Corresponding States Interpretation of Adsorption in Gate-Opening Metal-Organic Framework $\text{Cu(dhbc)}_2(4,4'\text{-bpy})$

Sarmishtha Sircar^a, Sanhita Pramanik^b, Jing Li^b, Milton W. Cole^c, and Angela D. Lueking^{*a,d}

^aDepartment of Energy & Mineral Engineering, ^cDepartment of Physics, ^dDepartment of Chemical Engineering, ^dEMS Energy Institute, The Pennsylvania State University, University Park, Pennsylvania 16802, USA,

^bDepartment of Chemistry and Chemical Biology, Rutgers University, Piscataway, NJ 08854, USA.

*Corresponding Author: 104 Materials Research Laboratory, adl11@psu.edu, 814-876-0005

Fax: 814-865-3248

ABSTRACT

The “universal adsorption theory” (UAT) extends the principle of corresponding states for gas compressibility to describe the excess density of an adsorbed phase at comparable reduced conditions. The UAT helps to describe experimental trends and provide predictive capacity for extrapolation from one adsorption isotherm to that of a different adsorbate. Here, we extend the UAT to a flexible metal-organic framework (MOF) as a function of adsorbate, temperature, and pressure. When considered via the UAT, the adsorption capacity and GO pressure of multiple gases to $\text{Cu}(\text{dhbc})_2(4,4'\text{-bpy})$ [H_2dhbc =2,5-dihydroxybenzoic acid, bpy=bipyridine] show quantifiable trends over a considerable temperature and pressure range, despite the chemical and structural heterogeneity of the adsorbent. Exceptions include quantum gases (such as H_2) and prediction of maximum capacity for large and/or polar adsorbates. A method to derive the heat of gate opening and heat of expansion from experimental trends is also presented, and the parameters can be treated as separable and independent over the temperature and pressure range studied. We demonstrate the relationship between the UAT and the common Dubinin analysis, which was not previously noted.

KEYWORDS: Adsorption, Gas Separations, Gas Storage, Porous Coordination Polymers

ABBREVIATIONS: GO: Gate-opening; GC; Gate-closing; MOF: Metal-organic framework; Pc: Critical pressure; Tc: Critical Temperature; UAT: Universal Adsorption Theory

GRAPHICAL ABSTRACT

INTRODUCTION

Metal-organic frameworks (MOFs) are promising for a variety of applications including adsorptive gas storage, gas separations, catalysis, and sensing and detection devices.¹ A subclass of MOFs, subsequently referred to as Gate-Opening (GO)-MOFs, have flexible structures that change shape to accommodate guest molecules.² GO-MOFs have unique adsorption isotherms, which are typified by a sharp discontinuity at a pressure associated with GO (P_{GO}), giving rise to an unusual isotherm with a pronounced S-shape. A similar discontinuity is observed in the desorption branch at a ‘gate closing’ pressure (P_{GC}). The adsorption and desorption branches show considerable hysteresis, such that $P_{GO} > P_{GC}$. Although this unusual S-shaped isotherm is certainly distinctive in the field of adsorption, isotherm discontinuities alone are insufficient evidence to demonstrate structural transformations, as other conditions (e.g. capillary condensation without structural change) also may exhibit such features. Slow diffusion into the material, accompanied by insufficient experimental time, may also lead to similar S-shaped isotherms,³ and molecular sieving effects have been invoked to explain hysteretic adsorption of H_2 at 77K to $Ni_2(bipy)_3(NO_3)_4$.⁴ In certain cases, significant adsorption below P_{GO} may occur, given sufficient induction time.⁵ Despite these alternative explanations, structural transformations in GO-MOFs have been confirmed by *in situ* characterization techniques, including powder X-ray diffraction (XRD),⁶ neutron diffraction⁷, and spectroscopy.⁸⁻¹¹ The structural transformations have been attributed to specific chemical interactions (e.g. H-bonding,¹² π -stacking interactions with polar molecules²) that are disrupted by the adsorbate, leading to subsequent changes in channel or pore or window sizes.^{2, 4, 12-13} In this paper, we

focus our analysis on the P and T of the GO transition and the maximum capacity of the adsorption branch (which will converge with the desorption branch at sufficient pressure).

