two components, as is the V-G method. Mixtures containing corrosive components can damage the inner surfaces of instrumentation, posing a challenge for all measurement methods. However, about one-third of the methods discussed here have been used with corrosive mixtures. The use of tubing coated with inert material and MFCs designed for use with corrosive gases may allow for some methods to be adapted for adsorption measurements with corrosive mixtures. In general, methods which use simpler instrumentation may be easier to adapt for complex or corrosive mixtures.

Beyond the adsorbent and mixture of interest, the kind of data desired may help determine which techniques are most appropriate. Experimental control over pressure and gas composition at equilibrium can allow for direct comparison of selectivity of different adsorbents for the same gas mixture under identical conditions. This can be desirable when metrics for selectivity or capacity are important, as can be the case in adsorbent materials screening. In general, open systems allow for control over gas composition and pressure. Breakthrough methods, CPC, TPC, and DCT are open systems which afford this kind of control. IET is one of the few closed systems which allows for control over pressure and gas composition at equilibrium. Other closed systems can afford some control over pressure at equilibrium through the use of a manostat. Manostat use is discussed in Section 3.1 as applied to the CV method, but, in principle, other closed systems could be used with a manostat or piston to control pressure at equilibrium. Only the isosteric method offers the ability to simultaneously control the composition and quantity of the adsorbed phase.

While there are at least 18 options to choose from for measurement methods, this list can be narrowed using the flow diagram in Figure 20. This chart seeks to use several heuristics to help determine which mixture adsorption instrument may be the most worthwhile investment. This chart does not seek to provide absolute guidance for which method is the best, but methods that do not follow these heuristics should, at a minimum, be considered with caution. The sample masses listed can be considered as minimum acceptable values, and we note that larger samples will usually give less measurement uncertainty. In some cases, much larger samples have been used successfully.45,114,164

As shown in Figure 21, the methods described above vary greatly in both difficulty of implementation and possible throughput. Generally, there is some trade-off between ease of setup, throughput, and robustness, where ease of setup refers to the degree of difficulty that could be expected in building and validating an experimental setup for each method, and throughput represents how many mixture adsorption equilibrium points can be measured in a given time. Complete robustness can be defined as the ability to experimentally measure adsorption of any mixture on any adsorbent across a useful range of different temperature and pressure. Systems which are not completely robust, shown by the color scale in Figure 21, are missing one or more of these criteria. For example, the Van Ness method is the least robust as it is not a purely experimental measurement, while other methods either do not work at all for some mixtures or pose challenges for some adsorbents (shown in pink) or require the use of isotopically labeled gases (light blue). Again we caution readers that there are many factors to consider when choosing a method, and while Figure 21 is a good starting point for choosing an experimental method, it is not a definitive guide. The presence of corrosive or hazardous species, presence of gases or vapors, need for precise temperature control, budget for MFCs or pressure transducers, and other factors may make one method more difficult than another for a specific application.

Applications where few measurements are required may benefit from using a system that favors ease of setup over high throughput. Often, a single measurement of selectivity for adsorption of one component from a representative mixture is sufficient to demonstrate the value of further research on that adsorbent.42,165−169 Conversely, many measurements of mixture adsorption may be required to develop a deeper understanding of how a system may respond to perturbations in input.41,170−173 Both kinds of research are required to further understanding of mixture adsorption phenomena and facilitate development of robust and selective adsorbents. Furthermore, the use of a very robust method may not be required if the experimentalist is interested in measuring adsorption of a limited set of mixtures and adsorbents.

The most desirable system would of course rank highest in all metrics. The two systems closest to fitting these criteria for ease of setup and throughput, however, are among the least robust presented in this work. As noted in Section 3.3, the Van Ness method is not a completely experimental measurement of mixture adsorption, while Section 6.3 explains why IR

**Figure 21.** Ease of setup, throughput, and robustness of each method. These are categorized qualitatively, and comparisons may not hold for every adsorbent-mixture system.
spectroscopy works only for select adsorbent—adsorbate mixture systems. The methods which are in the next tier of easily set up, high-throughput systems are ZLC, CPC, and DCT. All of these methods are highly robust, but none are widely used when compared to the CV method and both breakthrough methods. There are two reasons that explain this discrepancy. First, ZLC and CPC data are not as easily analyzed as that from other methods. Second, DCT is relatively new and has not yet had time to rise to the level of popularity we expect it might reach. Breakthrough methods and the CV method are the most popular techniques because both are highly robust, relatively easy to set up, and offer straightforward data analysis.

The most widely used method at present (based on information obtained from the BISON-20 data set) is SB, which offers straightforward setup, good robustness, and control over gas pressure and composition, although at the cost of relatively low throughput. However, SB users must use care in making dead volume measurements and be cautious of roll-up and wall channeling phenomena during measurements. Care should be taken to run experiments to equilibrium and interpret experimental data correctly when mixtures contain a strongly adsorbing component like water vapor. Second in popularity is the CV method, which is equally robust and can give higher throughput but with greater complexity of equipment and less control over the equilibrium conditions. Meanwhile, specialty methods like IR spectroscopy can offer very sensitive measurements but only for some adsorbent—adsorbate mixture systems. It is important to remember that several commercial options exist for measuring mixture adsorption. Any of these commercial options offer easier setup than a custom lab-built system, although likely at higher cost.

