Computational Investigation of Correlations in Adsorbate Entropy for Pure-Silica Zeolite Adsorbents [†]

Christopher Rzepa,[‡] Daniel W. Siderius,^{*,¶,§} Harold W. Hatch,[¶]

Vincent K. Shen,[¶] Srinivas Rangarajan,^{*,‡,§} and Jeetain Mittal[‡]

[‡]Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, USA

¶Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8320, USA §Corresponding Author

E-mail: daniel.siderius@nist.gov; srr516@lehigh.edu

 $^{^\}dagger Official$ contribution of the National Institute of Standards and Technology; not subject to copyright in the United States.

Abstract

Vast numbers of unstudied hypothetical porous frameworks continue to spark interest in optimizing adsorption and catalytic processes. Evaluating the use of such materials depends on the accessibility of thermodynamic metrics such as the free energy, which, in turn, depend on the satisfactory estimation or calculation of the adsorption entropy, which often remains elusive. Previous works using simulations and experimental data have demonstrated relationships between the entropy and system descriptors, allowing for sensible predictions based on more-easily obtained physical parameters. However, the resultant conclusions were either based on experimental data for industrially relevant alkanes or lacked a significant sample size. In this paper, we evaluate correlations between gas-phase and adsorbed-phase entropies for a larger and more chemically diverse set of adsorbate molecules by using force fields and statistical mechanical expressions to calculate those entropies. In total, we perform calculations for 37 molecules across 10 chemical categories available in the TraPPE force field set, as adsorbed in five siliceous zeolites. Our results show that linear correlations between the gas- and adsorbed-phase entropies persist for the larger and diverse set of adsorbate molecules studied here, proving a broader applicability and justifying the use of simple correlations for many adsorbates and, presumably, adsorbent materials.

1 Introduction

Zeolites are crystalline, microporous frameworks that consist of unique channels and cages and have a propensity for gas adsorption. They have been historically used in light-gas separations and cracking of petrochemical feedstocks^{1,2}. Moreover, millions of hypothetical structures of zeolites have been proposed purely based on geometric and energetic considerations³. As a result, much work has been devoted to optimizing additional applications, such as methane storage^{4,5}, carbon capture⁶ and flue-gas treatment⁷. However, due to the large number of frameworks, identifying a zeolite whose geometry is well-suited to adsorb a particular molecule is difficult. This is further exacerbated by diffusion limitations⁸, the realities of framework synthesis⁹, thermal and mechanical stability, and postsynthesis treatment^{10,11}. Amidst these practical challenges, a reasonable first criterion for finding a suitable candidate is based on the thermodynamic spontaneity of the adsorption process, which is provided by the free energy of adsorption or, equivalently, the contributions from energetic and entropic effects.

Within siliceous zeolites and other neutral frameworks, the adsorption enthalpy is related to the strength of the van der Waals interactions between the molecule and pore¹². On the other hand, the adsorption entropy can be interpreted as the measure of confinement associated with adsorption¹³⁻¹⁵, where a molecule loses mobility and its degrees of freedom become hindered. The largest contributors to the entropy, translation and rotation, are the first to be impaired, while the smallest contributor, vibration, is commonly assumed to be preserved. Techniques, such as gravimetry¹⁶, chromatographic adsorption¹⁴, and infrared operando spectroscopy¹⁷, provide experimental routes in measuring the adsorption entropy. However, performing experiments for many molecule-framework combinations is impractical. Computational experiments of adsorption therefore make for an attractive alternative. Nevertheless, there remain caveats. For example, quantifying the entropy using ab initio-based methods (such as density functional theory) is computationally demanding¹⁸⁻²² or relies on approximations¹⁹. Such approximations include (1) limiting translation to the surface area of the zeolite²³, which artificially restricts the entropy to a surface term; (2) invocation of the "harmonic approximation" based on the assumption of a very strong fluid–solid interaction that renders translations and rotations unimportant; or (3) employing the hindered translator/rotor model²⁴. On the other hand, (classical) Monte Carlo (MC) and molecular dynamics simulations have proven successful in accurately calculating the adsorption entropy²⁵, with the primary limitation being the number of force fields available to accurately model the adsorbate–adsorbent interaction. Although these simulations are numerically cleaner compared to experiment because they involve analyzing efficiently a greater number of molecule–zeolite combinations, it remains overwhelming to apply them to the millions of hypothetical frameworks. Novel topology-based, data-driven approaches have been shown to be adequate in predicting specific features such as adsorption capacity⁶ and selectivity²⁶. However, there are currently no similar models for entropy.

The use of empirical correlations offers an expedient route in predicting sensible thermodynamic quantities without resorting to experiments or simulations. De Moor et al.¹² used ab initio simulations to show that adsorption enthalpies and entropies for *n*-alkanes within acidic zeolites are linearly correlated with their carbon number. Campbell and Sellers compiled a collection of experimental alkane entropies on two-dimensional catalytic surfaces^{27,28}. The key finding of their work was that the ratio of the adsorbed-phase entropy to the gas-phase entropy was approximately two-thirds. They proposed a general and elegant explanation, suggesting that the adsorption of a molecule from an unhindered gas phase onto a two-dimensional (2D) surface would eliminate a dimension of translational freedom, i.e., the adsorbate behaves as a 2D gas. This correlation was found to hold across many molecules, spanning 50 *R* of entropy space with a standard deviation of only 2 *R* (where *R* is the universal gas constant). Campbell and Sellers' correlation was observed for other two-dimensional surfaces: Otyepková et al. calculated the adsorption entropy of a chemically diverse set of molecules adsorbed onto organic "van der Waals" materials using inverse gas chromatography and ab initio simulations^{29,30}. Their results showed an entropic loss of approximately 40% relative to the gas-phase entropy. Likewise, Budi et al. calculated the adsorption entropy of a set of chemically diverse molecules adsorbed on mineral surfaces using density functional theory ³¹. Although predicting a larger entropic loss relative to Campbell and Sellers' correlation, their data showed a strong linear dependence between the adsorbed-phase entropy and the gas-phase entropy. Dauenhauer and Abdelrhaman¹³ expanded this idea to three-dimensional frameworks by compiling experimentally determined adsorption entropies for alkanes adsorbed in nine aluminosilicate zeolites. They showed that the entropic loss upon adsorption can be linearly correlated with the molecule's gas-phase translational and rotational entropies and that the occupiable volume of a zeolite is a useful descriptor in predicting such losses.

While the simple elegance of this nearly linear correlation of entropies is suggestive of an underlying physical origin, the extent of its applicability is unknown. This is of special concern considering that the aforementioned data is almost entirely for industrially relevant alkanes. Therefore, within this paper, we avoid this practical constraint by using Monte Carlo simulations to quantify the adsorption entropies for a diverse assortment of molecules in zeolite-like materials. In particular, we use the Transferable potentials for Phase Equilibria (TraPPE)³² force fields to calculate the adsorption entropies for 37 molecules across 10 functional categories within five pure-silicate zeolites. Our simulation results for this broad set of adsorbate molecules reveal that the correlation of the adsorbed-phase and gas-phase entropies persists, suggesting that these correlations may be much more broadly applicable than reported thus far. As a result, such correlative relationships may be exploited to predict sensible adsorption entropies for a wide range of industrially relevant fluids in zeolites and possibly other host materials.

The order of this paper is as follows: Section 2 briefly derives the thermodynamic and statistical mechanical expressions for the entropy that we use for our calculations (full derivations are in the Appendix section). In Section 3 we describe the models of our adsorption systems (i.e., the adsorbates and adsorbents) and how the adsorption entropy was calculated. Section 4 presents the results of our model-based calculations of the adsorbed-phase entropy and discusses the correlation of this entropy with the bulk, gas-phase entropy. This section further presents how the entropy correlations can be cast primarily in terms of adsorbent characteristics and how a more detailed model can be generated based on physically intuitive arguments. Finally, in Section 5 we summarize the paper, offer conclusions, and discuss opportunities for future work.