There are multiple emerging theoretical explanations of the thermodynamics of the GO phenomenon. Early work described adsorption to GO-MOFs as the superposition of the isotherms of a first ('closed') structure and a second ('open') structure.² First principle considerations of structural changes associated with an 'imbibition-transition' for the model graphene-silica slit pore system found pore dilation to be a consequence of Newton's third law.¹⁴ To generalize to any size pore, structural changes and/or pore expansion or contraction occur when the change leads to minimization of the free energy of the system. Specifically, insertion of an adsorbed film into the graphene-silica slit pore will occur when the energetics of film formation exceed the energy cost of expanding the slit.¹⁴⁻¹⁵ At low pressure, low film coverage is insufficient to drive pore expansion, but at higher pressure, there is enough net free energy incentive to adsorb additional molecules to drive the pore expansion. The pore expansion is proportional to gas density, a force imparted to the pore by the adsorbate, and inversely related to compressibility modulus (or spring constant) of the material. This treatment suggests that pore expansion/contraction is a universal phenomenon, although it will be particularly pronounced in materials that have a small spring constant due to weak cohesive interactions and/or variable conformations. This theory also suggests that a force imparted by a particular gas-surface interaction can be useful in predicting behavior of all gases. Similarly, Neimark et al. argued that breathing transitions are a response to the development of a threshold adsorption stress within pores which corresponds to the external pressure that triggers the transition.¹⁶⁻¹⁹

Simulations of the GO process include the statistical osmotic ensemble, which extends the Grand Canonical ensemble to account for the possibility of a flexible host by varying the unit cell.¹⁹⁻²¹

This treatment assumes energies of adsorption and the host configuration as separable additive variables (which is common). Application of the osmotic potential ensemble has relied on fits of experimental isotherm data to yield host free interaction energies of expansion for the structure, i.e. the material “spring constant”.²⁰ Experimental data at the distinct P_{GO} transition point is used to account for the free energy of GO, as it is presumed the open and closed structures have equal free energies at this condition. To apply this model, adsorption to the rigid host (had it not opened) is extrapolated from the ‘flat’ portion of the isotherm (i.e. the lower portion of the ‘S’-shaped isotherm). Alternatively, the host’s free energy of interaction with the adsorbate can be calculated from molecular dynamics or Monte Carlo simulations of the GO process.²²⁻²⁴

Molecular-level first principle simulations of adsorption to GO-MOFs come with considerable computational expense, however, particularly when/if structural dynamics are included. It is often desirable to perform a preliminary estimate of adsorption behavior to down-select materials that warrant a detailed study, and furthermore, to have a reliable means to extrapolate from the modeling study (and/or experimental isotherm) of one adsorbate to another.

A unifying theory that would include predictive behavior of the effects of T , P , and adsorbate on both the capacity and the GO transition point of GO-MOFs would provide insight into the gas-surface potential and the mechanism for adsorption-induced structural transformations. From a practical standpoint, predictive relationships would greatly facilitate optimization of adsorption conditions, as well as provide a means to design a system for a given gas separation. A means to extend the molecular-level thermodynamic theories (described in the preceding paragraph) to

predict experimental trends, and extrapolate from one gas measurement to another, has not yet emerged, to the best of our knowledge. An alternative approach is to apply relationships that are grounded in theory, but tend to be more empirical. For example, Yamakazi et al.²⁵ attempted to correlate extensive experimental data by use of the Dubinin-type analysis. Discussed further below, this treatment relates the ‘adsorption potential’ (i.e. chemical potential of the adsorbate) to a characteristic adsorption curve for a solid, generally over a limited temperature range. In the development below, we show how the Dubinin-type analysis is quite similar to the universal adsorption theory (UAT) previously observed by Quinn to describe adsorption of six gases to four different activated carbons.²⁶ The convergence of adsorption isotherms shown in Quinn’s treatment suggests that when thermodynamic variables are scaled appropriately, the guest-host surface potential exerted is possibly the same irrespective of the guest.²⁷⁻²⁸ This is the same principle applied in the Dubinin-type analysis; also the analogy between the two theories has not previously been noted. Our previous development of the UAT²⁷ (described further in the theory section below) extends the law of corresponding states to consideration of excess adsorption, demonstrating a novel approach to arrive at the Dubinin approach. Although MOFs and GO-MOF have a significantly more complex and non-uniform surface potential than the activated carbons studied by Quinn, previous adsorption data for GO-MOFs from our laboratory hint towards the applicability of the UAT to these more complex materials. Specifically, adsorption capacities of N₂ and Ar for adsorption to [Zn₂(bpdc)₂(bpee)]·2DMF (bpdc = biphenyldicarboxylate, bpee = 1,2-bipyridylethene; DMF = N,N-dimethyl formamide) converged at their boiling points, which corresponded to a T_R of ~0.6.³ Here, we further explore the applicability of the UAT to adsorption to Cu(dhbc)₂(4,4’-bpy) [H₂dhbc=2,5-dihydroxybenzoic acid, bpy=bipyridine], subsequently abbreviated as Cu(db), which is perhaps the most

