

**Unusual Entropy of Adsorbed Methane on Zeolite-Templated Carbon**

Supporting Information

Part 1: The Effects of Omitting Considerations **a-c**

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## On Fitting Adsorption Data

Figure S1 shows a comparison of the methane adsorption isotherms on MSC-30 fitted in four ways: by linear interpolation (worst case) and by a generalized-Langmuir fitting equation omitting **a-c**, omitting only **b**, and omitting none (best case). In the stage of fitting the adsorption isotherms, disregarding either Gibb's definition of excess adsorption (**a**) or a growing adsorption phase volume (**c**) are essentially equivalent, the effects of which are readily apparent (Figure S1b). Interestingly, the incorporation of considerations **a** and **c** without acknowledgement of gas non-ideality (**b**), even with the use of seven independent fitting parameters, the two-site Langmuir model cannot accurately represent the measured data in the region of highest pressure and lowest temperature (Figure S1c). This demonstrates the necessity to measure sufficient adsorption data in the region of the phase diagram above the excess maximum for dependable interpretation of the parameters, even when a "real gas" equation of state is employed. With all relevant considerations taken, the goodness of fit of the non-ideal two-site Langmuir equation is excellent across the entire range of temperature and pressure (Figure S1d); the residual sum of squares across all materials in this study was always  $< 0.02 \text{ mmol g}^{-1}$  per data point.

It is important to notice that in the case of all three materials, the use of a linearly increasing adsorbed layer volume gives satisfactory fits to the data up to 10 MPa. However, the accuracy of this approximation becomes more questionable in the case of significant adsorbate-adsorbate interactions. Further analysis of this effect would be necessary to determine whether a more sophisticated approximation is warranted at higher pressures and lower temperatures.