2 Thermodynamics of Gas Adsorption

The thermodynamic quantity of primary interest here is the adsorption entropy, henceforth Δs_{ads} , which is the change in entropy of the adsorbate species upon transfer from the bulk (unconfined) state to the adsorbed (confined) state, on a molar basis. Quantification of Δs_{ads} from laboratory or computational measurements depends on both the thermodynamic constraints on the starting and ending states (e.g., fixed pressure, fixed volume, etc.) and the thermodynamic conditions of the measurement (e.g., low pressure or infinite dilution, high pressure or near-saturation loading). The entropy results presented in ref 13 are obtained from various approaches, often based on either the Langmuir adsorption model or a modification thereof using the Henry's law constant^{33,34} or a high-level quantum-mechanical calculation¹², among others. Comparison between varying sources for the adsorption entropy is facilitated by the historical belief that Δs_{ads} is largely unaffected by temperature^{35,36} and, for the purposes of those papers, by ignoring the effect of adsorbate loading. As a generalization, however, the adsorption entropy can be defined through the principal thermodynamic relationship

$$\Delta G_{\rm ads}^0 = \Delta H_{\rm ads}^0 - T \Delta S_{\rm ads}^0 \tag{1}$$

where ΔG_{ads}^0 and ΔH_{ads}^0 are the Gibbs free energy of adsorption and the enthalpy of adsorption, respectively, where the superscript ⁰ indicates that the change is measured at some standard state (usually 298 K and 1 bar). From an experimental perspective, one can obtain ΔH^0 and ΔG^0 through measurements of the isosteric heat of adsorption $(Q_{\rm st})$ and an adsorption equilibrium constant, respectively, which can then yield $\Delta s^0_{\rm ads}$ by manipulation of eq 1.

For example, and as done for some of the data presented in ref13, eq 1 may be manipulated by introduction of the Langmuir isotherm to express the adsorption entropy as 37,38

$$\frac{\Delta s_{\rm ads}^0}{R} = \frac{\Delta h_{\rm ads}^0}{RT} + \ln\left(\frac{k_{\rm H}p^0}{\Gamma^\infty}\right) \tag{2}$$

in which $k_{\rm H}$ is the Henry constant, $p^0 = 1$ bar is the standard-state pressure, and Γ^{∞} is the adsorption capacity; lowercase s and h identify those thermodynamic quantities as intensive molar quantities. Inherent in the transformation of eq 1 to eq 2 are a number of assumptions, including (1) the aforementioned Langmuir isotherm describing the adsorbed phase, (2) ideal gas behavior for the bulk adsorptive phase, and (3) $p >> p^0$ such that the adsorption condition approaches the maximum loading Γ^{∞} . (Additionally, we note that eq 2 is derived from an excess view of adsorption, with the usual caveat that the excess adsorption is an acceptable representation of the absolute adsorption^{37,39,40}.)

Equation 2 and similar expressions (cf. ref 38) are, of course, not the only routes to quantification of the adsorption entropy. An alternative limiting case is that of infinite dilution or the Henry's law regime which facilitates the use of statistical mechanics for defining a version of Δs_{ads} that, in turn, is easily implemented in numerical calculations. For a full discussion of the statistical mechanics and thermodynamics of adsorption in the Henry limit, we point the reader to the work of Sarkisov⁴¹. In particular, Sarkisov presented the key results for the Henry coefficient and differential enthalpy of adsorption for a system composed of a nondeformable adsorbent and a rigid (no internal degrees of freedom) adsorbate:

$$k_{\rm H} = \frac{\langle \exp\left[-\beta U_{\rm fs}\left(\mathbf{r},\boldsymbol{\psi}\right)\right] \rangle}{RT\rho_{\rm S}}$$

$$\Delta h_{\rm ads}^{\infty} = -R \left[\frac{\partial \ln k_{\rm H}}{\partial(1/T)}\right]_{\Gamma} = \frac{\langle U_{\rm fs}\left(\mathbf{r},\boldsymbol{\psi}\right) \exp\left[-\beta U_{\rm fs}\left(\mathbf{r},\boldsymbol{\psi}\right)\right] \rangle}{\langle \exp\left[-\beta U_{\rm fs}\left(\mathbf{r},\boldsymbol{\psi}\right)\right] \rangle} - RT \qquad (3)$$

(We note that $\Delta h_{\rm ads}^{\infty} = -Q_{\rm st}^{\infty}$, where $Q_{\rm st}$ is the isosteric heat of adsorption.) In eq 3, R is the universal gas constant, $\rho_{\rm S}$ is the density of the adsorbent, $U_{\rm fs}$ is the adsorbate–adsorbent (i.e., fluid–solid) potential energy, and $(\mathbf{r}, \boldsymbol{\psi})$ identifies the adsorbate positions and orientations, respectively. Additionally, the $\langle \rangle$ brackets in this case indicate an average over all positions and orientations. Finally, the superscript $^{\infty}$ notation denotes the limit of infinite dilution.

The expressions in eq 3 show that the Henry coefficient and infinite dilution differential enthalpy of adsorption can be computed from spatial averages of terms related to $U_{\rm fs}$. It is easy to compute these quantities in the context of (classical) molecular simulation after introducing some model of the fluid–solid potential energy (e.g., an all-atom Lennard-Jones (LJ) model, point charges, and appropriate combining rules⁴²). In fact, no actual molecular simulation is necessary as both expressions in eq 3 are spatial averages that may be computed via Monte Carlo integration.

Given the limit of infinite dilution $(N/V \rightarrow 0)$, we may represent the adsorption process as the transfer of a single adsorbate molecule from a bulk gas state to a confined (adsorbed) state, where both states are represented by canonical ensembles at the same T and volume V, i.e.,

$$\Delta s_{\text{ads}}^{\infty} = S_{\text{ads}} \left(N = 1, V, T \right) - S_{\text{gas}} \left(N = 1, V, T \right) \tag{4}$$

As we describe in the Appendix section, the entropy S can be related to the canonical ensemble partition function, eventually resulting in the following expression for the adsorption entropy in the limit of infinite dilution:

$$\frac{\Delta s_{\text{ads}}^{\infty}}{R} = \frac{\Delta h_{\text{ads}}^{\infty}}{RT} + \ln\left[RT\rho_S k_{\text{H}}\right] + 1 \tag{5}$$

where $k_{\rm H}$ and $\Delta h_{\rm ads}^{\infty}$ are identical to the definitions in eq 3. We point out the similarity of the above equation to the adsorption entropy given in eq 2; the adsorption enthalpy and logarithm of the Henry constant appear in both. In contrast, however, the standard state chosen for our expression for $\Delta s_{\rm ads}^{\infty}$ is the low-pressure limit, which may be interpreted as one adsorbate per simulation cell. In this low-pressure regime, the adsorbate entropy is highly sensitive to coverage. In particular, Campbell, Sprowl, and Árnadóttir have shown that the molar entropy of adsorbates on Pt(111) increases by 2.303 R for every factor of 10 decrease in its coverage⁴³.

Our expression for the adsorption entropy offers an important computational advantage over the Langmuir-based approach in eq 2: all of the terms may be computed in a single Monte Carlo integration. As mentioned earlier, after selecting models of the adsorbent and the adsorbate–adsorbent potential energy, one can compute the adsorption entropy via straightforward integration. These integrations are rapid in comparison to full Monte Carlo simulation (which would be necessary to compute both the Henry constant and adsorption capacity that are used in the Langmuir theory).

Finally, since the calculations we present in the following sections are actually for the adsorbed-phase entropy (s_{ads}^{∞}) as a function of the gas-phase entropy (s_{gas}^{0}) , it is necessary to clarify how those quantities are calculated. First, the molar bulk-phase entropy for our model molecules is calculated from a sum of rigorous statistical mechanical expressions for the single-molecule translational and rotational entropies for rigid molecules (denoted s_{trans}^{0} and s_{rot}^{0} in this work)^{44,45} and the molar vibrational entropies (s_{vib}^{0}) as obtained from the NIST CCCBDB⁴⁶. We note that the translational entropy is computed using a volume corresponding to one molecule of an ideal gas at the selected standard state of 300 K and 1 bar. We admit that this is a mixing of reference states (a nonzero-pressure standard state for the gas phase, but infinite dilution for the adsorbed phase), but some choice along these lines is necessary to avoid a divergence in the gas-phase entropy that would appear at zero pressure. This convention is similar to that used in refs 27 and 13. Finally, the adsorbed-phase entropy is estimated by

$$s_{\rm ads}^{\infty} = s_{\rm gas}^0 + \Delta s_{\rm ads}^{\infty} \tag{6}$$

Before proceeding, we briefly reiterate our reasoning for the use of our entropy approximation in eq 6. The adsorption entropy of the infinitely dilute state, e.g., one adsorbate per simulation cell, serves as a proxy for the actual, concentration-dependent adsorption entropy. Use of this adsorption entropy is a computationally advantageous choice, as it allows for the use of rapid Monte Carlo integration for the computation of the Henry constant and isosteric heat, as opposed to the comparatively lengthy simulation of the full adsorption isotherm that would be necessary at a nondilute adsorbate concentration. Consequently, the Monte Carlo integration approach allows us to investigate many more adsorbates than would be possible via full simulation.