extensively studied GO-MOF, including published experimental adsorption isotherms by Kitagawa et al.² and Yamakazi et al.²⁵ We extend this published data set to include additional high- and low-pressure data. Although the UAT is approximate, our overall goal is to develop predictive relationships to explain key features of the adsorption isotherms and adsorption energetics, which are applicable to a multitude of adsorbates, temperatures, and pressures. Unlike previous treatment with limited temperature- and pressure- applicability, our results suggest the existence of a *universal gate-opening adsorption behavior* that implies scaling behavior of the corresponding force imparted by the gas-surface interaction.

METHODS

Materials

Cu(db) (illustrated in Figure 1) was synthesized by a modified procedure from previously reported synthesis.² A diethyl ether solution (20ml) containing 4-4'bpy (156.7mg, 1mmol) is poured carefully on the top of an aqueous solution (20ml) containing a mixture of Cu(NO₃)·3H₂O (240.8mg, 1mmol) and 2,5-dihydroxybenzoic acid (308.2mg, 2mmol). The glass tube containing both the layered solutions was then kept in room temperature undisturbed. After 5 days, plate-like green crystals were formed between the two layered solutions. The crystals were then collected by filtration and washing with water and dried in air. The samples were structurally characterized by powder X-ray diffraction technique and their thermal properties were evaluated by thermogravimetric analysis (see Figures S1 and S2, Supporting Information).

Figure 1. Crystal structure of the as-synthesized Cu(dhbc)₂(4,4'-bpy), a.k.a. Cu(db). a) 1D chain structure constructed by Cu^{II}, 4,4'-bpy, and dhbc along the *b* axis (Cu, cyan; O, red; C, gray; N, blue). b) 2D layer structure in the *ab* plane. c) 3D π -stacked pillared layer structure of Cu(db). Solvent molecules are omitted for clarity.

Experimental

Low pressure adsorption measurements ($P \leq 1$ bar) were performed for N₂ and Ar at 77 and 87K on a commercial volumetric adsorption unit (ASAP 2020, Micromeritics). After sample degassing and evolution of the synthesis solvent, typical sample mass used on this unit was ~50 mg. Moderate pressure ($P < 20$ bar) H₂ (at 77K and 87K) and N₂ (at 195 K) measurements were

performed on a high-pressure gravimetric unit (Hiden IGA-003) with ~80 mg of dry sample. The operation of this equipment has been described in detail in previous reports, and the estimated uncertainty of measurement is <1 cc/g at 20 bars.²⁹ Based upon our experience of the time necessary to meet a mass stability criteria of <10⁻⁴ µg/min, a minimum of 1 hour and a maximum of 4 hours was used for each adsorption point. (The IGA software moves to the next adsorption pressure if the rate data approaches a limiting value within a specific tolerance after the minimum time.) High pressure adsorption measurements (P<90 bar) of N₂ (273 K and 298 K) were performed on a differential volumetric adsorption unit, using Method M-BC described in our previous report.³⁰ Method M-BC references a helium blank measurement to calibrate the unit free space. The estimated uncertainty was < 2 cc/g for 300 mg sample.