## On Calculating $-\Delta H_{ads}$

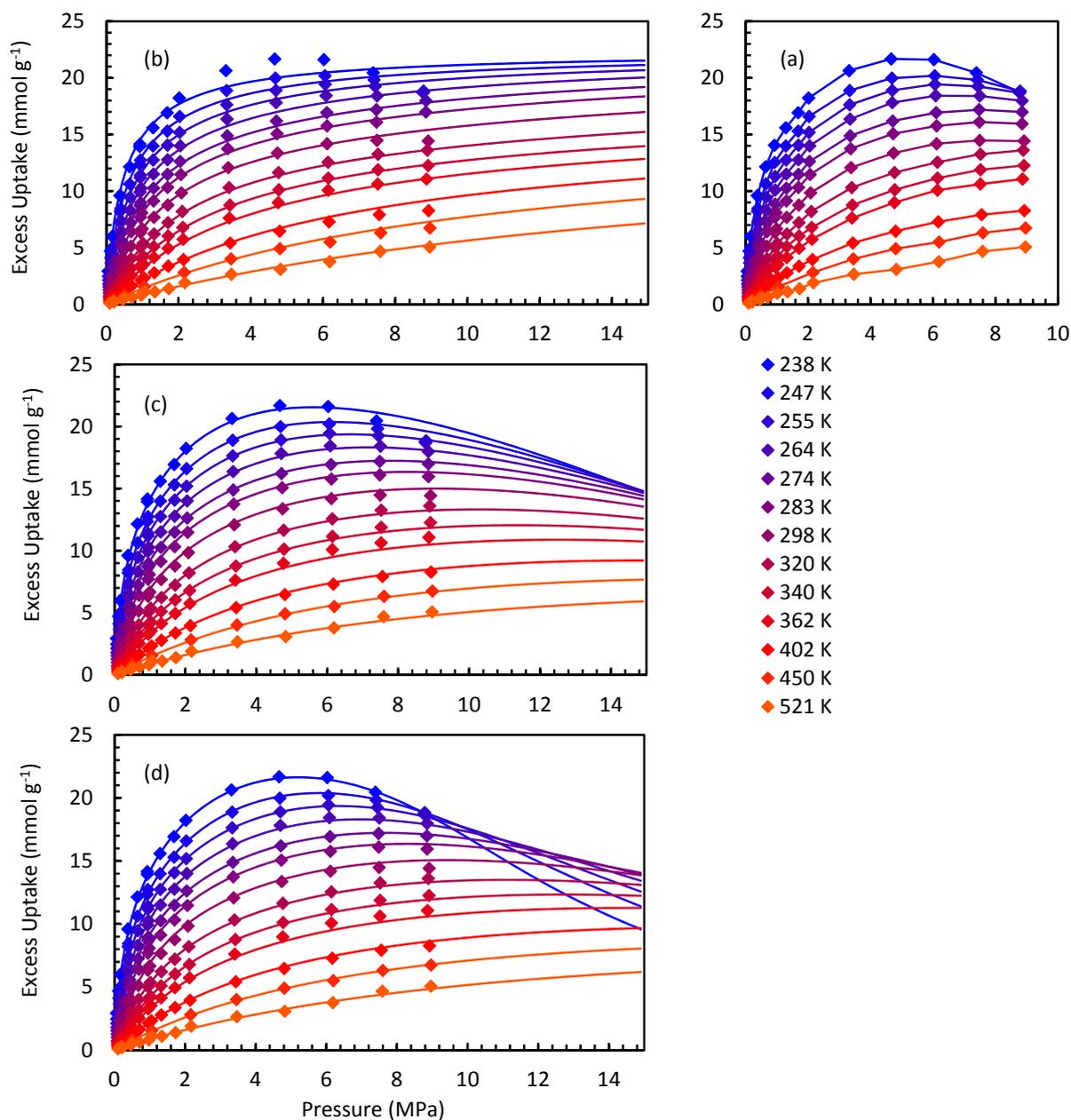
The effects of disregarding various considerations in the calculation of the isosteric enthalpy of adsorption are shown in Figure S2. If the adsorption data are fitted by a completely general, model-less approach (linear interpolation, omitting **a-c**) the "isoexcess" (constant excess quantity of adsorption) enthalpy can be directly calculated via the Clausius-Clapeyron equation, as shown in Figure S2a. This is the most straightforward approach to obtaining an experimental estimate of the change in enthalpy due to adsorption, and its role here is to demonstrate the typical limitations reflected in other simple approaches (e.g., fitting the data to an arbitrary functional form, such as a Virial-type equation, which does not exhibit physically realistic and consistent relationships between the thermodynamic variables). Two classic pitfalls commonly encountered when excluding considerations **a-c** are evident: the temperature dependence is lost in the noise that arises from small errors in the interpolated isoexcess equilibria and the adsorption uptake dependence shows an unphysical behavior at high quantities of excess uptake. The latter effect is well known, and common practice to account for this limitation is to disregard the data above a certain quantity of uptake where it is estimated that considerations **a-c** become most significant. The temperature dependence of the isosteric enthalpy of adsorption is much less discussed (a temperature average is typically reported), likely because of the finer approach needed for its determination. Without a rigorous understanding of the effects of **a-c** in the region of interest, the results of this type of analysis are not accurate or insightful. Nevertheless, it is important to note that even with such a completely model-less approach and using the ideal gas (Clausius-Clapeyron) "isoexcess" method, it is still possible to obtain an average Henry's law enthalpy of adsorption that is sufficiently accurate, in other words consistent with all other increasingly detailed approaches: e.g.,  $14.7 \text{ kJ mol}^{-1}$  for  $\text{CH}_4$  on MSC-30. Therefore, such an approach can be used as an effective general screening tool for comparing materials and analytical methods.