3 Computational Models and Methods

The following section describes the computational techniques that we used to calculate the adsorption entropy and, hence, the adsorbed-phase entropy from a relationship given in eq 5, as derived in the Appendix section. Our technique requires the selection of models for the zeolite adsorbents and adsorbate species and adaptation of a Monte Carlo integration technique (cf. Widom test particle method^{47,48}) to our adsorption system.

The adsorption system for our calculations is composed of a zeolitic adsorbent material and an adsorbate species. The adsorbents used here are the faujasite (FAU), Linde type A (LTA), mordenite (MOR), mordenite framework inverted (MFI), and ferrierite (FER) zeolite topologies, in their pure-silicate forms (i.e., no aluminum substitutions). The idealized structure of each silicate was obtained from the IZA database⁴⁹, and then periodically replicated to form an adsorbent cell of adequate size (cf. discussion of the cutoff radii below). The adsorbent framework was kept entirely rigid. The adsorbate species used within this study were selected on the basis of (1) having an implicit hydrogen-based TraPPE force field, (2) the availability of vibrational entropy from the NIST Computational Chemistry Comparison and Benchmark Database (CCCBDB)⁴⁶, and (3) the ability to physically fit within our smallest cage framework (i.e., omitting molecules such as cyclo-octadecane and 2-ethylhexyl acrylate). The geometry of each adsorbate was obtained by using Open Babel⁵⁰ to convert the SMILES strings of each molecule into three-dimensional coordinates and relaxing the structure by minimization of the GAFF potential⁵¹. These energy-minimized structures were used for the subsequent test particle insertions in the unaltered form, which allowed us to ignore energy terms related to bond bending, stretching, or rotation. The respective gas-phase entropies were calculated by summing the ideal gas equations for translational, rotational, and vibrational entropies at the same conditions (see Sec. 2). The gas-phase vibration entropy was obtained from the CCCBDB⁴⁶ with a CCSD(T) level of theory and a cc-pVDZ basis set and was assumed to be preserved upon adsorption. As mentioned previously, the adsorbates were modeled using the TraPPE force field^{32,52} (i.e., Lennard-Jones parameters and point charges for constituent pseudo-atoms), while the adsorbents were modeled using the TraPPE-Zeo⁵³ force field. As specified in both TraPPE and TraPPE-Zeo, Lorentz–Berthelot combining rules were used to determine the cross-site Lennard-Jones parameters. The Ewald sum technique was used to compute the Coulomb energy of adsorbates whose TraPPE parameters include point charges, with consistent Ewald damping parameter $\alpha = 6.0/L_{min}$ (L_{min} is the smallest side length of the simulation cell) and Fourier vectors with $k^2 < 27$.

The calculation of the adsorption entropy (as defined by eqs 3 and 5) was done via Monte Carlo integration (equivalent to the Widom test particle method^{47,48}), in the same mode described by Sarkisov⁴¹. First, a position and orientation of the adsorbate is generated randomly, and the adsorbate–adsorbent potential energy $U_{\rm fs}$ ($\mathbf{r}, \boldsymbol{\psi}$) for that position/orientation is computed for the TraPPE-derived model. Then, the appropriate terms in eq 3 are accumulated, and the procedure is repeated for 10⁷ random positions and orientations. This number of trials was satisfactory for numerical convergence for nearly all adsorbent/adsorbate combinations, where the $\Delta s_{\rm ads}^{\infty}$ measurements were considered converged when the change in the measured value associated with an order-of-magnitude increase in the number of trials was less than 5 %. The two exceptions to these convergence criteria were FAU/1,3,5-dioxane and MOR/ethyl-methyl-ether which were still varied by approximately 10 % when the number of trials was increased from 10⁷ to 10⁸. Subsequent calculations at 10⁹ trials for these two systems reduced the variation to less than 6 %. More importantly, the longer runs for these two systems did not affect any of the trends or conclusions that we discuss in the following sections. Finally, we also computed appropriate moments of the accumulated terms to allow for the estimation of uncertainty in the Monte Carlo integrals (which was not visible on the scale of plots presented here).

The actual Monte Carlo integrations were done using the FEASST⁵⁴ molecular simulation package developed at NIST. FEASST is primarily designed for Markov chain Monte Carlo molecular simulation, but its library functions may also be utilized for the position/orientation generation step and the subsequent energy calculations. Essentially, our program used conventional FEASST operations to build the system model and then run a loop that generated trial positions/orientations and called the energy calculator for the specified number of trial insertions. An example script implementing the Monte Carlo integration (Widom insertion) routine in FEASST v0.6.0 for the TraPPE Ethane/LTA silicate system is provided in the Supporting Information. Finally, we used conventional molecular simulation choices in our calculations: periodic boundaries were applied at all edges of the replicated zeolite cell, Lennard-Jones and Ewald real-space energies were cut at 15 Å, and the zeolite unit cells were periodically replicated to ensure that the length of each side of the simulation cell was at least twice this cutoff distance. By constructing the simulation cell to be at least twice the cutoff distance in each Cartesian direction, an adsorbate cannot interact with its periodic image and, thus, the spatial averages in eq 3 are truly the infinitely dilute limit, i.e., the partial occupancy of a unit cell does not affect the partition function⁴³.

4 Results and Discussion

4.1 Linear Correlation of Adsorbed- and Gas-Phase Entropies

The adsorbents for our calculations consisted of the pure-silicate forms of FAU, LTA, MOR, MFI, and FER. The set of adsorbates consisted of 37 species among 10 functional categories:



Figure 1: Plots of the adsorbed-phase entropy $(s_{ads}^{\infty} = s_{gas}^{0} + \Delta s_{ads}^{\infty})$ versus the respective gasphase standard entropy $(s_{gas}^{0} = s_{trans}^{0} + s_{rot}^{0} + s_{vib}^{0})$ for the adsorbates listed below, adsorbed in FAU, LTA, MOR, MFI, and FER, at T = 300 K, as calculated using the infinitely dilute adsorption entropy described in Section 2. Points are the raw calculations from Monte Carlo (MC) integration, and lines are linear regressions of the MC data forced through the origin. The set of adsorbate molecules used to generate the plots consisted of 37 species in the following categories: aldehydes (2), alkanes (8), alkenes (7), ethers (5), sulfides (5), ketones (2), nitrile (1), cyclic alkanes (2), cyclic ethers (4), and aromatic molecules (1). The 95 % confidence interval of each regression is represented by the shaded region of the corresponding color. The 95 % confidence intervals for the fitted slopes (η) are FAU, 0.84–0.89; LTA, 0.86– 0.88; MOR, 0.83–0.85; MFI, 0.76–0.77; FER, 0.73–0.75.

two aldehydes, eight alkanes, seven alkenes, five ethers, five sulfides, two ketones, one nitrile, two cyclic alkanes, four cyclic ethers, and one aromatic species; this yields 185 adsorbentadsorbate combinations. (A complete list of adsorbates is given in Table S1 of the Supporting Information.) Tabular results of Δs^{∞}_{ads} from our Monte Carlo integrations, the components of s_{gas}^0 , and the resultant s_{ads}^∞ are given in Tables S2–S6 of the Supporting Information. Figure 1 shows our calculated adsorbate entropies defined by eq 5, and plotted against their respective gas-phase entropies at the same temperature. The confidence intervals in s_{ads}^{∞} were below 0.02% of $\Delta s_{\rm ads}^{\infty}$, and were therefore omitted. The primary and most important observation is that, for the most part, the adsorbed-phase entropy shows a remarkable degree of linear correlation with the gas-phase entropy. Based on this visual linearity, we performed a leastsquares regression of our data, with the requirement that the trend line passes through the origin, e.g., $s_{ads}^{\infty} = \eta_i s_{gas}^0$. Similar to ref 13, this added constraint is based on the conjecture that the adsorbed-phase entropy must be both positive and smaller than the gas-phase entropy, i.e., $0 < \eta_i < 1$. The R^2 correlation coefficients ¹, except for that of FAU, are close to unity, indicating low deviation from the linear trend lines; the notable deviations for FAU will be discussed later.

