

A Collection of More than 900 Gas Mixture Adsorption Experiments in Porous Materials from Literature Meta-Analysis

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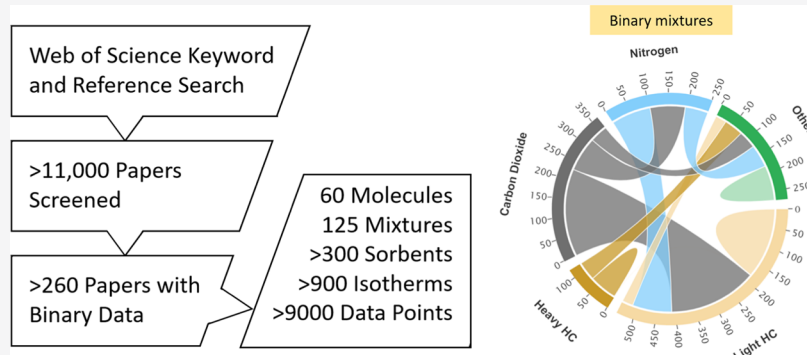
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ABSTRACT: Information on mixture adsorption equilibrium is vital in developing adsorption-based separation processes. Because measuring mixture adsorption is more difficult than measuring single-component adsorption, far more data of the latter kind are available. Previous efforts to compile experimental mixture adsorption data for gases have given data sets with at most a few dozen examples. Here, we report the results of systematic literature meta-analysis that produced a data set of more than 900 gas mixture adsorption experiments. This collection includes data from 125 different binary mixtures including 60 different molecular species and information from 333 different adsorbents. We refer to this data set as the Binary adsorption ISOtherm ExperimeNtal 2020 (BISON-20) Database. Because the BISON-20 data set enormously expands the number and variety of experimental results for binary gas adsorption that are readily available, it will be a useful resource for future efforts in developing new materials or processes for gas separations. As initial applications of the BISON-20 data set, we show how identifying replicate measurements can be used to assess the reliability of binary adsorption data, how the accuracy of Ideal Adsorbed Solution Theory (IAST) can be systematically tested using experimental data, and how trends in selectivity for gas separations across many materials can be examined.

INTRODUCTION

Energy-efficient chemical separations are a critical step in many large-scale chemical processes.¹ Adsorption of gases or liquids into porous materials is an attractive mode of chemical separations that is already used commercially, for example, in air purification and hydrocarbon processing² and has been widely considered for CO₂ capture.³ Enormous numbers of distinct porous adsorbents exist,^{4,5} making comprehensive experimental screening of adsorbents for targeted separation applications challenging. This observation has driven efforts to use computational models to rapidly predict the adsorption equilibrium of diverse sets of chemical species in large libraries of porous materials.^{6–8}

Assessing the performance of an adsorbent for a chemical separation requires information on the adsorption of the relevant chemical mixtures. Despite the self-evident nature of this statement, information on single-component adsorption is far more prevalent in the scientific literature than mixture adsorption data. This situation is in large part because single-component experiments are far easier to perform than

experiments with mixtures, but it is also widely thought that approximate mixing theories such as Ideal Adsorbed Solution Theory (IAST)^{9,10} or heuristic performance metrics^{11,12} can give useful insight using only single-component data. Multiple situations are known, however, where IAST is expected to be inaccurate,¹⁰ and comparisons between simple performance metrics and detailed process models have pointed to the limitations of these metrics.¹¹ As a result, experimental data on binary or multicomponent adsorption equilibria have significant value.

Several previous sources have compiled published mixture adsorption data. Wu and Sircar reviewed data of this kind in

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2016,¹³ reporting on 44 binary adsorption isotherms from 29 separate published sources. More recently, Kaur et al. collected 37 binary isotherms from published experiments in their work on a mixing theory for adsorption that goes beyond IAST.¹⁴ An interesting feature of these two collections of data is that they are nonintersecting; that is, none of the papers used in one study also appeared in the other study. This observation motivated us to ask how many examples of binary adsorption in porous materials can be found in the literature. We initially examined the NIST/ARPA-E Adsorption Database, which has aimed to systematically locate adsorption data from experiments and simulations.¹⁵ This database primarily contains single-component data, but a number of entries are flagged as being from adsorbed mixtures. Our initial analysis of the NIST database identified examples of 70 experimental binary adsorption isotherms. Surprisingly, there was little overlap between these examples and the data collections by Wu and Sircar as well as Kaur et al. Specifically, there was only one example that appeared in both the NIST database and one of these other two sources.

The analysis described above suggests that the totality of binary mixture adsorption data in the scientific literature has not been captured in any prior effort to survey this data. In this paper, we describe a literature meta-analysis that gives a more comprehensive collection of binary mixture data than any previous effort. The search strategy we implemented to this end is conceptually simple and could readily be adapted to other contexts. We identify 908 distinct binary adsorption isotherms where direct experimental data are available. Of these examples, 630 also reported single-component adsorption data for the same conditions. This data set allows us to examine various interesting topics such as the kinds of mixtures and adsorbents for which data are available, the ability of IAST to predict binary mixture adsorption, and whether examples exist where multiple independent replicates are available. These results provide a tool that will be valuable to the separation community in accelerating the modeling and design of adsorption separations of complex mixtures.

METHODS

A typical search strategy when finding published data of a desired kind is to use targeted search terms in one or more databases of publications. The limited overlap between previous collections of binary adsorption data noted above illustrates the potential shortcomings of this approach. We supplemented this direct search approach with a forward and backward citation search in which for selected papers we examined all of the papers cited in the published paper (a backward search) and also all of the papers that cite the published paper (a forward search). Conceptually, this approach relies on the assumption that it is rare for papers to report binary adsorption data without citing some earlier examples of measurements of this kind.

The specifics of our search strategy were as follows. We used the Web of Science as the search engine for automated literature searches. Searching for papers that contained the keywords “adsorption isotherms,” “binary mixture,” and “experiment” in the “Topic” entry gave 303 separate published sources. We then collected all papers that either cited one of these 303 references or was cited by one of these references.

Using the backward and forward search methods defined above and eliminating papers for which data were already available in the NIST database generated a collection of 11 586

papers. Analysis of these papers followed the flow chart in Figure S1. Each paper was examined to separate the papers containing experimental binary gas adsorption data from those that do not. Papers in both categories were further examined to determine if they reported binary gas experimental data in other sources. If sources of this kind were identified that were not in either our original collection of 11 586 papers or the NIST database, these sources were added to our collection. This step increased the size of our collection of papers to 11 672. Each of these papers was examined by at least one person. Analysis of these papers identified 236 unique papers (2.02% of the total) that reported binary gas adsorption data. We did not include papers that reported partial adsorbed amounts calculated using the so-called Van Ness method because this method does not yield unambiguous information.¹⁶ A list of papers of this kind is shown in Table S9.

Each paper that reported experimental binary gas adsorption data was further analyzed to determine whether the data sets were complete. Throughout the discussion below, we define an isotherm to be a collection of measurements from a single adsorbed mixture in a single adsorbent at a single temperature. We consider isotherms that only include a single adsorbing component separately, even though they could be described as limiting cases of the mixture data; we return to this point below. To be considered complete, a data set needed to specify the temperature, total pressure, gas-phase mole fractions, and adsorbed amounts for both components (or total adsorbed amount and adsorbed fractions for both components, see Figure S2). Incomplete data sets were discarded during this process. Data that were not available in tabulated form were obtained via digitizing the original figures. The resulting collection of binary gas adsorption data is given in the Supporting Information. An example of collected data is shown in Table S1. The Web of Science ID was used to label the paper in which the data was obtained. Other identification numbers such as digital object identifier (DOI) and thesis dissertation numbers were also given if available. Adsorbing species were designated with International Union of Pure and Applied Chemistry (IUPAC) names. Adsorbent names were taken directly from the original report. We refer below to adsorption isotherms, defined as a collection of data for the same adsorbent material, adsorbing species, and temperature and also to individual data sets, defined as data from an adsorption isotherm for which either the pressure or the composition was kept constant while changing the other property for multiple data points.

The collected data records the adsorbed amounts (q_i) and the units for this quantity reported by the original authors. The gas-phase compositions (y_i) were collected in mole fractions or volume fractions as reported by the original authors. Otherwise, adsorbed fractions (x_i), total adsorbed amounts (q_{tot}), or selectivity ($S_{1/2}$) were recorded. All data and units were tabulated as reported and comments were also recorded with the data to record information such as cases when the data reported excess adsorption. The type of experiment and the specific detector used were also collected. In breakthrough experiments, the total pressures we report are for noncarrier gases only. In these instances, a note is included with the data indicating what carrier gas was used.

We included experimental binary isotherms from the NIST/ARPA-E database during our data collection process. As of August 2020, this database contained 13 303 data points for binary mixtures from experiments (labeled as “exp”) or

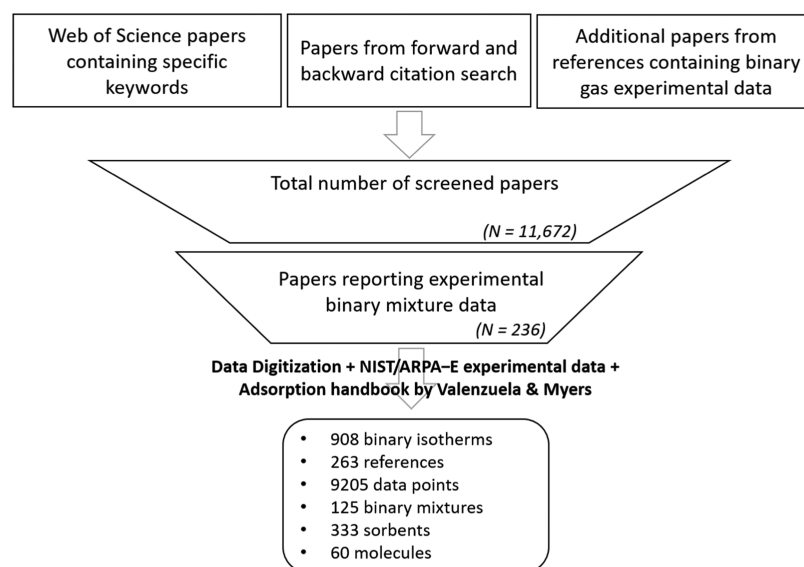


Figure 1. Schematic illustration of binary data collection from paper search strategy. The number of papers at each stage is shown in parentheses (N).

computational simulations (labeled as “mod” or “sim”). Focusing on the 8643 binary data points labeled as “exp”, we reviewed each reported isotherm and excluded liquid adsorption data and incomplete isotherms using the same procedure discussed. We found that 16 papers in NIST that were labeled as experimental data in fact did not report experimental binary data (see Table S10 in the Supporting Information). This analysis of the NIST/ARPA-E database yielded 70 complete gas mixture experimental binary isotherms reported by 25 distinct papers.