Previously published adsorption data by Kitagawa et al.² and Yamakazi et al.²⁵ was digitized to extend the adsorption data considered. In brief, Kitagawa et al.² utilizes a moderate pressure gravimetric unit, whereas Yamakazi et al.²⁵ used a low pressure (P<1bar) volumetric unit. Not all low-pressure isotherms from Yamakazi et al. were collected at pressures sufficient for saturation, and data that was not close to a plateau value has been excluded; data which we estimate have reached > ~90% of the plateau value is so noted below. Throughout the paper, the phrase “complete data set” refers to the combined data from all three sources. For isotherms that lack a sharp GO transition, the PGO is selected to be the lowest pressure where a significant increase in the isotherm is noted.

THEORY

Universal Adsorption Theory for Consideration of Excess Adsorption Isotherms

The law of corresponding states (LOCS) expresses the bulk properties of gases as a nearly universal function when ‘scaled’ via their values at the critical point, viz:

$$n_R = g(P_R, T_R) \quad (1)$$

Where g is the universal function, and n_R , P_R , and T_R , are the bulk density, pressure, and temperature of the gas, scaled by their values at the critical point, i.e. $n_R = n/n_c$, $P_R = P/P_c$, $T_R = T/T_c$. The origin of the remarkable convergence at comparable reduced conditions can be traced to the near universality of the *functional form* of the interparticle interaction, $U(\mathbf{r})$:

$$U(r) = \varepsilon U^*\left(\frac{r}{\sigma}\right) \quad (2)$$

The universality of the function U^* arises by scaling the distance ($\mathbf{r}$) and energy (U) by the appropriate characteristic parameters, namely the hard-core diameter (σ) and well depth (ε), respectively. Insofar as $U^*(r)$ is universal, it follows that the critical properties (T_c, P_c, n_c) are universal constants, when scaled appropriately by ε and σ (i.e. by ε/σ^3 and σ^3 respectively).

Thus, the LOCS dictates that the one energy scale is necessarily (strictly) proportional to T_c (i.e. $\varepsilon/13T_c \text{ K}^{31-32}$). These conclusions are rigorously valid when both quantum effects and many-body interactions are negligible. When this universal reduced interaction is assumed, one finds that the various thermodynamic energies (i.e. chemical potential, enthalpy, etc.) converge into universal functions when considered at similar reduced conditions. This is an underlying premise of the UAT: All energies converge when considered at comparable reduced conditions.

Additional length and energy scales associated with adsorption preclude a rigorous derivation of a similar expression for corresponding states behavior in complex porous media. One might

hypothesize, nevertheless, an analogous expression to describe excess adsorption (N_{ex}) in porous media:

$$N_{ex} = f(P_R, T_R, \epsilon_{GS}) \quad (3)$$

Where f is the universal adsorption function, and ϵ_{GS} is the gas-surface well depth. ϵ_{GS} is related to the intermolecular potential (ϑ of Equation 2 via a geometric mean (i.e., $\epsilon_{GS} = (\epsilon \epsilon_{solid})^{1/2}$),³¹⁻³² where ϵ_{solid} is the characteristic energy of the solid. Thus, for fixed adsorbent, $\epsilon_{GS} \sim \epsilon^{1/2} \sim T_c^{-1/2}$. The proposed universal adsorption theory (UAT) for a given adsorbent reduces to:

$$N_{ex} = f(P_R, T_R) \quad (4)$$

The UAT implies isotherms of multiple gases at multiple temperatures and pressures should converge when plotted at reduced conditions. This was exactly that observed by Quinn²⁶ for adsorption of five ‘classical’ gases to four different activated carbons, despite considerable variations in pore structure. Hydrogen did not follow the trends for the other five gases, and the calculations of Kim et al. showed the deviation could be attributed to quantum effects and to an unusually large hydrogen-surface interaction²⁷ similar to the shortcomings seen for the LOCS to describe bulk properties.