Linearity in the correlation of s_{ads}^{∞} with s_{gas}^{0} is the key feature of the results in Fig 1, as it corresponds to qualitatively similar observations in the entropy correlations disclosed in refs 13, 31, and 27. More importantly, though, our results show that apparent linearity in the correlation of s_{ads}^{∞} with s_{gas}^{0} persists for a larger set of chemically diverse adsorbates than was previously seen. As discussed in those references, such a simple correlation is an obvious opportunity for the development of an engineering correlation that allows for prediction of the adsorption entropy from a limited set of measurements (whether experimentally or computationally derived). Furthermore, we aim to build on the conclusions in refs 13, 31, and 27 by examining our own data in light of the physical arguments presented previously. As a brief review, the apparent linearity in adsorption entropy correlations derives from

 $R^{2} = 0.85, 0.97, 0.98, 0.96, \text{ and } 0.91 \text{ for FAU, LTA, MOR, MFI, and FER, respectively.}$

fundamental physical considerations. In ref 27, where their linear trend in the entropy correlations was approximately two-third, the authors offered a simplified explanation that the linear trend reflected a loss of approximately one-third of the translational and rotational entropies owing to adsorption. Dauenhauer and Abdelrahman¹³ extended this argument to acidic zeolites by considering an additional loss of rotational entropy dependent on the adsorbate size and the pore volume. (Pure linear correlation of s_{ads}^{∞} with s_{gas}^{0} is broken by the arguments in ref 13, but a visual linear correlation persists. We return to this point later in our work.) Before proceeding, we also note that a numerical comparison between our entropy values and those of ref 13 must be done with care; the gas-phase rotational and translational entropies (i.e., the x-axis of Fig 1) of our TraPPE-model molecules differ from experimental values. This is because the TraPPE molecules include pseudo-atoms, which represent hydrogens implicitly. Although the mass of the TraPPE-model molecules does not change, the symmetry number and principal moments of inertia within the rotational entropy equation are different.



Figure 2: Comparison of the linear correlation of adsorbed- and gas-phase entropies for MFI adsorbent, from the present simulation/model-based results (at 300 K) and the experimental calculations (at various temperatures) from Dauenhauer and Abdelrahman¹³. As noted in the figure, the slopes of the linear trend lines are 0.76 and 0.65 for the simulation and experimental data sets, respectively. The simulation/model results are for the diverse set of adsorbates studied here, whereas the experimental results are for alkanes of up to eight carbons, with propane as the smallest adsorbate (and the corresponding smallest s_{gas}^0). We note that the model-based entropies are offset compared to the experiment due to the pseudo-atom structure of TraPPE molecules mentioned in the text.

The linear trend lines in Fig 1 yield the following slopes: FAU:0.86, LTA:0.87, MOR:0.84, MFI:0.76, FER:0.74. The slopes appear to be related to zeolite size as this sequence of decreasing slope corresponds to the sequence of decreasing pore size. Further discussion on this point is reserved for later in this paper (cf. Section 4.2). We immediately point out that all of these slopes are larger than the proposed two-third based on adsorption to a flat surface. Given that the x-axis is the total entropy, not just translational and rotational contributions, we should not expect a precise slope of two-third. These slopes are, additionally, larger than the slopes for linear trend lines computed from the data of Dauenhauer and Abdelrahman (not present in their paper, but easily obtained using data in the Supporting Information of ref 13): FAU: 0.80, MOR: 0.75, MFI: 0.65, and FER: 0.59 (and other topologies not studied here). As a specific example, Fig 2 reproduces the entropy correlation for MFI (same as Fig 1) but includes the data from ref 13 for the same material; the slope based on experimental measurements is 0.65 versus 0.76 for our model-based measurements. Qualitatively identical differences were found for FAU and MOR, the other two zeolite structures common to the two sets of results. We highlight two points in examining this difference. First, our results are for stock (i.e., nontuned), model-based representations of the adsorbates (e.g., rigid molecules composed of TraPPE pseudo-atoms) and adsorbents (e.g., LJ and point charge representations of silicon and oxygen). Second, the adsorbents are nonacidic, pure silicates in our models, versus aluminum-substituted (with varying Si–Al ratios) and cation-balanced zeolites in the experiments. From our perspective, the most critical result is that the linear scaling appears for a wide range of adsorbate species even without specifically tuning the potential energy models for our adsorption systems or simulating the actual zeolites. This is again suggestive of the arguments for systematic entropy loss given in the previous works. However, the difference in slopes highlighted in Fig 2 is an important distinction between our work and that referenced above. Our results suggest that while the appearance of a linear trend in the correlation of adsorbed-phase and gas-phase entropies may derive from underlying, common physical effects, the strict details of the total entropy loss function for our model systems differ from the experiment.

4.2 Correlation of Adsorbed-Phase Entropy with Adsorbent Characteristics



Figure 3: Ratio of the adsorbed-phase to gas-phase entropy, $s_{ads}^{\infty}/s_{gas}^{0}$, for each adsorbate molecule identified by an integer label. (See Table S1 of the Supporting Information for the mapping of integer labels to the adsorbates.) Connecting lines are simply an aid to the eye, with no physical interpretation implied. The symbol and connecting line colors identify the adsorbent framework type and correspond to the color scheme in Fig 1. As discussed in the text, the outliers are small adsorbates and chemically unique cyclic ethers.

In this section, we discuss the variance of the linear correlations in Fig 1 across the set of adsorbates and adsorbents studied here. The first metric we examine more closely is the ratio $s_{ads}^{\infty}/s_{gas}^{0}$ for each adsorbate-adsorbent combination, as forcing the trend lines in Fig 1 through the origin is analogous to taking this ratio to be constant for each adsorbent. In doing so, we look more closely at how constant that ratio actually is. Figure 3 plots $s_{ads}^{\infty}/s_{gas}^{0}$ for all 185 adsorbate-adsorbent combinations, with the adsorbate species identified

by an integer on the x-axis (mapping in Table S1 of the Supporting Information) and the adsorbents identified by the same color coding as in Fig 1. Adsorbates are also grouped by chemical type (see Table S1 of the Supporting Information), though we stress that the x-axis integers should not be used to draw any correlative conclusions; the purpose of this figure is to put every entropy ratio from our calculations on a single plot. As expected from the results in Fig 1, for a given adsorbent, the entropy ratio is remarkably uniform across the adsorbates, with only a few noticeable outliers. Furthermore, the data in the figure appear to be clustered into three adsorbent groupings. Based on the "largest cavity diameter" (LCD) descriptor of First et al.⁵⁵ (the LCD being the diameter of the largest sphere that the adsorbent can accommodate), our zeolites are grouped into the following adsorbent categories: (1) spherical pores with an LCD of \approx 7 Å (FER and MFI), (2) cylindrical channels with an LCD of ≈ 7 Å (MOR), and (3) spherical pores with an LCD of ≈ 12 Å (FAU and LTA)². The implication is that the entropy ratio is effectively a constant for materials with similar characteristic pore size and shape and that (again, except for a few prominent outliers) the adsorbate characteristics are relatively unimportant. This raises the possibility that models based primarily on adsorbent characteristics may be an effective tool for modeling the adsorbed-phase entropy.