For publications that were not listed in the NIST/ARPA-E database, we digitized the published experimental binary adsorption data. For the 25 papers that were included in the NIST/ARPA-E database we used the data reported in that database. We also compared our sources with the 1989 book by Valenzuela and Myers, which reports 12 papers with experimental binary adsorption data.¹⁷ Two papers were listed by Valenzuela and Myers that were not already in our collection so these were added to our list. In total, this data collection effort identified 908 distinct binary isotherms from 263 references. This collection of data contains 9205 data points from 125 unique binary mixture pairs adsorbing on 333 different sorbents. This is by far the largest and most diverse data set of this kind that has been reported to date. The process that led to this data set is summarized in Figure 1. We will refer to this data set as the Binary adsorption Isotherm Experimental 2020 (BISON-20) Database.

Many of the 263 papers that reported mixed gas data also reported single-component adsorption data. Because the latter data can be viewed as a special case of mixed gas data where the bulk-phase mole fraction of one species is zero, the single-component data from these papers were also digitized. These results are available in the Supporting Information, where the isotherm labels from the binary database were also used to label the single-component isotherms. In this way, one can easily find the corresponding single-component data that corresponds to a binary isotherm, if it is available. Among all 908 binary isotherms reported in the database, 630 of these reported single-component isotherms in the same paper.

Among the sources we examined, two examples have been found that contain identical data without citing each other. One example comes from a DOE report (DE-FC26-00NT40924_Rep) and a peer-reviewed paper accessed by Web of Science (DOI 10.1016/j.fuel.2005.05.002). Binary data were digitized using the peer-reviewed paper in this case. Another example has two peer-reviewed papers that appear to have identical contents but were published in different journals within a year of each other (DOI 10.1002/1521-4125(20021105)25:11<1060::AID-CEAT1060>3.0.CO;2-7 and 10.1023/A:1022206031461). In this case, only the paper that was published earlier was used in our data collection.

The adsorbents used for the 908 binary isotherms in the BISON-20 data set were classified into four categories: zeolites, metal–organic frameworks (MOFs), activated carbons, and other (see Figure 2). Zeolites make up 42% of the adsorbents, but each category is represented by many isotherms. A more detailed breakdown of the adsorbent types is shown in Figures S2–S5. Information on how we accounted for adsorbents with multiple names in the published literature is given in Tables S3–S5.

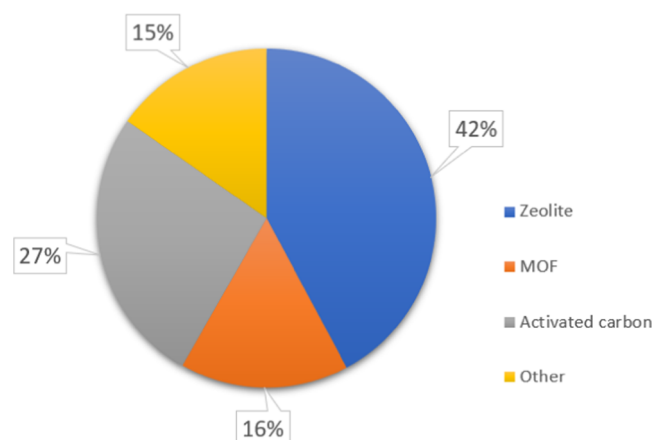


Figure 2. Adsorbent types among the examples available in the BISON-20 database ($n = 908$).

To indicate the gases for which data are available, it is useful to separately consider carbon dioxide, nitrogen, light hydrocarbons (light HC), and heavy hydrocarbons (heavy HC). For this purpose, we took light HCs to include C_1 – C_3 species and heavy HCs to be all larger hydrocarbons (see Tables S6–S8). Figure 3 shows the number of binary isotherms containing

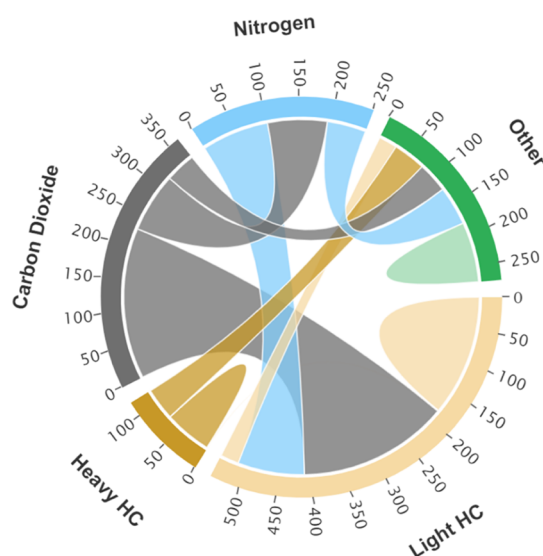


Figure 3. Binary mixture pairs in the BISON-20 database ($n = 908$). The circumference of the circle shows the number of isotherms available for the indicated component, while shaded areas inside the circle indicate the number of binary mixture isotherms with the indicated components.

gases from each of these categories in the BISON-20 data set. Species that are not described by the four categories listed above are shown in Figure 3 as “Other”. There are, for example, 219 isotherms of light HC– CO_2 mixtures and 96 isotherms of light HC– N_2 mixtures.

In addition to categorizing the available mixture data in terms of adsorbents and adsorbing gases, it is interesting to ask what bulk-phase compositions are represented in the data. The composition histogram in Figure 4 shows that a large number of measurements used equimolar bulk mixtures (1588 data points, 17.3% of the total), while measurements using dilute mixtures, that is with $y_1 > 0.925$ or $y_1 < 0.075$, make up 17.9% of the measurement (1637 data points).

A significant fraction of the data we collected was digitized from figures. To assess the quality of the digitizing process, we picked the data for CO_2/CH_4 in MIL-53(Al) at 30 °C reported by Finsy et al.¹⁸ The original paper reported the data in both graphical and tabular form, with the tabular data rounded to one decimal point. The authors also kindly shared their exact experimental data with us, that is, their graphical data with no rounding. A comparison between our digitized pressures and adsorption loadings and the values reported by Finsy et al.¹⁸ shows that the pressures can be digitized, in average, within $\pm 1.3\%$ of the original values (see Tables S10 and S11). Although digitized loadings are, on average, within $\pm 5.9\%$ (CH_4) and 1.2% (CO_2) of the tabular values reported by Finsy et al.,¹⁸ they are, on average, within $\pm 1.2\%$ (CH_4) and 0.4% (CO_2) of their exact experimental values. This example suggests that the uncertainties associated with our digitizing process are small, although it also highlights the value of including tabulated data for published figures¹⁹ provided the

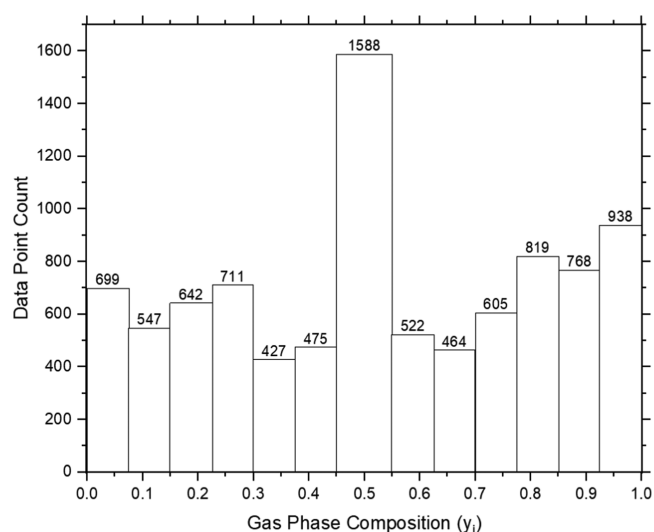


Figure 4. Histogram of bulk-phase composition for all data points in the BISON-20 database ($n = 9205$). Each gas composition was defined in terms of the component in the binary mixture with the lower molecular weight of the two components.

full data for the figure is included. When digitizing data from figures, it is possible for values of 0 or 1 for a gas or adsorbed phase fraction to be read as slightly negative values near 0 or slightly larger than 1. Similarly, a very small or zero absolute adsorption loading may be read as a slightly negative value. In such cases, we rounded the values to the closest integer values (either 0 or 1) so that the physical limits on these quantities are correct.

The BISON-20 data set provides useful insight into the range of experimental methods that can be used to measure binary gas adsorption. The experiments compiled in this data set were collected using 15 distinct experimental methods that can be broadly grouped into breakthrough, volumetric, gravimetric, desorption, isotopic, and specialty methods. The majority ($\sim 75\%$) of the papers represented in the database used either a breakthrough or a volumetric method. There has been a clear shift in the last decade in the use of breakthrough methods relative to all other methods. Only 21% of papers in the data set published before 2010 used a breakthrough method, while 57% of papers from after 2010 used this approach. The use of desorption methods and isotopic methods has greatly decreased over time; these methods represented 13% of all isotherms collected before 2010, but just 1.4% of isotherms after that year.

Historical trends up to 2019 for the adsorbent materials and gas mixtures were extracted from the BISON-20 data set. Figure 5a shows the trends for different gas mixtures measured over time using the same gas categories for light and heavy HC as shown in Figure 3. Three gas mixtures, light HC– CO_2 , CO_2 – N_2 , and light HC– N_2 , show a sharp increase in the figure after the 1980s. These trends are also seen if the data are normalized with the total number of reported isotherms for the decade (see insert in Figure 5a). The trends among adsorbents reaching back almost a century are shown in Figure 5b. A sharp increase in the accumulated number of isotherms line began around 1980. It is interesting that the number of reports with zeolites remains larger than the number of reports for MOFs, despite the intense interest in the latter materials in the research community.