8. OUTLOOK

The study of mixture adsorption presently relies to great extent on home-built systems. Although the most popular methods are SB and the OV and CV techniques, a wide variety of other methods have been developed. Many of these have risen in popularity even as SB systems have become more widespread. This trend suggests that there will not be a lone method that will emerge as the preferred technique for all future measurements of mixture adsorption. Rather, a small group of methods, each with their own advantages, is likely to make up the bulk of mixture adsorption measurements in the future.

If the future of mixture adsorption measurement follows a similar path to pure gas adsorption measurement, use of commercial instruments will overtake that of home-built systems as commercial instruments become more accessible. Nevertheless, at present, the home-built systems still represent the vast majority of published mixture adsorption measurements. Among the various techniques presented in this review, there are three which merit further discussion as part of the future of mixture adsorption measurement: SB, CPC, and IR spectroscopy.

Despite its relatively low throughput, SB is currently the most widespread method for measuring mixture adsorption and is likely to account for the majority of such measurements in the next decade. The simplicity of the equipment required for this technique is among the greatest of any method presented in this work. SB has found great favor among those developing novel adsorbent materials, who might have small adsorbent samples and require a single measurement of selectivity for a component in a representative mixture for benchmark testing. These single-point selectivity measurements do not provide information on how the system responds to different gas compositions or pressures. However, there is a simple possibility to address this weakness. The OV and DCT systems use much of the same equipment as SB systems with the addition of effluent flow rate measurement. Experimentalists who perform routine SB measurements can adapt SB systems to perform OV or DCT measurements. Adaptation offers the possibility to measure multiple equilibrium points per activation of the adsorbent, greatly increasing throughput. This adaptation is likely not trivial but may be less daunting than building an OV or DCT system from the ground up.

While SB has been widely used, CPC has not found such popularity. Researchers have lamented that the treatment of experimental data to calculate equilibrium loadings is not trivial. A variety of data treatment methods exist, which are becoming better able to handle highly selective adsorption at the cost of increasing complexity. This method, like SB, uses relatively simple equipment and offers higher throughput than SB. The introduction of robust software for the data fitting methods required to use CPC would make this technique more broadly accessible.

The use of IR spectroscopy to directly probe the composition of the adsorbed phase offers unique advantages when this method can be applied. In situ measurement of adsorbate composition allows high sensitivity and removes the need for careful material balances on the gas phase of the system. If this technique can be applied to adsorbents beyond zeolites and silica gels, IR spectroscopy could see widespread use in the near future. This technique faces some challenges as it has yet to be applied to any MOFs, which are becoming a widely studied class of adsorbents.

We close by highlighting several issues that are relevant to producing and reporting high quality mixture adsorption data. Systematic meta-analysis of experimental replicates of single component adsorption have suggested that approximately 20% of reported single component isotherms are inconsistent with other reported data. Fewer experimental replicates are available for mixture adsorption, but analysis by Cai et al. of the BISON-20 data set also suggested that differences between measurements with nominally equivalent materials are not uncommon. This situation is exacerbated by the observation that in studies focused on materials discovery it is common for materials to appear just once in the literature with no subsequent instances of the same material being synthesized. When aiming to produce high quality mixture adsorption data, it is highly advisable to first provide data showing the ability to reproduce single component isotherms that are known with a high degree of reliability. For CO2 and CH4 adsorption, multilaboratory studies have established isotherms of this kind with readily available reference zeolites, and additional examples with multiple replicates are available for CO2 and alcohols. For mixture adsorption, the BISON-20 data set presents a comprehensive collection of extant mixture data including examples for which replicates have been reported, so careful comparisons to data from this source should be made in any new study of mixture adsorption. In addition, standard practices to enhance data reproducibility and reuse such as reporting experimental uncertainties and tabulating numerical data in readily available ways should always be followed when reporting mixture adsorption data.
While the study of mixture adsorption has seen tremendous innovation in its history, some central problems remain unsolved. Several challenges were identified in Talu’s 1998 examination of the state of the art of mixture adsorption experiments, and many of these challenges remain unsolved more than two decades later. Direct measurement of mixture adsorption equilibria is still complicated and time consuming, and researchers remain heavily reliant on IAST to predict mixture adsorption in the absence of a robust, accessible, high-throughput method for measurements. Although SB has emerged as the closest candidate to this vision, many other methods maintain advantages for certain applications such as the ability of IR to directly monitor adsorbate concentrations. The ability of IR to directly monitor adsorbate concentrations observed has been difficult to achieve.

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ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acs.iecr.1c03756. Information on three additional little-used methods for measurement of mixture adsorption (PDF)

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