While the predominant trend in Fig 3 is a roughly uniform entropy ratio for each adsorbent across our set of adsorbates, there are some noticeable outlier adsorbates, particularly for the FAU and LTA topologies. For example, adsorbates 1, 5, 8, 11, and 26 are acetaldehyde, methane, ethane, ethylene, and dimethyl ether, respectively; these are all relatively small molecules. Furthermore, the adsorbents (FAU and LTA) have small secondary pores that are connected to the primary pores (LCD ≈ 12 Å) via inaccessible apertures. It is known that these small pores can be accessed by small adsorbates in Monte Carlo-type simulations since the adsorbate positions are generated randomly rather than by physical trajectories⁵⁷, resulting in unphysically large adsorption, which would be reflected in a larger entropy of

² The pore size descriptors for FAU, LTA, MOR, MFI, and FER are MSD = 11.24, 11.05, 6.7, 6.36, and 6.31 Å⁵⁶; LCD = 11.9, 11.7, 6.5, 7.0, and 7.0 Å⁵⁵, $V_{\rm occ} = 370.0, 311.4, 223.0, 177.4$, and 198.8 Å³ ⁵⁶

adsorption and, hence, smaller entropy ratio. Our integration technique also relies on the random generation of adsorbate positions; we have confirmed by direct visualization that these outliers result from adsorbates accessing pores that are actually inaccessible. The other group of prominent outliers are adsorbates 22, 24, and 32, corresponding to 1,3-dioxolane, 1,3,5-trioxane, and acetonitrile, respectively. These adsorbates are two cyclic ethers and one nitrile. In this case, we suspect that the unique chemical functionality of these adsorbates, in comparison to the other TraPPE species, results in a larger-than-expected entropy loss.



Maximum Included Sphere Diameter & Limiting Cavity Diameter [Å]

Figure 4: Plot of η from Fig 1 versus the LCD, MSD, and occupiable volume (see the main text for definitions and values²). Symbols are color-coded as follows. Blue: materials with an LCD of ≈ 7 Å, with spherical pores; orange: material with an LCD of ≈ 7 Å, with cylindrical channels; purple: materials with an LCD of ≈ 12 A, with spherical pores. Connecting lines are an aid to the eye to identify the MSD (solid green), LCD (dotted green), and occupiable volume (solid red) for each material. Zeolite graphics are from the Zeomics online database 55 .

Finally, the η slopes in Fig 1 and the examination of adsorbate-specific entropy ratios in Fig 3 are suggestive of an entropy loss model based primarily on certain adsorbent characteristics. As pointed out above, η is roughly the same for (1) FAU and LTA and (2) FER and

MFI; the adsorbents in each of these two groups have roughly the same LCD and predominantly cage-like, spherical pores. The MOR topology has, as mentioned previously, an LCD similar to FER and MFI but with channel pores. Other pore descriptors are, of course, available as well, and we examine two others here. First, as a complement to the LCD descriptor, we include the "maximum included sphere diameter" (MSD), which is the largest sphere pore identified in a calculated pore size distribution⁵⁶. Second, we also include a different type of geometric descriptor, the "occupiable volume" (V_{occ}) , which is defined as the volume per 1000 Å of the crystal cell that can be accessed by the center of probe molecules with diameter 2.8 Å^{56} . These three pore size descriptors capture both the size of the largest pore features and the overall pore volume. In Fig 4, we plot the η slope for each adsorbent as a function of these three pore metrics; diameter-based metrics are on the lower x-axis and occupiable volume is on the upper x-axis. The important result shown in Fig 4 is that, regardless of the metric used to characterize the zeolite adsorbent, the slope of the entropy relationship in Fig 1 follows the same qualitative trend. Starting at the largest pore adsorbents in terms of any of the three metrics, η decreases slowly with decreasing pore size, before decreasing more rapidly to values in the vicinity of $\eta = 0.75$. Despite plotting all three metrics on the x-axes of Fig 4, we imply no quantitative relationship between MSD/LCD and $V_{\rm occ}$; the purpose is to show the common trend in the correlation of η with different size metrics. (As an aside, we note that the upper and lower x-axes have common scaling, i.e., they share a common x = 0 origin [though not visible] given the upper bounds of LCD/MSD = 12 Å and $V_{\rm occ} = 408 \,\text{\AA}^3$; we acknowledge that the trend in the figure can be distorted by adjusting the scale and/or origin. Our plot attempts to avoid biasing the interpretation of the data by using a common origin.) Based on Fig 4, one may be motivated to construct an empirical fit of η as a function of one or more pore size metrics, from which one could then approximate the adsorbed-phase entropy from the gas-phase entropy. However, we suggest that a larger set of zeolites with more variation in pore size be examined computationally to provide a better basis for generating an empirical predictor of η .

Overall, we wish to stress that the entropy ratio is primarily a function of the adsorbent characteristics and that it may be quite adequate for engineering purposes to approximate the adsorbed-phase entropy as a fraction of the gas-phase entropy, with that fraction being largely independent of the adsorbate identity. This simple, fractional scaling of s_{ads}^{∞} with s_{gas}^{0} is, of course, a highly simplified model of the adsorbed-phase entropy and includes minimal physical insight or intuition. As shown in the next section, one can introduce physically intuitive arguments into more complicated models of entropy than that presented above.

4.3 Empirical Model of Entropy Based on Adsorbent Identity

While the linear entropy scaling in Figures 1 and 3 is quite successful for the TraPPEbased adsorption systems, it is ultimately an oversimplified correlation. We seek a physicsbased structure–topology–entropy relationship that is generic and applicable across molecule classes and zeolites. As a first step to this end, motivated by the arguments in refs 27 and 13, we considered a simple linear model wherein each contributor to the entropy is affected differently. However, it has been argued that the translational contribution to the adsorbate entropy (for alkanes) is relatively uniform across frameworks, with the emphasis being on the disparate rotational contributions^{13,58}. For example, Denayer et al. have demonstrated that the driving force behind the zeolitic separation of alkane/isoalkane mixtures is exclusively the difference in rotational loss, represented by a ratio between the molecule's radius of gyration with the cavity's largest inscribed van der Waals radius⁵⁸. Therefore, we consider a model where s_{ads}^{∞} is composed of (1) two-third translational entropy (equivalent to the loss of onethird of the gas-phase translational entropy) and (2) a fraction of the gas-phase rotational entropy. As mentioned previously, the vibrational entropy is assumed to be unaffected by adsorption or confinement.

We propose the simplest model consistent with the proposition that the adsorbed-phase entropy is composed of the translational and rotational entropies and all of the vibrational entropy of the gas state. Mathematically, this may be stated as

$$s_{\text{ads}}^{\infty} = \alpha s_{\text{trans}}^{0} + \beta s_{\text{rot}}^{0} + s_{\text{vib}}^{0} \quad \text{where} \quad \alpha = 2/3 \quad \text{and} \quad 0 < \beta < 1 \tag{7}$$

Then, motivated by our previous results, which showed that the linear correlation of adsorbedand gas-phase entropies could be based primarily on adsorbent identity, we make the further approximation that β is constant for each adsorbent species irrespective of the adsorbates. In other words, the loss in rotational entropy is dictated exclusively by the adsorbent characteristics and the loss in translational entropy is the aforementioned one-third of the gas-phase term. We make this approximation owing to the results in the previous sections showing the predominant effect of the adsorbent in correlations for the adsorption entropy.



Figure 5: Plot of the adsorbed-phase entropy s_{ads}^{∞}/R as computed from the multilinear regression in eq 7 versus that calculated in the Monte Carlo integration ("simulation") described in Section 3. Particular zeolite topologies are identified by the color codes in the legend. The y = x line is plotted for evaluation of the multilinear fit.

Based on these arguments, we performed a simple multilinear least-squares regression of our entropy data with eq 7 and the constraints shown. The full set of results are shown in Fig 5, where the calculated ("simulated") s_{ads}^{∞} is on the *x*-axis and the predicted value (eq 7 is on the y-axis. The β values from the regressions are given in Table 1, with the α parameter held constant at two-third. As is hoped for this type of model, the data are clustered around

Table 1: Fitting Parameters for β ($\alpha = 2/3$) for the Multilinear Regression of s_{ads}^{∞} to eq 7 for Each Zeolite Popology Studied Here with It's Respective MSD

Topology	MSD(LCD)	β
FAU	11.2(11.9)	1.00
LTA	11.1(11.7)	1.00
MOR	6.7(6.5)	1.00
MFI	6.4(7.0)	0.80
FER	6.3(7.0)	0.71

the y = x line, with only a few prominent outliers. In fact, the three most noticeable outliers are for the FAU material, and these correspond to 1,3,5-trioxane, acetaldehyde, acetonitrile outliers already pointed out in our discussion of Fig 3. The RMSE of the multilinear fits are 2.6, 1.8, 1.1, 1.4, and 1.8 for FAU, LTA, MOR, MFI, and FER, respectively. The α and β coefficients may be thought of as survival coefficients for the translational and rotational entropy, so trends in them may be helpful for physical interpretation of the predicted results. First, we note that the zeolite materials are in order of decreasing MSD in Table 1. The table then reveals that β decreases with decreasing pore size. The simplified model thus offers the following physical interpretation: decreasing pore size results in a proportionately larger loss of rotational entropy, entirely consistent with the previous results¹³. In other words, smaller pores are a hindrance to free rotation of an adsorbate, resulting in the loss of rotational entropy.