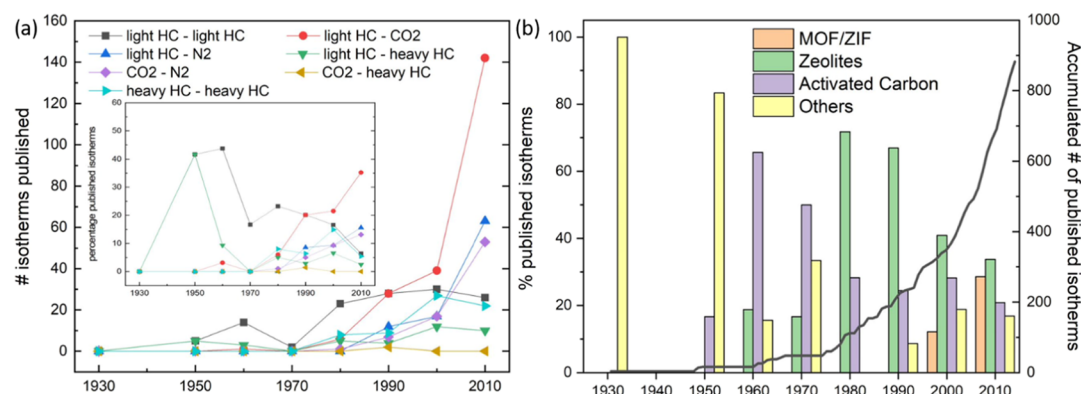


Figure 5. (a) Summary of isotherm number as a function of the decade based on gas mixture components in the BISON-20 data set. The inset shows the percentage of kind of isotherm published within each decade. (b) Summary of percentage of published isotherms (left axis) based on adsorbent types in the BISON-20 data set for the decade starting in the year indicated. The accumulated number of isotherms as a function of time is shown as a solid curve (right axis).

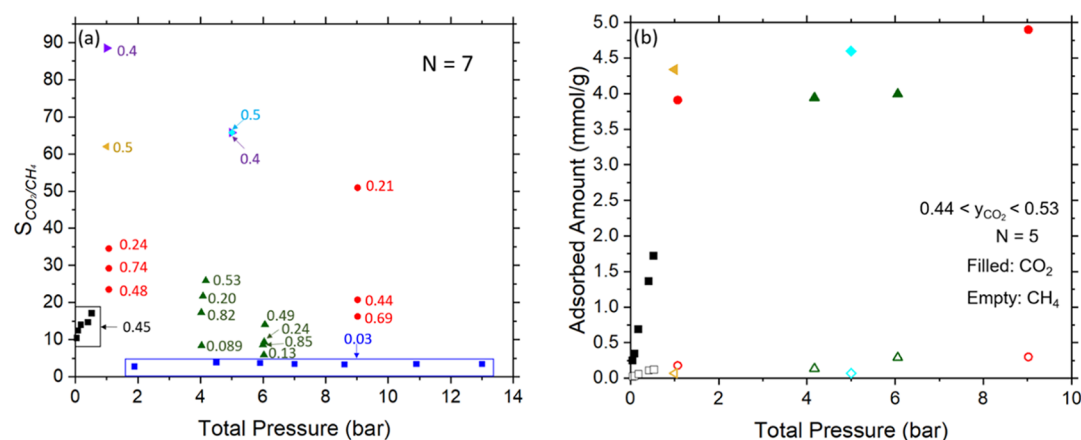


Figure 6. (a) Selectivity from replicate isotherms measured on CO₂–CH₄ mixtures on zeolite 13X at 303 ± 5 K. Different symbols represent different published papers. CO₂ gas-phase compositions are indicated next to the data points. Points in purple, light blue, red, and yellow come from breakthrough experiments. (b) Reported loadings from CO₂–CH₄ mixtures on zeolite 13X at 303 ± 5 K for a CO₂ gas-phase composition range of 0.44–0.53 using the same color notation as in (a). CO₂ and CH₄ loadings are shown as filled and empty symbols, respectively.

Replicate Measurements of Binary Gas Adsorption.

One immediate application of the BISON-20 data set is to search for replicate experiments. Identifying replicate experiments in distinct published reports can be a useful way to assess the reliability of published data.^{20,21} Systematic analysis of replicates of single-component adsorption of CO₂ and alcohols in nanoporous materials has suggested that ~20% of published experimental single-component isotherms are inconsistent with repeat measurements of the same example.^{22,23} Interlaboratory studies that perform many replicate experiments in a well-defined material provide a useful path to defining material standards and allowing careful tests of modeling methods.²⁴ Because of the relatively small number of experimental binary isotherms available in previous collections of this data, we are not aware of any examples of replicate binary adsorption experiments that have been identified previously.

Our discussion in this section focuses on measurements reported for the same gas mixture on the same adsorbent within a small temperature and pressure range. Our first example is the adsorption of CO₂/CH₄ mixtures on zeolite 13X (Figure 6). The BISON-20 data set includes seven papers reporting binary adsorption isotherms at 303 ± 5 K for this example.^{25–31} This is the largest number of replicates we have

found among the BISON-20 data. Four of these papers used breakthrough measurements (purple, light blue, red, and yellow data points in Figure 6) and three of these reported only one or two data points in this temperature range. Figure 6b shows the reported adsorption loadings from the five reports with 0.44 < y_{CO_2} < 0.53. The measurements are in broad agreement that the zeolite is strongly selective for CO₂ over CH₄, but there is considerable variation in the CH₄ loadings. This variation leads to disagreement between the various reports as to the selectivity of adsorption (Figure 6a). In particular, the data from three of the four breakthrough measurements report much higher adsorption selectivities than the other available data at comparable bulk-phase compositions. Even among the remaining data, there is disagreement on whether the adsorption selectivity increases or decreases as the bulk-phase composition is increased. Zeolite 13X is hydrophilic, so differences in sample pretreatment may account for some of the variations between the different reports. The data in Figure 6 also point out an intrinsic difficulty with accurately measuring selectivity in highly selective adsorbents, namely that small uncertainties in the adsorption loadings of the more weakly adsorbing species lead to large uncertainties in adsorption selectivity.

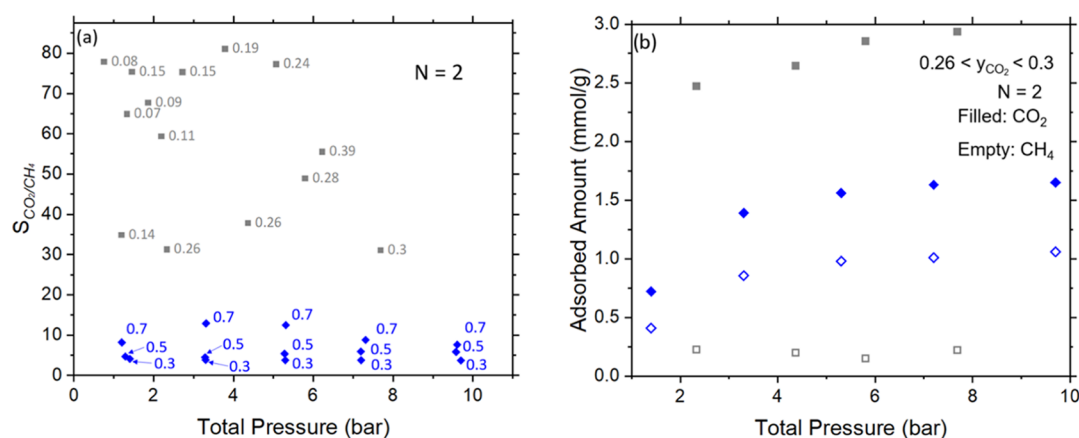


Figure 7. (a) Selectivity from replicate isotherms measured for CO_2/CH_4 mixture on zeolite 5A at 323 ± 5 K. Different symbol colors represent different published sources. CO_2 gas-phase compositions are noted next to the data points. (b) Adsorption loadings for CO_2/CH_4 mixtures on zeolite 5A at 323 ± 5 K with CO_2 gas-phase compositions in the range 0.26–0.3. The same color notation as in (a) is used. CO_2 and CH_4 loadings are shown with filled and empty symbols, respectively.

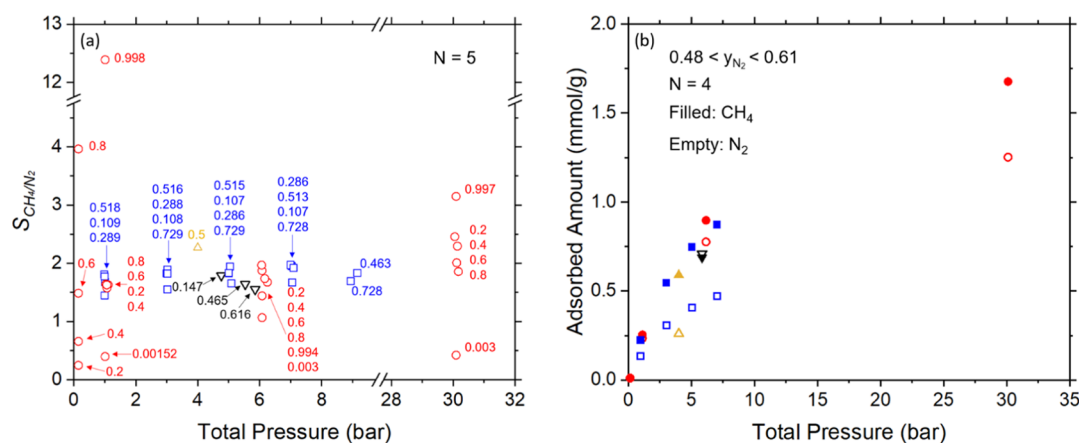


Figure 8. (a) Selectivity from replicate isotherms measured for N_2/CH_4 mixture on zeolite 5A at 298 ± 5 K. Different symbol colors represent different published sources. N_2 gas-phase compositions are noted next to the data points. (b) Adsorption loadings for N_2/CH_4 mixtures on zeolite 5A at 298 ± 5 K with N_2 gas-phase compositions in the range 0.48–0.61. The same color notation as in (a) is used. CH_4 and N_2 loadings are shown with filled and empty symbols, respectively.