Universal Adsorption Theory to Describe Phase Transitions such as Gate Opening

The Clausius-Clapeyron equation has been used^{25, 33} to calculate the molar enthalpy of GO (ΔH_{GO}) from the $P_{GO}(T)$ behavior of the adsorption branch:

$$\frac{\partial(\ln P_{GO})}{\partial(1/T)} = \frac{-\Delta H_{GO}}{R} \quad (5)$$

A perfectly analogous relation for two-dimensional monolayer films can be derived (See Supporting Information). We may argue heuristically that films, in general, are intermediate

between two- and three-dimensional, and since there are Clausius-Clapeyron relations in both limits, it seems plausible that such a relation is applicable more generally to describe any film transition. For UAT consideration, Equation (5) is divided by the energy-scaling parameter T_C :

$$\frac{\partial(\ln P_{GO}^R)}{\partial(1/T_R)} = \frac{-\Delta H_{GO}}{RT_C} = \frac{-\Delta H_{GO}^R}{R} \quad (6)$$

Where the latter expression defines reduced enthalpy as the energy term scaled by T_C .

Experimental Determination of Heat of Expansion and Validation of the UAT

Previously,²⁰ the heat of gate-opening (ΔH_{GO}) has been assumed to be a separable linear combination of heat of adsorption (ΔH_{ADS}) and heat of structural expansion (ΔH_{EXP}):

$$\Delta H_{GO} = \Delta H_{ADS} + \Delta H_{EXP} \quad (7)$$

As developed above, for a given host, the heat of adsorption is approximately proportional to T_C when corresponding states behavior applies. Inserting a pseudo proportionality constant (α) leads to:

$$\Delta H_{GO} = \alpha T_C + \Delta H_{EXP} \quad (8)$$

Or in terms of reduced enthalpies:

$$\Delta H_{GO}^R = \alpha + \Delta H_{EXP}^R \quad (9)$$

As developed above, an underlying premise of the UAT is that various thermodynamic energies scaled by the reduced temperature are universal for multiple gases. Insofar as this universal behavior applies, convergence of ΔH_{GO}^R for multiple gases, temperatures and pressures is validation of the UAT. Applicability of the UAT (i.e. convergence of ΔH_{GO}^R) then implies the reduced enthalpy of expansion (ΔH_{EXP}^R , Equation 9) also converges at reduced conditions, as α 's

also a constant for a given host. As the heat of expansion, ΔH_{EXP} , is generally considered to be the ‘spring constant’ of the host, independent of guest, the equality of Equation 9 is valid only if different guests expand the structure by different amounts. Subject to the UAT axiom and the separation of adsorption and expansion energies, Equation 9 thus suggests a continuum in the degree of structural expansion rather than a fixed integral number of structural configurations.

UAT versus Dubinin-Polyani analysis

Although the development of the UAT above is semi-empirical, it is quite notable that assertion of a universal function (i.e. Equation 4) is the same basic premise of the Dubinin theory³⁴ which is an extension of the earlier work of Polyani,³⁵ with the Dubinin theory used extensively to describe physisorption, particularly to activated carbons. Interestingly, the tie between the UAT and the Dubinin analysis has not been previously noted, despite application of both theories to activated carbons. Although numerous other models exist to describe adsorption, a Dubinin-type analysis was used previously in consideration of a subset of the data considered here,²⁵ and we thus elaborate on the similarities and differences of this model to the UAT. The key difference is that the UAT utilizes the straightforward and readily available parameter T_C as a measure of the characteristic energy of interaction between gas and surface, whereas the characteristic energy scaling parameter of the Dubinin theory goes unspecified, although many candidates have been proposed (such as the experimentally determined initial heat of adsorption,³⁶ the heat of immersion in the bulk liquid,³⁷ the polarizability, molar volume, and/or molecular parachor³⁸). Scaling of the adsorption isotherms in the UAT allows for comparison (and convergence) at reduced conditions, which is not always a part of the Dubinin analysis. Furthermore, the Dubinin-Polyani theory utilizes an exponential function to relate excess adsorption to a

‘characteristic energy’,³⁵ which can be derived from a generalized Boltzmann principle of adsorption (see Supporting Information for derivation). The final exponential dependence is:

$$\int e^{-V(\vec{r})/kT} d\vec{r} = A \sqrt{\frac{2\pi}{T}} e^{-E/kT} \quad (10)$$