Perhaps surprisingly, even once a physically realistic fitting equation has been established, the three considerations **a-c** have a profound effect on both the temperature and uptake dependence of  $-\Delta H_{ads}$ . This is observed by comparing Figures S2b-S2d. In all three cases, a generalized Langmuir model has been used to interpolate the data and the derivative  $dP/dT$  of the resulting isosteric equilibria has been used to calculate  $-\Delta H_{ads}$  in both steps making the same set of assumptions. It is already apparent from the comparison of Figures S2b-S2d to S2a that the use of a physically realistic fitting equation (one that is monotonically increasing and based on a self-consistent physical model) serves to clarify the temperature and adsorption site occupancy (i.e., uptake) dependence of the results. This is desirable for obvious reasons, but care is needed in order to determine whether the delivered results are accurate and meaningful. The comparison of Figures S2b and S2c elucidates the role of non-ideality of the gas phase: at high pressures (corresponding to high uptake), the isosteric enthalpy decreases rapidly when non-ideality is acknowledged, while that of the ideal gas case remains constant. This effect is especially evident at lower temperatures. The temperature dependence of the isosteric enthalpy remains mostly intact between Figure S2b and S2c (i.e., with and without consideration **b**). However, upon acknowledgement of the finite adsorbed phase volume, the temperature dependence of the isosteric enthalpy is significantly affected. Comparing Figures S2c and S2d, it can be seen that an increasing dependence of the isosteric enthalpy of adsorption on temperature only remains intact in the Henry's law limit; above a fractional adsorption site occupancy of  $\sim 0.1$ , the temperature dependence is reversed. This is clearly a result of widely varying changes in molar volume upon adsorption,  $\Delta v_a$ , which in this work correspond to relative differences as low as 0.1% (0.1 MPa, 526 K) and as high as 40% (9 MPa, 238 K). Further, the dependence of the isosteric enthalpy of adsorption on uptake amount, with and without consideration **c**, is to reinforce the effects of including/omitting **b**: isosteric enthalpy decreases more rapidly with uptake. In summary, the combined results of considering **a-c** and discounting all inapplicable approximations in the calculation of isosteric enthalpy of adsorption is a rapidly decreasing enthalpy of adsorption at high surface occupancy, and a complex dependence of this enthalpy change on the temperature. To better understand how the elimination of the various approximations leads one closer to the true thermodynamic quantities, we must turn to the corresponding entropy calculations which can be readily compared to simple statistical mechanics.