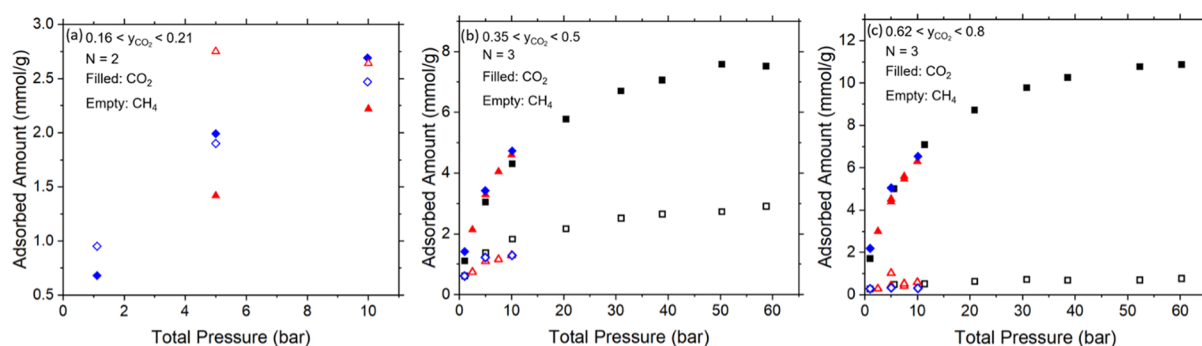


Figure 9. Replicate isotherms for CO_2/CH_4 mixture on Norit activated carbon at 298 ± 5 K at CO_2 gas-phase composition range (a) $0.16 < y_{\text{CO}_2} < 0.21$, (b) $0.35 < y_{\text{CO}_2} < 0.5$, and (c) $0.62 < y_{\text{CO}_2} < 0.8$. Different symbol colors represent different paper sources.

Figure 7 compares the two replicate isotherms that are available for the CO_2/CH_4 mixtures in zeolite 5A at 323 ± 5 K. Each paper presented more than ten measured data points.^{32,33} It is clear that the two sets of measurements are not consistent with each other; one gives selectivities of 30–80 while the other gives selectivities of 5–10. The data marked in gray in Figure 7 were collected on zeolite 5A regenerated at 573 K for

6 h prior to adsorption, while the data marked in blue used a 473 K regeneration temperature for 3 h.^{32,33} Because zeolite 5A is hydrophilic, it is likely that these different preparations led to materials with different amounts of water content and that this difference can account for some of the differences in adsorption between the two reports.

Another set of replicate binary isotherms is shown in Figure 8 for N_2/CH_4 mixtures on zeolite 5A at 298 ± 5 K.^{34–37} At the pressures and bulk-phase compositions that can be directly compared the four independent sets of experimental data are consistent and show selectivities of 1–3 favoring CH_4 over N_2 . There are a small number of data points from one set of experiments (shown with red symbols in Figure 8) for which the measured selectivity falls outside the range of the other experiments, but most of these data points come from experiments in which one component was very dilute (e.g., $y_{\text{N}_2} = 0.003$ or 0.998) and/or the total loading was small. At these conditions, the uncertainty in the measured selectivity is large because one or both components have a very small loading in the adsorbent.

A nonzeolite material for which replicate data are available is Norit activated carbon. Figure 9 compares three separate reports of CO_2/CH_4 adsorption in this material.^{38–40} The results for CO_2 adsorption are consistent among the different reports when $y_{\text{CO}_2} > 0.35$, but less consistency in the data is seen with lower y_{CO_2} . The results for CH_4 , which is the more weakly adsorbed component, are less consistent among the different reports. This variation leads to strong deviations among the adsorption selectivities from different measurements (see Figure S6). Two replicates presented in Figure 10

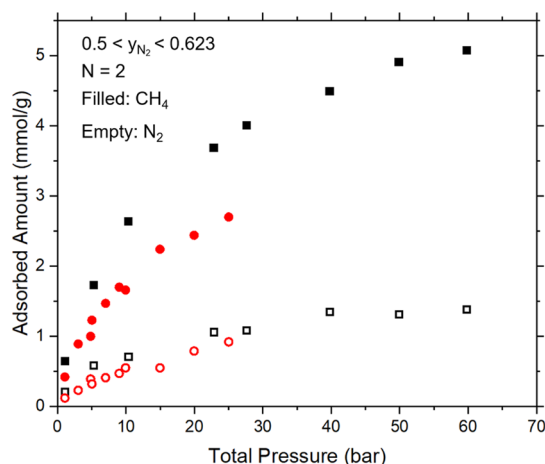


Figure 10. Replicate isotherms for N_2/CH_4 mixture on Norit activated carbon at 298 ± 5 K at gas-phase compositions of $0.5 < y_{\text{N}_2} < 0.623$. CH_4 and N_2 loadings are represented with filled and empty symbols, respectively.

are also available for N_2/CH_4 adsorption in Norit activated carbon.^{38,41} In this case, the reported loadings for N_2 , the more weakly adsorbing component, are quite similar in the two reports, but there are deviations in the reported CH_4 loading. This means that the two reports give rather different adsorption selectivities.

The replicate experiments discussed above give several useful insights into the challenges of reliably measuring binary adsorption experimentally. First, they underline the observation that measuring selectivity accurately is considerably more challenging than measuring adsorbed loadings, especially in examples where one component is weakly adsorbed. Second, similar to earlier studies of replicate single-component adsorption experiments,^{22,23} experimental studies exist that are outliers in the sense that they are inconsistent with other self-consistent sets of replicate data. The results above for

CO_2/CH_4 mixtures on zeolite 13X are the most striking example of this, possibly because this is the example for which the largest number of replicate studies was found. Although outliers of this kind can arise because of problems with the reported data, it is more likely that each set of experiments was performed carefully and the differences that are found stem from systematic differences in sample preparation or similar issues.^{20,21,24,42} Identifying and controlling the source of experimental variation of this kind has significant value. Finally, this discussion raises the question of how future experiments or equipment should be validated before generating new binary adsorption data. The variation seen among replicates above hints that attempting to perform this validation by comparing to a single previous published study may be suboptimal. A more reliable strategy would be to choose a gas mixture, adsorbent, and conditions from the examples above where consistent results have been obtained in multiple previous experiments. An even more powerful approach, which would require concerted work by the adsorption community, would be to coordinate an interlaboratory study using a widely available reference material, similar to work that has recently been reported for single-component CO_2 adsorption.⁴²

Trends in Adsorption Selectivity. Another immediate use of the BISON-20 data set is to consider the adsorption selectivity for a specific gas mixture across all materials for which experimental data is available. We illustrate this use of the database with $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$ mixtures and CO_2/CH_4 mixtures.

In Figure 11, we show all of the available data for $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$ mixture adsorption at 298 ± 10 K and $1 < P_{\text{total}} < 1.44$ bar in terms of the reported selectivity as a function of the total loading. Examples that reported a range of adsorption conditions indicate the range of reported outcomes as error bars. This collection of data comes from 16 papers,^{43–58} including three papers reporting replicate measurements with zeolite 13X^{51,56,58} and two papers that report selectivity data from more than one material.^{48,52} Out of the 16 materials reported, 13 are selective for ethane over ethylene, while zeolite 13X, Mg-MOF-74 and NUS-6(Hf)-Ag are reported to be selective for ethylene over ethane. The results are consistent with the idea that MOF materials such as Mg-MOF-74 and NUS-6(Hf)-Ag with open metal sites that have specific interactions with the pi-bond in ethylene can give $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ selectivity.^{51,53} If the differences between independent replicates that are seen in Figure 11b for zeolite 13X are similar for other materials for which no replicates are currently available then it is difficult to say with any certainty which materials are the “winning” materials in terms of $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$ mixture adsorption. This is a surprising conclusion given the industrial importance of this separation and the considerable research effort that has been applied to finding adsorbents for it.

Figure 12 shows a second example of surveying adsorbent selectivity, in this case for CO_2/CH_4 mixtures at 298 ± 5 K and $0.88 < P_{\text{total}} < 1.16$ bar. Further details of the low total loading and selectivity range is shown in Figure S8. The BISON-20 data set includes 22 papers with data under these conditions,^{18,25,29,33,39,59–75} including two replicate measurements for zeolite 13X^{25,29} and seven papers reporting selectivity data for two different materials.^{18,29,60,63,65,67,75} Among these 28 adsorbents, half are MOFs, three are zeolites, and five are activated carbons. Most of the selectivities are less

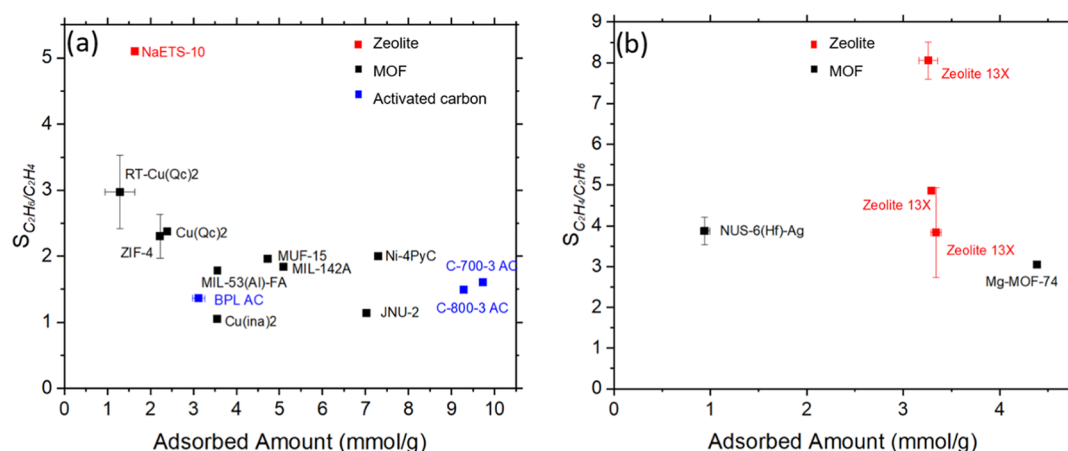


Figure 11. Reported selectivity for ethane–ethylene mixtures from all adsorbents in the BISON-20 data set at 298 ± 10 K and $1 < P_{\text{total}} < 1.44$ bar range. (a) Adsorbents selective for ethane over ethylene. (b) Adsorbents selective for ethylene over ethane. Measurements with different gas-phase compositions are presented as error bars. The symbol colors represent the adsorbent type used.