Where $\vec{r}$ is the vector describing the distance between the adsorbate and the surface, $V(\vec{r})$ is the surface holding potential, E is the characteristic energy for an equipotential surface, and A is integration constant. The prefactor yields just a logarithmic T -dependent correction to the chemical potential. To render the Dubinin analysis analogous to the UAT, we have scaled the “adsorption potential” of the Dubinin analysis (μ by T_C to lead to a reduced adsorption potential:

$$\mu_R = \frac{\mu}{T_C} = -R \frac{T}{T_C} \ln \left(\frac{P}{P_C} \right) = RT_R \ln P_R \quad (11)$$

Our adapted reduced-Dubinin approach uses P_C as the reference pressure, rather than an extrapolated saturated vapor pressure ($P_o = P_C(T/T_C)^2$), which was used by Yamazaki et al.²⁵ in a similar analysis. We note also that previous attempts to use T_C as a scaling parameter in the Dubinin analysis found that it holds for light gases with $T_C < 390\text{K}$,³⁸ which is the case for gases considered here. One should note the sign convention we are using leads to population of highly favorable sites at high adsorption potential (i.e. low pressure and/or low temperature). In our analysis, we have used effective Lennard-Jones radii³¹ to calculate the molecular volumes of the adsorbates.

RESULTS AND DISCUSSION

Effect of Reduced Conditions on Isotherms and Adsorption Capacity

Previously, Kitaura et al. published hysteretic adsorption isotherms of four gases (N_2 , O_2 , CH_4 and CO_2) to Cu(db) at 298K and pressures up to 100 atm.² These four isotherms are represented in Figure 2 at reduced conditions (blue data). Additional N_2 adsorption isotherms for N_2 at 298, 273, 195, 87 and 77K; and Ar at 87K have been added to extend the temperature range (green data, Figure 2). The common N_2 298K isotherm is fairly consistent, despite differences in methodology, equipment, and equilibration times. Multiple steps in the adsorption isotherm may be indicative of a partially opened structure, suggesting there is not a simple and immediate transition from the open to the closed state, which is discussed elsewhere.⁵

A general correlation between T_R and adsorption capacity emerges when the high-pressure data is plotted at reduced conditions. The correlation will become apparent in subsequent paragraphs, but first let us consider the unprocessed data. Adsorption capacity increases as T_R is decreased (Figure 2), as expected. Perhaps unexpectedly, there are also apparent groupings in capacity with T_R , independent of adsorbate: at $T_R \sim 2$, N_2 and O_2 converge at ~ 60 cc/g (see isotherms labeled 1.9, 2.2, and 2.4, Figure 2); at $T_R = 1.6$, N_2 and CH_4 converge at ~ 80 cc/g, close to the value of CO_2 at $T_R = 0.98$. Similar groupings are found in the data of Yamazaki et al.⁴³ when considered at similar reduced conditions (Figure S4, Supporting Information). The groupings in capacity at fixed T_R are generally consistent with the UAT, i.e. the adsorption isotherms should converge when considered at comparable reduced conditions. Variations in the shape of the isotherm,

particularly at the GO discontinuity, are discussed in the next section. At low temperature and comparable reduced conditions, H_2 significantly exceeds the capacity of the other gases (i.e. $T_R=2.32$, see Figure S3, Supporting Information), as observed previously²⁶ and explained elsewhere.²⁷ For this reason, H_2 is not considered further in the remainder of this paper.

Figure 2: Excess adsorption (closed) and desorption (open symbols) isotherms considered with reduced pressure and temperature show grouping of adsorption capacities. Blue isotherms are at 298K for N_2 (diamonds, $T_R=2.4$), O_2 (circles), CH_4 (squares), and CO_2 (triangles) are from Ref. ², reconsidered at reduced conditions. Green isotherms are measured in our laboratory for N_2 at a T_R of 2.4, 2.2, 1.6, 0.7, 0.6 (i.e. 298, 273, 195, 87, 77 K) and Ar (squares with cross) at $T_R = 0.58$ ($T=87K$). The low-temperature data ($T_R<0.7$) has been included in this figure by using a secondary (expanded) x-axis for reduced pressure and the same y-axis so that the subcritical measurements could be considered on the same graph

to emphasize the effect of reduced conditions. These subcritical measurements showed no discernible isotherm steps or adsorption-desorption hysteresis. The data in this figure, combined with those in Yamazaki et al.⁴³ comprise the ‘combined data set’ analyzed in this paper.