However, we stress that further work is needed to clarify whether the trend in β is a real effect or an artifact of an oversimplified model. By the same token, we emphasize that our pool of molecules excludes especially large species; we anticipate that data sets with extraordinarily hindered molecules will have much lower β values, but will ultimately follow a similar trend.

Ultimately, we find that the adsorbed-phase entropy can be fit to a simple model based on the survival of components of the gas-phase entropy and that this model is quite accurate except for a few outliers. Thus, in addition to the extremely simple linear correlation of the adsorbed- and gas-phase entropies presented in Fig 1 and associated discussion, we offer a more complex, but more physically intuitive, model based on eq 7 that may be used to predict the adsorbed-phase entropy solely from the gas-phase entropy with a satisfactory degree of accuracy.

5 Summary and Conclusions

The entropy of an adsorbed molecule is an important thermophysical property in evaluating the use of adsorbent for applications including, but not exclusive to, gas separation, catalysis, and energy storage. The number of actual and hypothetical zeolite materials, as only one example of a class of industrially relevant and resilient adsorbent materials, necessitates the provision of predictive models for the adsorbed entropy, whether those models are based on robust physical principles or engineering correlations. Previous works^{12,13,27} have demonstrated that the adsorbed-phase entropy may be predicted with good accuracy by applying straightforward loss functions to the gas-phase entropy, though the extent of those correlations was not clear as the correlations were generated for a limited set of adsorbates, primarily alkanes.

Here, we examined a larger and more chemically diverse set of adsorbates by computing the entropy in a model-based approach using 37 adsorbates available in the TraPPE force field library and five pure-silicate zeolites, for a total of 185 unique calculations. Our results show that linear correlation of the adsorbed- and gas-phase entropies persists for adsorbates and adsorbents not previously considered, though the form of the linear correlation differs from previous work^{13,27}. Furthermore, the correlation may be cast as a highly simplified linear scaling function applied to the gas-phase entropy, where the scaling coefficient is a constant for a particular adsorbent material, independent of the identity of the adsorbate species (Fig 3). Additionally, our data suggest that the scaling coefficient correlates with pore size characteristics (Fig 4), though more adsorbent materials need to be evaluated to confirm the observed correlation. Beyond the simple linear scaling of s_{ads}^{∞} with s_{gas}^{0} , we also fit the adsorbed-phase entropy to a multilinear expression based on physical arguments about the loss of translational and rotational entropies (eq 7). The multilinear fitting model successfully reproduced the TraPPE-model-based entropy calculations, which offers an alternative approach to modeling the adsorbed-phase entropy. In addition, this multilinear model is suggestive of opposing trends in the translational and rotational entropies (decreasing rotational entropy and increasing translational entropy with decreasing pore size), but more work is needed to determine whether this is a mathematical artifact or a real trend. Regardless, our model is consistent with prior approaches that model the adsorbed-phase entropy according to survival functions applied to the rotational and translational entropies.

Finally, as an overall summary, our results suggest that simple linear models can be used to approximate the entropy of an adsorbed phase, whether through a single scaling factor $(\eta \text{ in eq } 5)$ or through a more complicated multilinear expression (eq 7). In either case, our results point to engineering correlations based on a limited set of actual measurements; for example, evaluation of a new material could be done by measuring the Henry constant and isosteric heat of a few adsorbates and then using that limited set of data to generate η or α and β , based on the trends identified here. While these correlations have been identified specifically for pure-silicate zeolites, it is anticipated that the resultant trends may also appear for materials such as metal-organic frameworks and microporous polymers, which should be the objective of future work.

Acknowledgement

Financial support from Lehigh University (through S.R.'s startup and a CORE award) is gratefully acknowledged. S.R. also acknowledges financial support from the American Chemical Society Petroleum Research Fund Grant # 59476, as well as the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by the National Science Foundation grant number ACI-1548562 [59].

Supporting Information Available

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.0c02671.

Full list of adsorbate molecules from the TraPPE database used for the entropy calculations here and 820 additional details regarding the TraPPE-model implementation; tables of (1) the adsorption entropy Δs_{ads}^{∞} ; (2) the components of the gas-phase entropy s_{trans}^{0} (translational), s_{rot}^{0} (rotational), and s_{vib}^{0} (vibrational); (3) the total gas-phase entropy s_{gas}^{0} ; and (4) the adsorbed-phase entropy s_{ads}^{∞} and the infinite dilution isosteric heat of adsorption Q_{st}^{∞} for the adsorbate-adsorbent combinations reported here (PDF).

Example scripts and supporting files for the calculation of adsorption entropy of TraPPE ethane adsorbed in LTA all-silica zeolite at 300 K using FEASST (ZIP)

This material is available free of charge via the Internet at http://pubs.acs.org/.

ORCID 🕩:

Christopher Rzepa 0000-0001-6482-2968 Daniel W. Siderius 0000-0002-6260-7727 Srinivas Rangarajan 0000-0002-6777-9421 Harold W. Hatch 0000-0003-2926-9145 Jeetain Mittal 0000-0002-9725-6402

Appendix

In the following appendix, we derive the entropy of adsorption in the case of infinite dilution and show how it may be related to familiar thermodynamic quantities (cf. eq 5). To begin, we define our adsorption entropy in the limit of infinite dilution via

$$\Delta s_{\rm ads}^{\infty} = \lim_{N/V \to 0} \left[\left(\frac{\partial S}{\partial N} \right)_{V,T,ads} - \left(\frac{\partial S}{\partial N} \right)_{V,T,gas} \right]$$
(8)

$$= S_{\rm ads} \left(N = 1, V, T \right) - S_{\rm gas} \left(N = 1, V, T \right)$$
(9)

where the subscripts "ads" and "gas" labels identify the adsorbed (confined) and gas (bulk) phases, respectively. Given the constraints of a fixed number of molecules (N), volume (V), and temperature (T), it is natural to continue working in the canonical ensemble. (As in the main text, lowercase symbols identify intensive molecular or molar properties, whereas the uppercase indicates an extensive property.) For the molecules that we examine in this work (e.g., rigid molecules with no internal degrees of freedom), the canonical partition function Q may be expressed as

$$Q(N, V, T) = Q_{\text{trans}}(N, V, T) Q_{\text{rot}}(N, V, T) Z(N, V, T)$$

$$(10)$$

where Q_{trans} and Q_{rot} are the translational and rotational partition functions (which are unaffected by confinement) and Z is the configurational partition function. The translational and rotational partition functions are available in the usual statistical mechanics texts^{44,45}, but are ultimately unimportant for the derivation that follows.

Continuing, the configurational partition function may be written as

$$Z(N, V, T) = \frac{1}{\Omega^N} \int_V d\mathbf{r}^N \int_{\psi} d\psi^N \exp\left[-\beta U\left(\mathbf{r}^N, \boldsymbol{\psi}^N\right)\right]$$
(11)

where $\beta = 1/k_{\rm B}T$ and $U(\mathbf{r}^N, \boldsymbol{\psi}^N)$ is the potential energy (no kinetic contributions) of a molecule at position \mathbf{r} and with Euler angles (orientation) $\boldsymbol{\psi}$. $\Omega = 8\pi^2 V$ is the "volume" of the configurational space (i.e., it includes both positional and orientational degrees of freedom). Using the bridge function for the Helmholtz free energy, $F = -k_{\rm B}T \ln Q$, the entropy is given by

$$S(N, V, T) / k_{\rm B} = \frac{3}{2} N + \beta E_{\rm rot} + \beta \langle U \rangle (N, V, T) + \ln Q_{\rm trans} (N, V, T) + \ln Q_{\rm rot} (N, V, T) + \ln Z (N, V, T)$$

$$(12)$$

where $\langle U \rangle$ is the ensemble average potential energy,

$$\langle U \rangle (N, V, T) = \frac{1}{\Omega^N} \frac{\int_V \int_{\psi} U(\mathbf{r}, \boldsymbol{\psi}) \exp\left[-\beta U(\mathbf{r}, \boldsymbol{\psi})\right] d\mathbf{r}^N d\boldsymbol{\psi}^N}{Z(N, V, T)},$$
(13)

and $E_{\rm rot}$ is the molecule-specific rotational kinetic energy. We note that the kinetic energy and partition functions for the translational and rotational degrees of freedom in eq 13 are constants independent of the adsorbent characteristics.