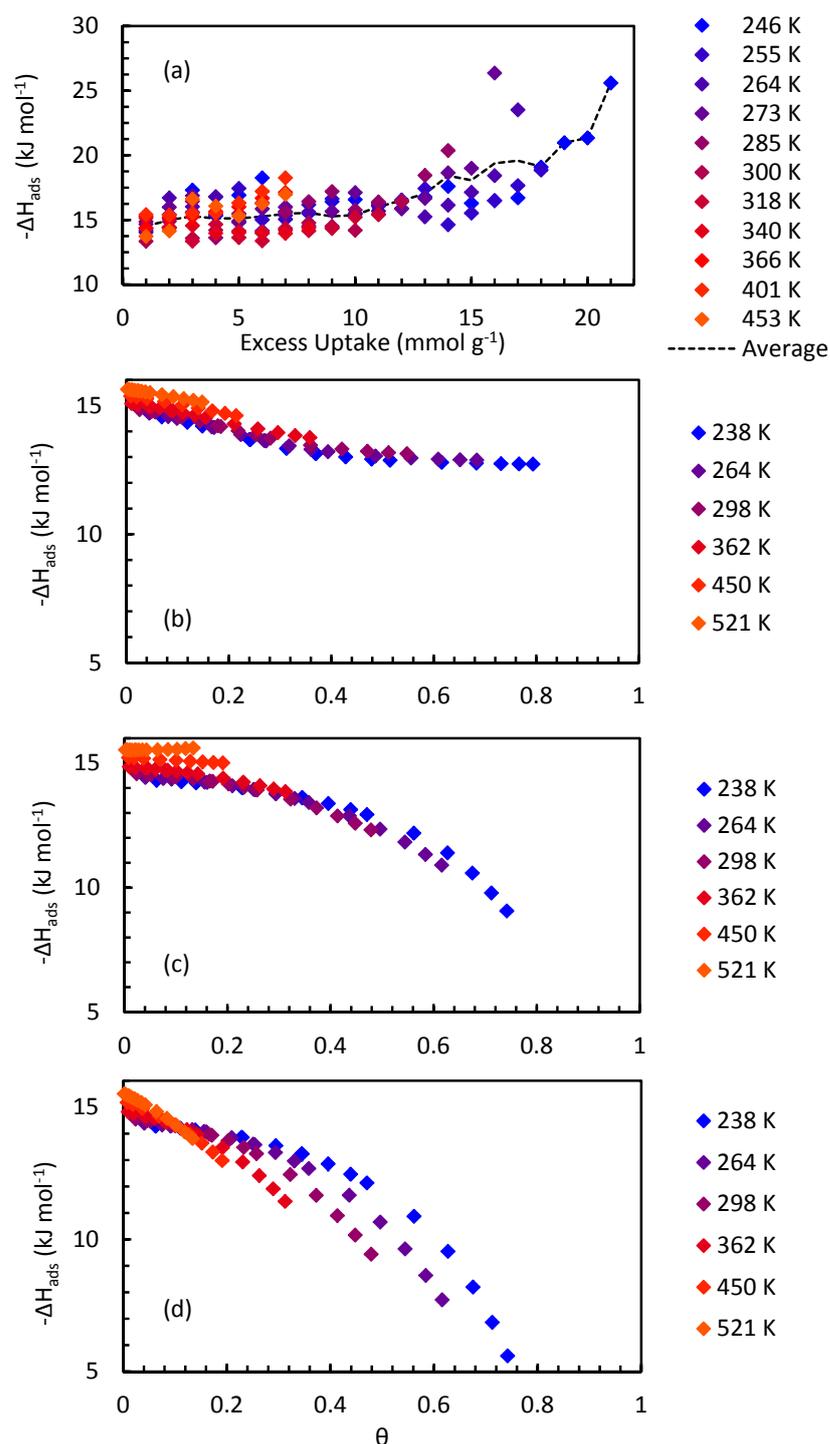
### On Calculating $S_{cum}$

The effects of disregarding various considerations in the calculation of the entropy of adsorbed methane on MSC-30 are shown in Figure S3. If the adsorption data are fitted by a completely general, model-less approach (linear interpolation, omitting **a-c**), the entropy of the adsorbed phase can be estimated by adding the entropy of an ideal gas to the "isoexcess" differential entropy of adsorption, as in Figure S3a. Even in this very simplistic analysis, some general trends can be extracted (e.g., the temperature dependence of the entropy in the dilute limit); however, the results are unreliable as adsorption uptake is increased, owing to the poor fit of the measured data and physical inconsistencies inherent in substituting the excess uptake amount for the absolute quantity present in the adsorbed phase. With the use of a physically realistic generalized-Langmuir fitting approach (Figures S3b-d), the temperature dependence of the entropy is clearly much more dependable in the entire range of analysis, closely following that of gaseous methane in all cases. However, the dependence of the cumulative entropy of the adsorbed phase as a function of increased site occupancy is significantly modified by the incorporation of considerations **a-c**, especially at high fractional site occupancy. In the case where the gas phase is treated as ideal and the adsorbed phase is approximated as having negligible volume (Figure S3b), the entropy is overestimated compared to calculations by statistical mechanics (e.g., up to 27% at 238 K). When gas phase non-ideality is considered (Figure S3c), the agreement is better overall, and within 1% error at all temperatures up to  $\theta = 0.2$ .