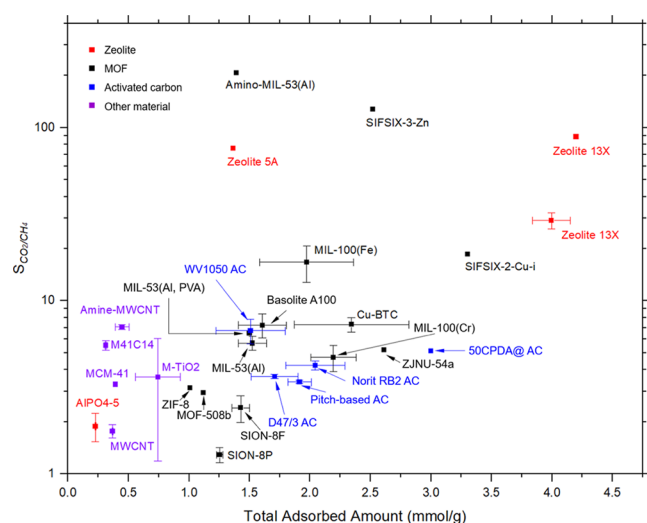


Figure 12. Summary of selectivity for CO_2/CH_4 mixtures in all adsorbents from the BISON-20 data set at 298 ± 5 K and $0.88 < P_{\text{total}} < 1.16$ bar. The range of reported results from measurements with different gas-phase compositions are indicated with error bars. Color represents the adsorbent type used.

than 10 with a total loading under 3.0 mmol/g. The highest total loading belongs to zeolite 13X. Even though there is a quantitative discrepancy between the reported selectivities for the two replicates with zeolite 13X, its high selectivity and loading relative to other materials point to its value as an adsorbent for this separation.⁷⁶

IAST Calculations. IAST is a mixing theory that has been widely used for the prediction of mixture adsorption.^{9,10} The BISON-20 data set along with the associated single-component adsorption described above offers interesting opportunities to assess the quality of IAST in describing binary mixture adsorption. Although a comprehensive assessment of this kind is outside the scope of this initial report, we illustrate the application of IAST to two examples with an emphasis on the effect of uncertainty of experimental data on the reliability of the IAST predictions. A variety of other mixing theories for adsorption have been developed in addition to IAST, but we do not attempt to systematically explore those theories here.

We used the pyIAST software⁷⁷ to perform IAST calculations. For each binary mixture system, all six adsorption models available in pyIAST (Langmuir, Quadratic, Brunauer–Emmett–Teller (BET), Henry, TemkinApprox, and DSLangmuir) were initially fitted to the corresponding single-component adsorption data. If one or more of these models fitted the single-component data adequately, the model with the lowest root-mean-square error was used.

The first example that we consider is the adsorption of N_2/O_2 mixtures in Laporte 4A molecular sieve pellets (L4AMSP) at 293.15 K as reported by Sorial.⁷⁸ As shown in Figure 13a, the single-component isotherms can be represented by Langmuir isotherms with a relative deviation of 2.5% (N_2) and 1.9% (O_2) compared to the experimental data. Figure 13b,c compares the predictions of IAST with the corresponding experimental data for binary adsorption. IAST predicts the mixture loadings of N_2 and O_2 with an average relative deviation of 3 and 5%, with maximum deviations of 21% for N_2 and 50% for O_2 . The quality of the IAST predictions drops when the gas-phase mole fraction of one component is small. IAST predicts the selectivities with an average relative deviation of 5.7% with a maximum relative deviation of 33%.

The second example we considered is the adsorption of ethane/propane mixtures in the MOF COSMOC-2 at 303 K.⁷⁹ None of the adsorption models available in pyIAST fitted the single-component experimental data well. Instead, we used a piecewise function similar to the original work of Couck et al.⁷⁹ to fit the single-component data (see Figure 13d). More details are given in the Supporting Information. The single-component isotherms of ethane and propane can be represented by the piecewise function approach with an average relative deviation of 8.2 and 1.2%, respectively, compared with the corresponding experimental data. Figure 13e,f compares the predictions of IAST with the corresponding experimental results for binary adsorption. The average relative deviation of the predicted loadings is 30.5% for ethane and 29.7% for propane, and the average relative deviation for the propane/ethane selectivity is 29.5%.

It is natural to ask whether IAST “works” for examples of interest. Before doing so, it is important to consider how uncertainty in experimental data can affect the IAST predictions. Couck et al.⁷⁹ reported experimental uncertainties of up to $\pm 30\%$ for ethane and $\pm 10\%$ for propane in their

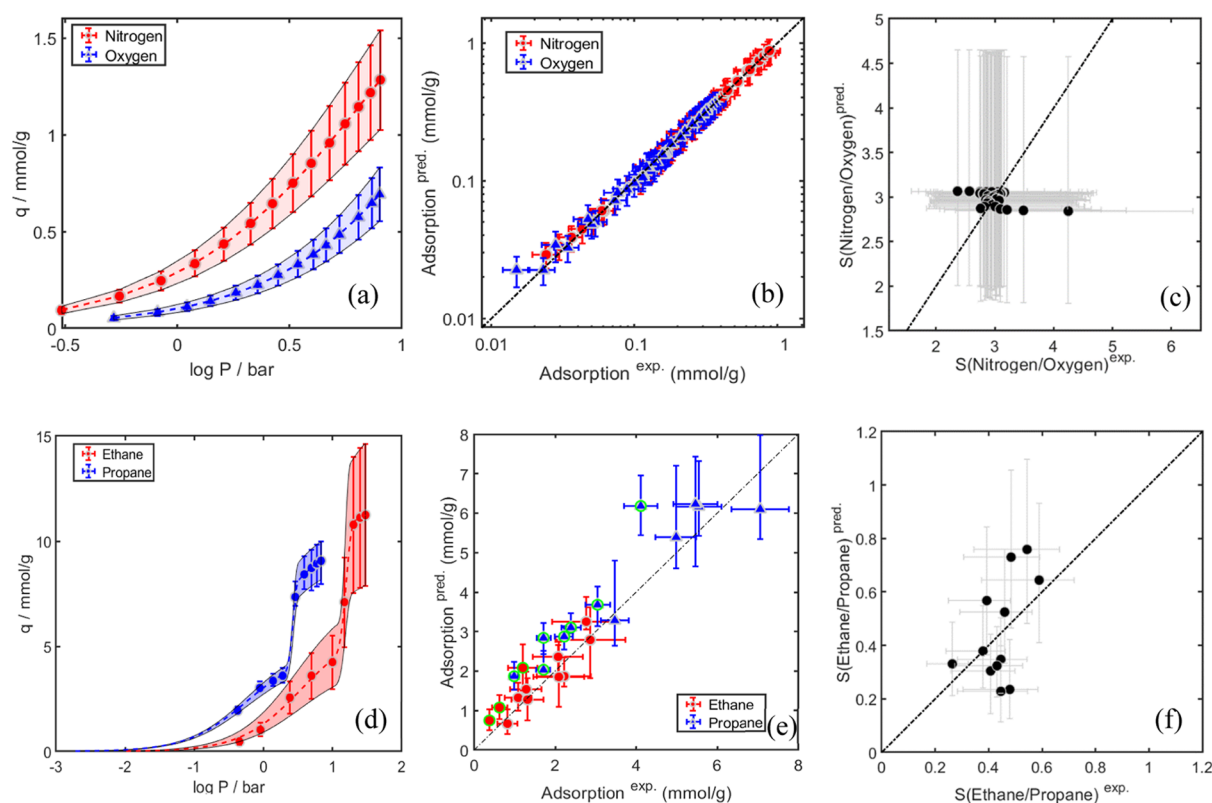


Figure 13. (a–c) Application of IAST to N_2/O_2 mixtures in L4AMSP at 293.15 K and (d–f) ethane/propane in COSMOC-2 at 303 K. The data are assumed to be $\pm 20\%$ uncertain. (d–f) Ethane/propane/COSMOC-2 at 303 K. In (a) and (d), experimental single-component data is shown with filled symbols, with fitted isotherms and uncertainties as described in the text. (b and e) Comparison between IAST predictions and the corresponding experimental values for binary adsorption loadings, with uncertainties shown as described in the text. (c and f) Comparison between the predicted selectivity values and their corresponding experimental values. The points in (e) that do not overlap the parity line within the specified uncertainties are highlighted in light blue (propane) and green (ethane).

binary adsorption data. These uncertainties are shown as horizontal error bars in Figure 13e. Although Couck et al.⁷⁹ did not report uncertainties for their single-component adsorption data, we assumed uncertainty analogous to the binary data, that is $\pm 30\%$ for ethane and 10% for propane. These uncertainties are shown as vertical error bars in Figure 13d. We estimated the uncertainty in the overall single-component isotherms by fitting isotherm models to the boundaries of the uncertain experimental data as shown by the shaded areas in Figure 13d. We then applied IAST to these uncertain isotherms to find the extremes of uncertainty in IAST predictions, as shown with vertical error bars in Figure 13e. The uncertainties in the binary experimental data and the IAST predictions were also carried into the selectivity results shown in Figure 13f. A conservative way to interpret these results is that a particular state point can only be judged to show that IAST is inaccurate if the IAST prediction and its associated error bars do not overlap the parity lines shown in Figure 13e,f.

We used a similar approach to consider the role of experimental uncertainty in N_2/O_2 adsorption in L4AMSP at 293.15 K. In this case, the experimental report did not estimate any uncertainties. We therefore assumed that all single-component and binary mixture loadings had uncertainties of $\pm 20\%$. This range of uncertainties is plausible when compared to the uncertainty found in a systematic analysis of replicate single-component isotherms^{22,23} and with the explicit uncertainties mentioned above in the work of Couck et al. The resulting uncertainties in the single-component data and IAST

predictions are shown in Figure 13a–c. In this example, all of the predicted binary loadings are, within uncertainty, in agreement with the experimental observations. Because the uncertainties in the selectivities are large, all of the IAST-predicted selectivities are consistent with the experimental results within uncertainty, even the handful of points that without considering uncertainties would probably be considered as evidence for IAST not being accurate. We repeated this analysis assuming smaller uncertainties of the measured loadings of $\pm 10\%$ (details in Figure S10), but this does not change the main observations from Figure 13a–c.