In the limit of N = 1, the adsorption entropy (eq 5) may thus be written as

$$\frac{\Delta s_{\text{ads}}^{\infty}}{k_{\text{B}}} = \beta \left\langle U_{\text{fs}} \right\rangle (1, V, T) + \ln Z_{\text{ads}} (1, V, T)$$
(14)

In the equation above, we have taken advantage of a number of simplifications. First, the volumes of the gas and adsorbed phases are taken to be identical; Q_{trans} is therefore identical for the two phases. Second, Q_{rot} is, by nature, identical in both phases. Third, we have exploited the fact that for a single adsorbed molecule the potential energy U is just the adsorbate-adsorbent potential energy U_{fs} . Finally, $\langle U \rangle = 0$ and $Z_{\text{gas}} = 1$ for a single, rigid gas molecule in isolation. Furthermore, the use of eqs 11 and 13 allows us to express the infinite dilution adsorption entropy for a rigid molecule as

$$\frac{\Delta s_{\text{ads}}^{\infty}}{k_{\text{B}}} = \frac{\int_{V} \int_{\psi} \beta U_{\text{fs}}\left(\mathbf{r}, \boldsymbol{\psi}\right) \exp\left[-\beta U_{\text{fs}}\left(\mathbf{r}, \boldsymbol{\psi}\right)\right] d\mathbf{r} d\boldsymbol{\psi}}{\int_{V} \int_{\psi} \exp\left[-\beta U_{\text{fs}}\left(\mathbf{r}, \boldsymbol{\psi}\right)\right] d\mathbf{r} d\boldsymbol{\psi}} + \ln\left[\frac{1}{\Omega} \int_{V} \int_{\psi} \exp\left[-\beta U_{\text{fs}}\left(\mathbf{r}, \boldsymbol{\psi}\right)\right] d\mathbf{r} d\boldsymbol{\psi}\right]$$
(15)

At this point, it is helpful to convert the integrals in eq 15 to spatial averages, consistent

with the approach of Sarkisov in ref 41:

$$\frac{\Delta s_{\text{ads}}^{\infty}}{k_{\text{B}}} = \frac{\langle U_{\text{fs}}\left(\mathbf{r}, \boldsymbol{\psi}\right) \exp\left[-\beta U_{\text{fs}}\left(\mathbf{r}, \boldsymbol{\psi}\right)\right] \rangle}{\langle \exp\left[-\beta U_{\text{fs}}\left(\mathbf{r}, \boldsymbol{\psi}\right)\right] \rangle} + \ln\left\langle \exp\left[-\beta U_{\text{fs}}\left(\mathbf{r}, \boldsymbol{\psi}\right)\right] \rangle$$
(16)

where the $\langle \rangle$ brackets now indicate (not ensemble) averages over the positional and orientational degrees of freedom. Finally, using Sarkisov's expressions for the Henry's law constant and infinite dilution enthalpy of the adsorption of rigid molecules⁴¹ in eq 3, the adsorption entropy reduces to the form shown in eq 5 (subject to appropriate conversions of energy quantities from molecular to molar basis).

References

- Corma, A. From Microporous to Mesoporous Molecular Sieve Materials and Their Use in Catalysis. *Chem. Rev.* 1997, 97, 2373–2420.
- (2) Corma, A. Inorganic Solid Acids and Their Use in Acid-Catalyzed Hydrocarbon Reactions. Chem. Rev. 1995, 95, 559–614.
- (3) Pophale, R.; Cheeseman, P. A.; Deem, M. W. A database of new zeolite-like materials. *Phys. Chem. Chem. Phys.* **2011**, *13*, 12407–12412.
- (4) Simon, C. M.; Kim, J.; Lin, L.-C.; Martin, R. L.; Haranczyk, M.; Smit, B. Optimizing nanoporous materials for gas storage. *Phys. Chem. Chem. Phys.* **2014**, *16*, 5499–5513.
- (5) Kim, J.; Maiti, A.; Lin, L.-C.; Stolaroff, J. K.; Smit, B.; Aines, R. D. New materials for methane capture from dilute and medium-concentration sources. *Nat. Commun.* 2013, 4, 1694.
- (6) Lee, Y.; Barthel, S. D.; Dłotko, P.; Moosavi, S. M.; Hess, K.; Smit, B. High-Throughput Screening Approach for Nanoporous Materials Genome Using Topological Data Analysis: Application to Zeolites. J. Chem. Theory Comput. 2018, 14, 4427–4437.

- (7) Sun, W.; Lin, L.-C.; Peng, X.; Smit, B. Computational screening of porous metalorganic frameworks and zeolites for the removal of SO2 and NOx from flue gases. *AIChE J.* 2014, 60, 2314–2323.
- (8) Haldoupis, E.; Nair, S.; Sholl, D. S. Pore size analysis of > 250 000 hypothetical zeolites. Phys. Chem. Chem. Phys. 2011, 13, 5053–5060.
- (9) Deem, M. W.; Pophale, R.; Cheeseman, P. A.; Earl, D. J. Computational Discovery of New Zeolite-Like Materials. J. Phys. Chem. C 2009, 113, 21353–21360.
- (10) Davis, M. E. Ordered porous materials for emerging applications. Nature 2002, 417, 813–821.
- (11) Slater, A. G.; Cooper, A. I. Function-led design of new porous materials. Science 2015, 348, aaa8075.
- (12) De Moor, B. A.; Reyniers, M.-F.; Gobin, O. C.; Lercher, J. A.; Marin, G. B. Adsorption of C2–C8 n-Alkanes in Zeolites. J. Phys. Chem. C 2011, 115, 1204–1219.
- (13) Dauenhauer, P. J.; Abdelrahman, O. A. A Universal Descriptor for the Entropy of Adsorbed Molecules in Confined Spaces. ACS Cent. Sci. 2018, 4, 1235–1243.
- (14) Denayer, J. F.; Baron, G. V.; Martens, J. A.; Jacobs, P. A. Chromatographic Study of Adsorption of n-Alkanes on Zeolites at High Temperatures. J. Phys. Chem. B 1998, 102, 3077–3081.
- (15) Denayer, J. F.; Souverijns, W.; Jacobs, P. A.; Martens, J. A.; Baron, G. V. High-Temperature Low-Pressure Adsorption of Branched C5–C8 Alkanes on Zeolite Beta, ZSM-5, ZSM-22, Zeolite Y, and Mordenite. J. Phys. Chem. B 1998, 102, 4588–4597.
- (16) Piccini, G. M.; Alessio, M.; Sauer, J.; Zhi, Y.; Liu, Y.; Kolvenbach, R.; Jentys, A.; Lercher, J. A. Accurate Adsorption Thermodynamics of Small Alkanes in Zeolites. Ab

initio Theory and Experiment for H-Chabazite. J. Phys. Chem. C 2015, 119, 6128–6137.

- (17) Li, H.; Kadam, S. A.; Vimont, A.; Wormsbecher, R. F.; Travert, A. Monomolecular Cracking Rates of Light Alkanes over Zeolites Determined by IR Operando Spectroscopy. ACS Catal 2016, 6, 4536–4548.
- (18) Beste, A. One-dimensional anharmonic oscillator: Quantum versus classical vibrational partition functions. *Chem. Phys. Lett.* **2010**, *493*, 200–205.
- (19) Piccini, G. M.; Sauer, J. Effect of Anharmonicity on Adsorption Thermodynamics. J. Chem. Theory Comput. 2014, 10, 2479–2487.
- (20) Alexopoulos, K.; Lee, M.-S.; Liu, Y.; Zhi, Y.; Liu, Y.; Reyniers, M.-F.; Marin, G. B.; Glezakou, V.-A.; Rousseau, R.; Lercher, J. A. Anharmonicity and Confinement in Zeolites: Structure, Spectroscopy, and Adsorption Free Energy of Ethanol in H-ZSM-5. J. Phys. Chem. C 2016, 120, 7172–7182.
- (21) Li, H.; Paolucci, C.; Schneider, W. F. Zeolite Adsorption Free Energies from ab Initio Potentials of Mean Force. J. Chem. Theory Comput. 2018, 14, 929–938.
- (22) Jørgensen, M.; Chen, L.; Grönbeck, H. Monte Carlo Potential Energy Sampling for Molecular Entropy in Zeolites. J. Phys. Chem. C 2018, 122, 20351–20357.
- (23) De Moor, B. A.; Reyniers, M.-F.; Gobin, O. C.; Lercher, J. A.; Marin, G. B. Adsorption of C2–C8 n-Alkanes in Zeolites. J. Phys. Chem. C 2011, 115, 1204–1219.
- (24) Sprowl, L. H.; Campbell, C. T.; Árnadóttir, L. Hindered Translator and Hindered Rotor Models for Adsorbates: Partition Functions and Entropies. J. Phys. Chem. C 2016, 120, 9719–9731.
- (25) Krishna, R.; Smit, B.; Calero, S. Entropy effects during sorption of alkanes in zeolites. *Chem. Soc. Rev.* 2002, *31*, 185–194.