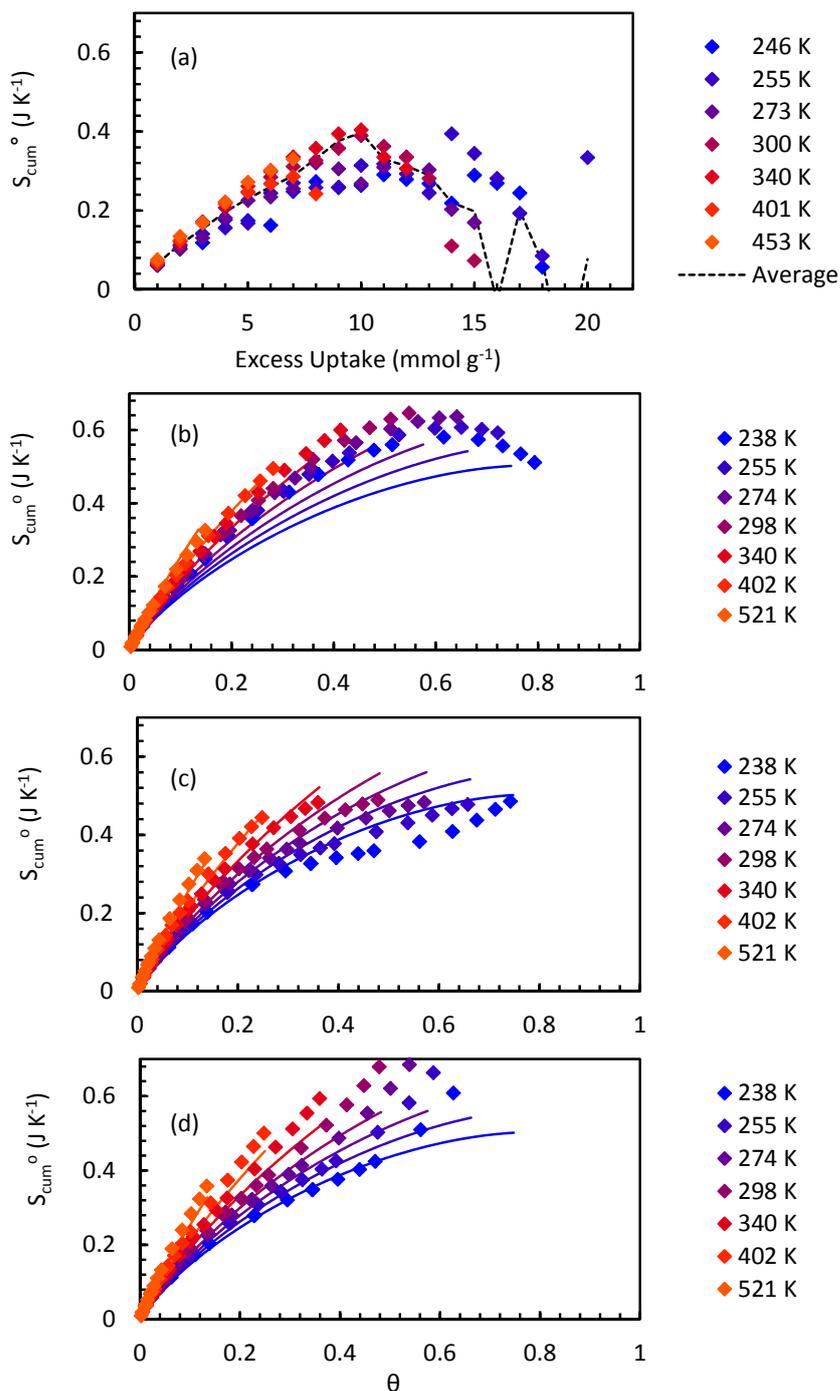
To achieve the greatest consistency between theory and experiment, the concepts of Gibbs excess, gas phase non-ideality, and a finite adsorbed phase volume must all be considered (Figure S3d), resulting in errors within 1% up to  $\theta = 0.4$ , and errors no larger than 2% up to  $\theta = 0.5$ , a remarkable range of agreement. This result provides clear evidence of the success of the adsorption model and thermodynamic analysis employed in the experimental part of this work, when incorporating considerations **a-c**, in providing an accurate physical picture of the adsorbed phase.



**Figure S1.** Equilibrium excess adsorption uptake,  $n_e$ , of methane on MSC-30, fitted by linear interpolation (S1a) and a two-site generalized Langmuir model with various considerations omitted for demonstration purposes: Gibbs excess (**a**), real gas interactions (**b**), and a finite volume adsorbed phase (**c**) all omitted (S1b), only **b** omitted (S1c), and none omitted, as in Equation 11 (S1d). The modelled fits are extended to 15 MPa to emphasize the importance of measuring data beyond the excess adsorption maximum where the behavior of the model with and without considerations **a-c** is significantly different.



**Figure S2.** Isosteric or “isoexcess” enthalpy of adsorption of methane,  $-\Delta H_{ads}$ , on MSC-30 as a function of adsorption site occupancy or uptake calculated by various methods for demonstration purposes: a model-less “isoexcess” approach (S2a), and Equation 12 omitting **b** and **c** (ideal gas and negligible  $v_a$ ) (S2b), omitting **c** (gas non-ideality and negligible  $v_a$ ) (S2c), and incorporating all considerations **a-c** (gas non-ideality and finite  $v_a$ ) (S2d).



**Figure S3.** Cumulative entropy of adsorbed methane,  $S_{cum}^o$ , on MSC-30 as a function of adsorption site occupancy,  $\theta$ , calculated by various methods for demonstration purposes: a model-less “isoexcess” approach (S3a), and a generalized-Langmuir approach omitting **b** and **c** (ideal gas and negligible  $v_a$ ) (S3b), omitting **c** (assuming negligible  $v_a$ ) (S3c), and incorporating all considerations **a-c** (S3d). Demonstrational experimental values are shown as filled diamonds and calculations of  $S_{cum}^o$  based on statistical mechanics (the same in each panel) are shown as solid lines.