The two examples we have considered illustrate several interesting aspects of using IAST to predict mixture adsorption. With N_2/O_2 adsorption in L4AMSP, the adsorbing species are chemically similar and the observed single-component isotherms have a simple form. These characteristics suggest that the assumptions of IAST may be justified and that IAST would therefore give accurate predictions. Our results are consistent with this expectation and the only data points where IAST at first glance appears somewhat imprecise are associated with large uncertainties. Adsorption of ethane/propane mixtures in COSMOC-2 is a contrasting case; the two molecules have differing sizes and more importantly the single-component isotherms are somewhat complex. The steps that appear in the single-component isotherms arise from structural changes in the adsorbent from a “small pore” to a “large pore” form. These so-called breathing transitions exist for a range of MOFs.⁸⁰ It is not simple to predict mixture adsorption

behavior in materials of this kind, since the adsorption of one component may cause the “opening” of the pore even though the adsorption of the other component would not do so if considered alone.^{81,82} It is therefore reasonable to expect that IAST may give inaccurate predictions for this example. Our results show, however, that once experimental uncertainties are considered the predictions of IAST are consistent with the experimental observations in many cases.

We began this discussion with the idea of finding whether IAST works in predicting binary adsorption data. A more nuanced view of this topic is to use the language of hypothesis testing from statistics. To this end, we aim to test the hypothesis that the predictions of IAST are consistent with the available mixture data, with the implied null hypothesis that IAST predictions do not describe the mixture data. To accept the null hypothesis using analysis similar to Figure 13, we would need to find a significant number of data points for which the envelope of uncertainty excludes the parity line. For the N_2/O_2 example in Figure 13, this null hypothesis is rejected for all data points, that is, the predictions of IAST are consistent with the available binary data in every case. For the adsorption of ethane/propane in COSMOC-2, there are a number of state points for which the null hypothesis can be accepted; these points are highlighted in Figure 13e. From this perspective, we can conclude that IAST is not adequate to describe this specific mixture/adsorbate pair under all conditions. An advantage of using the language of hypothesis testing is that it forces us to articulate the idea that is being tested. In practical settings, the relative accuracy of a mixing theory may be more important than whether the predictions are fully consistent with the mixture data. In other words, in a practical setting, it does not matter if the mixing theory is fully justified if it is “good enough”. This approach would require a different hypothesis to be tested than the one we described above.

The discussion above indicates that to carefully test IAST or any mixing theory for binary adsorption it is important to minimize the uncertainty in the underlying data. We emphasize that using data from the BISON-20 data set we have focused exclusively on examples for which mixture data and single-component data is available from the same set of experiments. This is important because systematic estimates from literature meta-analysis have suggested that in the absence of other information it is reasonable to estimate the uncertainty in adsorbed loadings from independent experiments to be $\pm 30\%$.²² It would of course be helpful for more literature reports to explicitly report estimates of experimental uncertainties. The challenges with reducing experimental uncertainties highlight the value of using adsorption data from molecular simulations, where single-component and mixture data can be obtained with high precision for well-defined molecular models of materials,⁸³ to test adsorption mixing theories. This approach has been used recently, for example, to systematically test the applicability of IAST for CO_2/CH_4 mixture adsorption in a large collection of atomically detailed amorphous materials.⁵

CONCLUSIONS

Gas adsorption in porous adsorbents is important in a wide range of chemical separations and related applications. In these settings, the properties of adsorbed mixtures are the primary quantity of interest. Despite this observation, the vast majority of experimental data that is available for gas adsorption is for

single-component adsorption. Although experiments to measure mixed gas adsorption have been performed for decades, previous attempts to collect this data in an organized form have been limited. We have introduced in this paper a resource that we anticipate will have considerable value for the adsorption community, a large, publicly available database of experimental binary adsorption data for gases. Using systematic search methods, we were able to compile a collection of binary adsorption data that is far larger than any previous data set. The BISON-20 data set, which we have introduced here, includes more than 9200 data points from experiments with 125 distinct binary mixtures of 60 distinct molecules.

Our initial use of the BISON-20 data set has addressed a number of useful questions that could not be answered previously. We analyzed the data set to find replicate experiments in which binary adsorption was measured independently at similar temperatures, pressures, and compositions for a given binary mixture and adsorbent. This analysis showed that at best a few examples exist for which self-consistent mixture data are available from independent experiments. We hope that this observation motivates future work to systematically compare binary adsorption data measured with different experimental methods and interlaboratory studies intended to develop material standards. We also used the data set to systematically consider the adsorption selectivities that have been reported among all materials for several industrially relevant separations. The availability of systematic data of this kind should provide a useful basis for assessing new materials for these separations.

In addition to collecting binary gas adsorption data, the BISON-20 data set includes a systematic collection of single-component isotherm data reported in the same experiments as mixture data. This allowed us to consider the applicability of IAST to binary adsorption without concerns about the experimental self-consistency of the single-component data that are used in IAST and mixture data to which predictions from IAST are compared. We showed that considering the implications of experimental uncertainty is critical in considering whether mixing theories for adsorption make accurate predictions, using IAST as an example. For the limited number of examples we examined the predictions of IAST were consistent with experimental observations of mixtures within uncertainty in most cases. It will be interesting to explore this issue more thoroughly for the large number of examples available in the BISON-20 data set in the future for IAST and for the other approximate mixing theories for adsorption that exist.

A theme that appeared in several of the uses of the BISON-20 data set we explored is the role of experimental uncertainty. We hope it is self-evident that uncertainty in adsorption selectivity is intrinsically larger than uncertainties in adsorption loadings. Indeed, the relative error in a selectivity is approximately the sum of the relative errors in the measured adsorption loadings. When one adsorption loading of an adsorbed mixture is small, either because the bulk-phase composition strongly favors the other component or the adsorbent is extremely selective or the bulk-phase pressure is low, the relative errors in that loading and the resulting selectivity are likely to be large. These observations highlight the importance of considering experimental uncertainties when choosing state points to study in mixture adsorption and the need to be skeptical of the precision of measured values of selectivity that are very high. We hope, in addition to

consideration of these ideas, that our analysis will motivate future experimenters to analyze and explicitly report uncertainties in their adsorption data and that the impact of uncertainty will be considered when ranking materials for possible end-use applications. In addition to unavoidable instrumental uncertainty, variability in adsorption experiments can also arise because of differences in materials synthesis and pretreatment. The availability of resources such as the BISON-20 data set should aid comparisons between experiments that will allow sources of variability of this kind to be understood systematically.

The BISON-20 data set is by far the largest collection of binary gas adsorption data available to date. Its limitations, however, indicate that this data barely scratches the surface of the full range of adsorbed mixtures that could be considered. The BISON-20 data set contains 60 distinct molecules, from which 1770 different binary pairs can be formed. Of these binary pairs, only 7% are represented by any experimental data in the BISON-20 data set. Recent work has argued that the possible binary mixtures that can be generated from industrially relevant molecules number in the millions.⁶ The BISON-20 collection includes data from 333 different sorbents. While this is an impressive number, collections of many thousands of crystalline sorbents exist and *in silico* generation of sorbent structures has indicated that hundreds of thousands of distinct material are possible.^{4,5} We hope that the compendium of data available in the BISON-20 data set will spur future experimental and modeling work that will aid the exploration of this chemically diverse area.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.0c05398>.

Information on categories of data and further details on selectivities in replicate experiments and IAST calculations (PDF document) (PDF)

Complete collection of data from binary adsorption experiments (XISX)

Complete collection of data from binary adsorption experiments in a simplified form (XISX)

Complete collection of data from single-component adsorption experiments reported in the same published sources as binary adsorption experiments (XISX)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Sholl, D. S.; Lively, R. P. Seven chemical separations to change the world. *Nature* **2016**, 532, 435–437.
- (2) Yang, R. T. *Gas Separation by Adsorption Processes*; Butterworth-Heinemann: Stoneham, MA, 1987.
- (3) Keskin, S.; van Heest, T. M.; Sholl, D. S. Can metal-organic framework materials play a useful role in large-scale carbon dioxide separations? *ChemSusChem* **2010**, 3, 879–891.
- (4) Chung, Y. G.; Haldoupis, E.; Bucior, B. J.; Haranczyk, M.; Lee, S.; Zhang, H.; Vogiatzis, K. D.; Milisavljevic, M.; Ling, S.; Camp, J. S.; Slater, B.; Siepmann, J. I.; Sholl, D. S.; Snurr, R. Q. Advances, Updates, and Analytics for the Computation-Ready, Experimental Metal–Organic Framework Database: CoRE MOF 2019. *J. Chem. Eng. Data* **2019**, 64, 5985–5998.
- (5) Thyagarajan, R.; Sholl, D. S. A Database of Porous Rigid Amorphous Materials. *Chem. Mater.* **2020**, 32, 8020–8033.
- (6) Gharagheizi, F.; Tang, D.; Sholl, D. S.; Snurr, R. Q. Advances, Updates, and Analytics for the Computation-Ready, Experimental Metal–Organic Framework Database: CoRE MOF 2019. *J. Chem. Eng. Data* **2019**, 64, 5985–5998.
- (7) Chong, S.; Lee, S.; Kim, B.; Kim, J. Applications of machine learning in metal-organic frameworks. *Coord. Chem. Rev.* **2020**, 423, No. 213487.
- (8) Ma, R.; Colon, Y. J.; Luo, T. Transfer Learning Study of Gas Adsorption in Metal-Organic Frameworks. *ACS Appl. Mater. Interfaces* **2020**, 12, 34041–34048.
- (9) Myers, A. L.; Prausnitz, J. M. Thermodynamics of mixed-gas adsorption. *AIChE J.* **1965**, 11, 121–127.
- (10) Walton, K. S.; Sholl, D. S. Predicting multicomponent adsorption: 50 years of the ideal adsorbed solution theory. *AIChE J.* **2015**, 61, 2757–2762.
- (11) Park, J.; Rubiera Landa, H. O.; Kawajiri, Y.; Realff, M. J.; Lively, R. P.; Sholl, D. S. How Well Do Approximate Models of Adsorption-Based CO₂ Capture Processes Predict Results of Detailed Process Models? *Ind. Eng. Chem. Res.* **2020**, 59, 7097–7108.
- (12) Leperi, K. T.; Chung, Y. G.; You, F.; Snurr, R. Q. Development of a General Evaluation Metric for Rapid Screening of Adsorbent Materials for Postcombustion CO₂ Capture. *ACS Sustainable Chem. Eng.* **2019**, 7, 11529–11539.
- (13) Wu, C.-W.; Sircar, S. Comments on binary and ternary gas adsorption selectivity. *Sep. Purif. Technol.* **2016**, 170, 453–461.
- (14) Kaur, H.; Tun, H.; Sees, M.; Chen, C.-C. Local composition activity coefficient model for mixed-gas adsorption equilibria. *Adsorption* **2019**, 25, 951–964.
- (15) Siderius, D. W.; Shen, V. K.; Johnson III, R. D.; van Zee, R. D. *NIST/ARPA-E Database of Novel and Emerging Adsorbent Materials*;

National Institute of Standards and Technology: Gaithersburg MD, 2019.