- (26) Simon, C. M.; Mercado, R.; Schnell, S. K.; Smit, B.; Haranczyk, M. What Are the Best Materials To Separate a Xenon/Krypton Mixture? *Chem. Mater.* 2015, 27, 4459–4475.
- (27) Campbell, C. T.; Sellers, J. R. V. The Entropies of Adsorbed Molecules. J. Am. Chem. Soc. 2012, 134, 18109–18115.
- (28) Campbell, C. T.; Sellers, J. R. V. Enthalpies and Entropies of Adsorption on Well-Defined Oxide Surfaces: Experimental Measurements. *Chem. Rev.* 2013, 113, 4106– 4135.
- (29) Otyepková, E.; Lazar, P.; Čépe, K.; Tomanec, O.; Otyepka, M. Organic adsorbates have higher affinities to fluorographene than to graphene. *Appl. Mater. Today* 2016, 5, 142–149.
- (30) Karlický, F.; Otyepková, E.; Lo, R.; Pitoňák, M.; Jurečka, P.; Pykal, M.; Hobza, P.; Otyepka, M. Adsorption of Organic Molecules to van der Waals Materials: Comparison of Fluorographene and Fluorographite with Graphene and Graphite. J. Chem. Theory Comput. 2017, 13, 1328–1340.
- (31) Budi, A.; Stipp, S. L. S.; Andersson, M. P. Calculation of Entropy of Adsorption for Small Molecules on Mineral Surfaces. J. Phys. Chem. C 2018, 122, 8236–8243.
- (32) Eggimann, B. L.; Sunnarborg, A. J.; Stern, H. D.; Bliss, A. P.; Siepmann, J. I. An online parameter and property database for the TraPPE force field. *Mol. Sim.* 2014, 40, 101–105.
- (33) Eder, F.; ; Lercher, J. A. Alkane sorption in molecular sieves: The contribution of ordering, intermolecular interactions, and sorption on Brønsted acid sites. Zeolites 1997, 18, 75–81.
- (34) Eder, F.; Stockenhuber, M.; Lercher, J. A. Brønsted Acid Site and Pore Controlled

Siting of Alkane Sorption in Acidic Molecular Sieves. J. Phys. Chem. B 1997, 101, 5414–5419.

- (35) Gelb, L. D.; Gubbins, K. E.; Radhakrishnan, R.; Sliwinska-Bartkowiak, M. Phase separation in confined systems. *Rep. Prog. Phys.* **1999**, *62*, 1573–1659.
- (36) Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution. *Pure Appl. Chem.* 2015, *87*, 1051–1069.
- (37) Myers, A. L. Thermodynamics of adsorption in porous materials. AIChE J. 2002, 48, 145–160.
- (38) Myers, A. L. Characterization of nanopores by standard enthalpy and entropy of adsorption of probe molecules. *Colloids Surf. A* 2004, 241, 9–14.
- (39) Myers, A. L.; Monson, P. A. Physical adsorption of gases: the case for absolute adsorption as the basis for thermodynamic analysis. *Adsorption* **2014**, *20*, 591–622.
- (40) Brandani, S.; Mangano, E.; Sarkisov, L. Net, excess and absolute adsorption and adsorption of helium. Adsorption 2016, 22, 261–276.
- (41) Sarkisov, L. Toward Rational Design of Metal–Organic Frameworks for Sensing Applications: Efficient Calculation of Adsorption Characteristics in Zero Loading Regime. J. Phys. Chem. C 2012, 116, 3025–3033.
- (42) Allen, M. P.; Tildesley, D. J. Computer Simulation of Liquids; Clarendon: New York, 1987.
- (43) Campbell, C. T.; Sprowl, L. H.; Árnadóttirr, L. Equilibrium Constants and Rate Constants for Adsorbates: Two-Dimensional (2D) Ideal Gas, 2D Ideal Lattice Gas, and Ideal Hindered Translator Models. J. Phys. Chem. C 2016, 120, 10283–10297.

- (44) Hill, T. L. An Introduction to Statistical Thermodynamics, 2nd ed.; Addison-Wesley: Reading, MA, 1962.
- (45) McQuarrie, D. A. Statistical Thermodynamics; University Science Books: Mill Valley, 1973.
- (46) Johnson III, R. D., Ed. NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101; National Institute of Standards and Technology: Gaithersburg, MD, 20899, Release 20, August 2019.
- (47) Widom, B. Some Topics in the Theory of Fluids. J. Chem. Phys. 1963, 39, 2808–2812.
- (48) Widom, B. Potential-Distribution theory and the statistical mechanics of fluids. J. Phys. Chem. 1982, 86, 869–872.
- (49) Baerlocher, C.; McCusker, L. B. Database of Zeolite Structures. 2020; http://www. iza-structure.org/databases/, Accessed 23 January 2020.
- (50) O'Boyle, N. M.; Banck, M.; James, C. A.; Morley, C.; Vandermeersch, T.; Hutchison, G. R. Open Babel: An open chemical toolbox. J. Cheminf. 2011, 3, 33.
- (51) Wang, J.; Wolf, R. M.; Caldwell, J. W.; Kollman, P. A.; Case, D. A. Development and testing of a general amber force field. J. Comput. Chem. 2004, 25, 1157–1174.
- (52) J. I. Siepmann Group, TraPPE Database. 2017; http://chem-siepmann.oit.umn. edu/siepmann/trappe/index.html, Accessed 23 January 2020.
- (53) Bai, P.; Tsapatsis, M.; Siepmann, J. I. TraPPE-zeo: Transferable Potentials for Phase Equilibria Force Field for All-Silica Zeolites. J. Phys. Chem. C 2013, 117, 24375–24387.
- (54) Hatch, H. W.; Mahynski, N. A.; Shen, V. K. FEASST: Free Energy and Advanced Sampling Simulation Toolkit. J. Res. Natl. Inst. Stand. Technol. 2018, 123, 123004.

- (55) First, E. L.; Gounaris, C. E.; Wei, J.; Floudas, C. A. Computational characterization of zeolite porous networks: An automated approach. *Phys. Chem. Chem. Phys.* 2011, 13, 17339–17358.
- (56) Treacy, M. M. J.; Foster, M. D. Packing sticky hard spheres into rigid zeolite frameworks. *Micropor. and Mesopor. Mater.* 2009, 118, 106–114.
- (57) Gómez-Álvarez, P.; Ruiz-Salvador, A. R.; Hamad, S.; Calero, S. Importance of Blocking Inaccessible Voids on Modeling Zeolite Adsorption: Revisited. J. Phys. Chem. C 2017, 121, 4462–4470.
- (58) Denayer, J. F. M.; Ocakoglu, R. A.; Arik, I. C.; Kirschhock, C. E. A.; Martens, J. A.; Baron, G. V. Rotational Entropy Driven Separation of Alkane/Isoalkane Mixtures in Zeolite Cages. Angew. Chem. Int. Ed. 2005, 44, 400–403.
- (59) Towns, J.; Cockerill, T.; Dahan, M.; Foster, I.; Gaither, K.; Grimshaw, A.; Hazlewood, V.; Lathrop, S.; Lifka, D.; Peterson, G. D. et al. XSEDE: Accelerating Scientific Discovery. *Comput. Sci. Eng.* **2014**, *16*, 62–74.

Graphical TOC Entry