(16) Van Ness, H. C. Adsorption of Gases on Solids. Review of Role of Thermodynamics. *Ind. Eng. Chem. Fundam.* **1969**, *8*, 464–473.

(17) Valenzuela, D. P.; Myers, A. L. *Adsorption Equilibrium Data Handbook*; Prentice Hall: Englewood Cliffs, NJ, 1989.

(18) Finsy, V.; Ma, L.; Alaerts, L.; De Vos, D. E.; Baron, G. V.; Denayer, J. F. M. Separation of CO₂/CH₄ mixtures with the MIL-53(Al) metal–organic framework. *Microporous Mesoporous Mater.* **2009**, *120*, 221–227.

(19) Sholl, D. S. Five Easy Ways To Make Your Research More Reproducible. *Langmuir* **2019**, *35*, 13257–13258.

(20) Han, R.; Walton, K. S.; Sholl, D. S. Does Chemical Engineering Research Have a Reproducibility Problem? *Annu. Rev. Chem. Biomol. Eng.* **2019**, *10*, 43–57.

(21) Agrawal, M.; Han, R.; Herath, D.; Sholl, D. S. Does repeat synthesis in materials chemistry obey a power law? *Proc. Natl. Acad. Sci. U.S.A.* **2020**, *117*, 877–882.

(22) Park, J.; Howe, J. D.; Sholl, D. S. How Reproducible Are Isotherm Measurements in Metal–Organic Frameworks? *Chem. Mater.* **2017**, *29*, 10487–10495.

(23) Bingel, L. W.; Chen, A.; Agrawal, M.; Sholl, D. S. Experimentally Verified Alcohol Adsorption Isotherms in Nanoporous Materials from Literature Meta-Analysis. *J. Chem. Eng. Data* **2020**, *65*, 4970–4979.

(24) Fang, H.; Findley, J.; Muraro, G.; Ravikovitch, P. I.; Sholl, D. S. A Strong Test of Atomically Detailed Models of Molecular Adsorption in Zeolites Using Multilaboratory Experimental Data for CO₂ Adsorption in Ammonium ZSM-5. *J. Phys. Chem. Lett.* **2020**, *11*, 471–477.

(25) Avijegon, G.; Xiao, G.; Li, G.; May, E. F. Binary and ternary adsorption equilibria for CO₂/CH₄/N₂ mixtures on Zeolite 13X beads from 273 to 333 K and pressures to 900 kPa. *Adsorption* **2018**, *24*, 381–392.

(26) Chen, S. J.; Fu, Y.; Huang, Y. X.; Tao, Z. C.; Zhu, M. Experimental investigation of CO₂ separation by adsorption methods in natural gas purification. *Appl. Energy* **2016**, *179*, 329–337.

(27) Gholipour, F.; Mofarahi, M. Adsorption equilibrium of methane and carbon dioxide on zeolite 13X: Experimental and thermodynamic modeling. *J. Supercrit. Fluids* **2016**, *111*, 47–54.

(28) García, E. J.; Pérez-Pellitero, J.; Pirngruber, G. D.; Jallut, C.; Palomino, M.; Rey, F.; Valencia, S. Tuning the Adsorption Properties of Zeolites as Adsorbents for CO₂ Separation: Best Compromise between the Working Capacity and Selectivity. *Ind. Eng. Chem. Res.* **2014**, *53*, 9860–9874.

(29) Peter, S. A.; Baron, G. V.; Gascon, J.; Kapteijn, F.; Denayer, J. F. M. Dynamic desorption of CO₂ and CH₄ from amino-MIL-53(Al) adsorbent. *Adsorption* **2013**, *19*, 1235–1244.

(30) Remy, T.; Peter, S. A.; Van Tendeloo, L.; Van der Perre, S.; Lorgouilloux, Y.; Kirschhock, C. E.; Baron, G. V.; Denayer, J. F. Adsorption and separation of CO₂ on KFI zeolites: effect of cation type and Si/Al ratio on equilibrium and kinetic properties. *Langmuir* **2013**, *29*, 4998–5012.

(31) Yan, B. L.; Yu, S.; Zeng, C. F.; Yu, L.; Wang, C. Q.; Zhang, L. X. Binderless zeolite NaX microspheres with enhanced CO₂ adsorption selectivity. *Microporous Mesoporous Mater.* **2019**, *278*, 267–274.

(32) Abdulkareem, F. A.; Shariff, A. M.; Ullah, S.; See, T. L.; Keong, L. K.; Mellon, N. Adsorption performance of 5A molecular sieve zeolite in water vapor-binary gas environment: Experimental and modeling evaluation. *J. Ind. Eng. Chem.* **2018**, *64*, 173–187.

(33) Mofarahi, M.; Gholipour, F. Gas adsorption separation of CO₂/CH₄ system using zeolite 5A. *Microporous Mesoporous Mater.* **2014**, *200*, 1–10.

(34) Rittig, F.; Aurentz, D. J.; Coe, C. G.; Kitzhoffer, R. J.; Zielinski, J. M. Pure- and Mixed-Gas Sorption Measurements on Zeolitic Adsorbents via Gas-Phase Nuclear Magnetic Resonance. *Ind. Eng. Chem. Res.* **2002**, *41*, 4430–4434.

(35) Hu, J.; Sun, T.; Liu, X.; Zhao, S.; Wang, S. Rationally tuning the separation performances of [M₃(HCOO)₆] frameworks for CH₄/N₂

mixtures via metal substitution. *Microporous Mesoporous Mater.* **2016**, *225*, 456–464.

(36) Bakhtyari, A.; Mofarahi, M. Pure and Binary Adsorption Equilibria of Methane and Nitrogen on Zeolite 5A. *J. Chem. Eng. Data* **2014**, *59*, 626–639.

(37) Sievers, W.; Mersmann, A. Single and multicomponent adsorption equilibria of carbon dioxide, nitrogen, carbon monoxide and methane in hydrogen purification processes. *Chem. Eng. Technol.* **1994**, *17*, 325–337.

(38) Dreisbach, F.; Staudt, R.; Keller, J. U. High pressure adsorption data of methane, nitrogen, carbon dioxide and their binary and ternary mixtures on activated carbon. *Adsorption* **1999**, *5*, 215–227.

(39) Goetz, V.; Pupier, O.; Guillot, A. Carbon dioxide-methane mixture adsorption on activated carbon. *Adsorption* **2006**, *12*, 55–63.

(40) Himeno, S.; Komatsu, T.; Fujita, S. Development of a New Effective Biogas Adsorption Storage Technology. *Adsorption* **2005**, *11*, 899–904.

(41) Rufford, T. E.; Watson, G. C. Y.; Saleman, T. L.; Hofman, P. S.; Jensen, N. K.; May, E. F. Adsorption Equilibria and Kinetics of Methane + Nitrogen Mixtures on the Activated Carbon Norit RB3. *Ind. Eng. Chem. Res.* **2013**, *52*, 14270–14281.

(42) Nguyen, H. G. T.; Espinal, L.; van Zee, R. D.; Thommes, M.; Toman, B.; Hudson, M. S. L.; Mangano, E.; Brandani, S.; Broom, D. P.; Benham, M. J.; Cychosz, K.; Bertier, P.; Yang, F.; Krooss, B. M.; Siegelman, R. L.; Hakuman, M.; Nakai, K.; Ebner, A. D.; Erden, L.; Ritter, J. A.; Moran, A.; Talu, O.; Huang, Y.; Walton, K. S.; Billefont, P.; De Weireld, G. A reference high-pressure CO₂ adsorption isotherm for ammonium ZSM-5 zeolite: results of an interlaboratory study. *Adsorption* **2018**, *24*, 531–539.

(43) Tang, Y.; Wang, S.; Zhou, X.; Wu, Y.; Xian, S.; Li, Z. Room temperature synthesis of Cu(Qc)₂ and its application for ethane capture from light hydrocarbons. *Chem. Eng. Sci.* **2020**, *213*, No. 115355.

(44) Zeng, H.; Xie, X. J.; Xie, M.; Huang, Y. L.; Luo, D.; Wang, T.; Zhao, Y.; Lu, W.; Li, D. Cage-Interconnected Metal–Organic Framework with Tailored Apertures for Efficient C₂H₆/C₂H₄ Separation under Humid Conditions. *J. Am. Chem. Soc.* **2019**, *141*, 20390–20396.

(45) Wu, H.; Chen, Y.; Yang, W.; Lv, D.; Yuan, Y.; Qiao, Z.; Liang, H.; Li, Z.; Xia, Q. Ethane-Selective Behavior Achieved on a Nickel-Based Metal–Organic Framework: Impact of Pore Effect and Hydrogen Bonds. *Ind. Eng. Chem. Res.* **2019**, *58*, 10516–10523.

(46) Peng, J.; Sun, Y.; Wu, Y.; Lv, Z.; Li, Z. Selectively Trapping Ethane from Ethylene on Metal–Organic Framework MIL-53(Al)-FA. *Ind. Eng. Chem. Res.* **2019**, *58*, 8290–8295.

(47) Qazvini, O. T.; Babarao, R.; Shi, Z. L.; Zhang, Y. B.; Telfer, S. G. A Robust Ethane-Trapping Metal–Organic Framework with a High Capacity for Ethylene Purification. *J. Am. Chem. Soc.* **2019**, *141*, 5014–5020.

(48) Lin, R. B.; Wu, H.; Li, L.; Tang, X. L.; Li, Z.; Gao, J.; Cui, H.; Zhou, W.; Chen, B. Boosting Ethane/Ethylene Separation within Isoreticular Ultramicroporous Metal–Organic Frameworks. *J. Am. Chem. Soc.* **2018**, *140*, 12940–12946.

(49) Hovestadt, M.; Friebe, S.; Helmich, L.; Lange, M.; Mollmer, J.; Glaser, R.; Mundstock, A.; Hartmann, M. Continuous Separation of Light Olefin/Paraffin Mixtures on ZIF-4 by Pressure Swing Adsorption and Membrane Permeation. *Molecules* **2018**, *23*, 889.

(50) Chen, Y.; Wu, H.; Lv, D.; Shi, R.; Chen, Y.; Xia, Q.; Li, Z. Highly Adsorptive Separation of Ethane/Ethylene by An Ethane-Selective MOF MIL-142A. *Ind. Eng. Chem. Res.* **2018**, *57*, 4063–4069.

(51) Pu, S.; Wang, J.; Li, L.; Zhang, Z.; Bao, Z.; Yang, Q.; Yang, Y.; Xing, H.; Ren, Q. Performance Comparison of Metal–Organic Framework Extrudates and Commercial Zeolite for Ethylene/Ethane Separation. *Ind. Eng. Chem. Res.* **2018**, *57*, 1645–1654.

(52) Liang, W.; Zhang, Y.; Wang, X.; Wu, Y.; Zhou, X.; Xiao, J.; Li, Y.; Wang, H.; Li, Z. Asphalt-derived high surface area activated porous carbons for the effective adsorption separation of ethane and ethylene. *Chem. Eng. Sci.* **2017**, *162*, 192–202.

- (53) Wang, Y.; Hu, Z.; Cheng, Y.; Zhao, D. Silver-Decorated Hafnium Metal–Organic Framework for Ethylene/Ethane Separation. *Ind. Eng. Chem. Res.* **2017**, *56*, 4508–4516.
- (54) Shi, M.; Lin, C. C. H.; Kuznicki, T. M.; Hashisho, Z.; Kuznicki, S. M. Separation of a binary mixture of ethylene and ethane by adsorption on Na-ETS-10. *Chem. Eng. Sci.* **2010**, *65*, 3494–3498.
- (55) Shi, M.; Avila, A. M.; Yang, F.; Kuznicki, T. M.; Kuznicki, S. M. High pressure adsorptive separation of ethylene and ethane on Na-ETS-10. *Chem. Eng. Sci.* **2011**, *66*, 2817–2822.
- (56) Danner, R. P.; Nicoletti, M. P.; Al-Ameeri, R. S. Determination of gas mixture adsorption equilibria by the tracer-pulse technique. *Chem. Eng. Sci.* **1980**, *35*, 2129–2133.
- (57) Reich, R.; Ziegler, W. T.; Rogers, K. A. Adsorption of Methane, Ethane, and Ethylene Gases and Their Binary and Ternary Mixtures and Carbon Dioxide on Activated Carbon at 212–301 K and Pressures to 35 Atmospheres. *Ind. Eng. Chem. Process Des. Dev.* **1980**, *19*, 336–344.
- (58) Danner, R. P.; Choi, E. C. F. Mixture Adsorption Equilibria of Ethane and Ethylene on 13X Molecular Sieves. *Ind. Eng. Chem. Fundam.* **1978**, *17*, 248–253.
- (59) Liang, W.; Liu, Z.; Peng, J.; Zhou, X.; Wang, X.; Li, Z. Enhanced CO₂ Adsorption and CO₂/N₂/CH₄ Selectivity of Novel Carbon Composites CPDA@A-Cs. *Energy Fuels* **2019**, *33*, 493–502.
- (60) Gladysiak, A.; Deeg, K. S.; Dovgaliuk, I.; Chidambaram, A.; Ordiz, K.; Boyd, P. G.; Moosavi, S. M.; Ongari, D.; Navarro, J. A. R.; Smit, B.; Stylianou, K. C. Biporous Metal–Organic Framework with Tunable CO₂/CH₄ Separation Performance Facilitated by Intrinsic Flexibility. *ACS Appl. Mater. Interfaces* **2018**, *10*, 36144–36156.
- (61) Billemont, P.; Heymans, N.; Normand, P.; De Weireld, G. IAST predictions vs co-adsorption measurements for CO₂ capture and separation on MIL-100 (Fe). *Adsorption* **2017**, *23*, 225–237.
- (62) Jiao, J.; Dou, L.; Liu, H.; Chen, F.; Bai, D.; Feng, Y.; Xiong, S.; Chen, D. L.; He, Y. An aminopyrimidine-functionalized cage-based metal-organic framework exhibiting highly selective adsorption of C₂H₂ and CO₂ over CH₄. *Dalton Trans.* **2016**, *45*, 13373–13382.
- (63) Molyanyan, E.; Aghamiri, S.; Talaie, M. R.; Iraj, N. Experimental study of pure and mixtures of CO₂ and CH₄ adsorption on modified carbon nanotubes. *Int. J. Environ. Sci. Technol.* **2016**, *13*, 2001–2010.
- (64) Wu, Y.-J.; Yang, Y.; Kong, X.-M.; Li, P.; Yu, J.-G.; Ribeiro, A. M.; Rodrigues, A. E. Adsorption of Pure and Binary CO₂, CH₄, and N₂ Gas Components on Activated Carbon Beads. *J. Chem. Eng. Data* **2015**, *60*, 2684–2693.
- (65) Jiang, G.; Huang, Q.; Kenarsari, S. D.; Hu, X.; Russell, A. G.; Fan, M.; Shen, X. A new mesoporous amine-TiO₂ based pre-combustion CO₂ capture technology. *Appl. Energy* **2015**, *147*, 214–223.
- (66) Rios, R. B.; Stragliotto, F. M.; Peixoto, H. R.; Torres, A. E. B.; Bastos-Neto, M.; Azevedo, D. C. S.; Cavalcante, C. L., Jr. Studies on the adsorption behavior of CO₂-CH₄ mixtures using activated carbon. *Braz. J. Chem. Eng.* **2013**, *30*, 939–951.
- (67) Nugent, P.; Belmabkhout, Y.; Burd, S. D.; Cairns, A. J.; Luebke, R.; Forrest, K.; Pham, T.; Ma, S.; Space, B.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M. J. Porous materials with optimal adsorption thermodynamics and kinetics for CO₂ separation. *Nature* **2013**, *495*, 80–84.
- (68) Heymans, N.; Vaesen, S.; De Weireld, G. A complete procedure for acidic gas separation by adsorption on MIL-53 (Al). *Microporous Mesoporous Mater.* **2012**, *154*, 93–99.
- (69) Hamon, L.; Heymans, N.; Llewellyn, P. L.; Guillermin, V.; Ghoufi, A.; Vaesen, S.; Maurin, G.; Serre, C.; De Weireld, G.; Pirngruber, G. D. Separation of CO₂-CH₄ mixtures in the mesoporous MIL-100(Cr) MOF: experimental and modelling approaches. *Dalton Trans.* **2012**, *41*, 4052–4059.
- (70) Chmelik, C.; Voß, H.; Bux, H.; Caro, J. Adsorption and Diffusion - Basis for Molecular Understanding of Permeation through Molecular Sieve Membranes. *Chem. Ing. Tech.* **2011**, *83*, 104–112.
- (71) Hamon, L.; Jolimaître, E.; Pirngruber, G. D. CO₂ and CH₄ Separation by Adsorption Using Cu-BTC Metal–Organic Framework. *Ind. Eng. Chem. Res.* **2010**, *49*, 7497–7503.
- (72) Bastin, L.; Bácia, P. S.; Hurtado, E. J.; Silva, J. A. C.; Rodrigues, A. E.; Chen, B. A Microporous Metal–Organic Framework for Separation of CO₂/N₂ and CO₂/CH₄ by Fixed-Bed Adsorption. *J. Phys. Chem. C* **2008**, *112*, 1575–1581.
- (73) He, Y.; Seaton, N. A. Heats of adsorption and adsorption heterogeneity for methane, ethane, and carbon dioxide in MCM-41. *Langmuir* **2006**, *22*, 1150–1155.
- (74) Keller, J. U.; Iossifova, N.; Zimmermann, W. Volumetric–Densimetric Measurements of the Adsorption Equilibria of Binary Gas Mixtures. *Adsorpt. Sci. Technol.* **2005**, *23*, 685–702.
- (75) Koh, C. A.; Montanari, T.; Nooney, R. I.; Tahir, S. F.; Westacott, R. E. Experimental and Computer Simulation Studies of the Removal of Carbon Dioxide from Mixtures with Methane Using AlPO₄-5 and MCM-41. *Langmuir* **1999**, *15*, 6043–6049.
- (76) Cavenati, S.; Grande, C. A.; Rodrigues, A. E. Adsorption Equilibrium of Methane, Carbon Dioxide, and Nitrogen on Zeolite 13X at High Pressures. *J. Chem. Eng. Data* **2004**, *49*, 1095–1101.
- (77) Simon, C. M.; Smit, B.; Haranczyk, M. pyIAST: Ideal adsorbed solution theory (IAST) Python package. *Comput. Phys. Commun.* **2016**, *200*, 364–380.
- (78) Sorial, G. A. Experimental data for the adsorption of oxygen, nitrogen and oxygen-nitrogen mixtures on five molecular sieve adsorbents at various temperatures and pressures and a comparison with theoretical models. Ph. D. Thesis, University of Bradford: Bradford, West Yorkshire, England, 1982.
- (79) Couck, S.; Van Assche, T. R.; Liu, Y. Y.; Baron, G. V.; Van Der Voort, P.; Denayer, J. F. Adsorption and Separation of Small Hydrocarbons on the Flexible, Vanadium-Containing MOF, COMOC-2. *Langmuir* **2015**, *31*, 5063–5070.
- (80) Qian, Q.; Asinger, P. A.; Lee, M. J.; Han, G.; Mizrahi Rodriguez, K.; Lin, S.; Benedetti, F. M.; Wu, A. X.; Chi, W. S.; Smith, Z. P. MOF-Based Membranes for Gas Separations. *Chem. Rev.* **2020**, *120*, 8161–8266.
- (81) Agrawal, M.; Bhattacharyya, S.; Huang, Y.; Jayachandrababu, K. C.; Murdock, C. R.; Bentley, J. A.; Rivas-Cardona, A.; Mertens, M. M.; Walton, K. S.; Sholl, D. S.; Nair, S. Liquid-Phase Multicomponent Adsorption and Separation of Xylene Mixtures by Flexible MIL-53 Adsorbents. *J. Phys. Chem. C* **2018**, *122*, 386–397.
- (82) Coudert, F. o.-X.; Mellot-Draznieks, C.; Fuchs, A. H.; Boutin, A. Prediction of Breathing and Gate-Opening Transitions Upon Binary Mixture Adsorption in Metal–Organic Frameworks. *J. Am. Chem. Soc.* **2009**, *131*, 11329–11331.
- (83) Chen, H.; Sholl, D. S. Efficient Simulation of Binary Adsorption Isotherms Using Transition Matrix Monte Carlo. *Langmuir* **2006**, *22*, 709–716.