To overcome inherent T_R scatter in consideration of the grouping of adsorption capacity for the full data set (Figure 2 plus the data from Yamazaki et al.⁴³), we considered trends in the maximum excess adsorption capacity (at the highest pressure of measurement) versus reduced temperature. Although a number of ways to plot the data were considered (see Figure S5, Supporting Information), the natural log versus inverse reduced temperature provided the least scatter, which follows the generalized Boltzmann principle of adsorption (i.e. Equation 10). With the exception of a few outliers (discussed in the next paragraph), the excess adsorption capacity converges for multiple adsorbates at a fixed reduced temperature, consistent with the UAT (Figure 3).

Outliers (i.e. > 20% deviation) from the trend include Xe, C₂H₄, and N₂O. These gases were not considered in Quinn’s original development of the UAT. CO₂ is an outlier for low temperature and pressure isotherms (i.e. 252 K < T < 273K, from Ref.²⁵), but follows the trend for the 298 K, 50 bar measurement (from Ref.²). The large pressure jump (despite a modest increase in temperature) suggests this may be due to differences in experimental protocols. The other outliers tend to be large (e.g. Xe and C₂H₄) and/or polar (N₂O, CO₂), suggesting (perhaps) packing effects may limit coverage. A more likely explanation relates to the heat of adsorption, however, as the outliers had the highest heats of adsorption of all the gases (Figure 3, Ref.²⁵), and the largest variation of ΔH_{GO} with coverage (Figure 2, Ref.²⁵). The use of T_C as a single

energy scaling parameter does not reflect the latter, and the effect is particularly pronounced due to the former. A decreased ‘effective’ T_C would shift the outliers to the left in Figure 3. Thus, use of T_C as a scaling parameter is applicable over the range of the isotherm in which the characteristic energy of adsorption has not deviated from that of low-coverage. Similarly, one should not expect the UAT to extend to dissimilar surfaces, i.e. the assumptions in the derivation of the UAT above assume a fixed characteristic energy of the solid.

Figure 3: The maximum excess adsorption capacity (at the highest pressure measured) trended with $1/T_R$ for all three data sets. Legends: Green symbols are data from our laboratory, blue from Ref. ², black from Ref. ²⁵ that have plateaued, while red symbols are from Ref. ²⁵ that are estimated to have reached $>\sim 90\%$ of the plateau value (by 1 bar). Outliers (circled) have high heats of adsorption that is coverage dependent (see text).

Yamakazi et al.²⁵ also looked to find trends in maximum excess adsorption capacity for their lowest temperature measurements, which is a large subset of this data (i.e. highest $1/T_R$ black data, Figure 3). However, they did not find consistent trends between excess adsorption capacity and adsorbate, which seems tied to an implied assumption that adsorption temperature is not

relevant when considering only the lowest temperature subset of the data. Clearly, Figure 3 shows that adsorption temperature cannot be ignored in assessing trends of adsorption capacity, and each gas does not have a unique maximum excess capacity, which was the implied assumption in this previous consideration. The relatively smooth transition of maximum excess capacity versus $1/T_R$ (Fig 4) for multiple adsorbates seems to imply that either (a) there is not a unique volume for the open structure and the degree of pore expansion is a function of temperature, or (b) the pores open to a fixed structure and become partially filled, and the degree of filling is temperature-dependent. The latter statement is inconsistent with development of Equation 9 which incorporates the UAT and treats the energies of adsorption and expansion as separable. Validation of the UAT for this data set thus implies statement (a) is true. Future work, including either structural measurements and/or adsorption tests with rigid materials (e.g. zeolites), would provide a more conclusive test of these two possible explanations.

Dubinin Analysis versus Universal Adsorption Theory

Yamakazi et al. proposed the Dubinin adsorption potential theory to generalize the data to “characteristic curves”, by transforming the adsorption isotherms to adsorbed volume versus adsorption [chemical] potential.²⁵ Without an energy scaling parameter, Yamakazi et al.’s characteristic curves coincided for a narrow temperature (see boxes, Figure 4a) and pressure ($P < 1\text{bar}$) range for a given adsorbate. However, there was no convergence for multiple adsorbates (see Figure 4a, and Figure 7 of Ref. ²⁵), and the temperature and pressure range was quite limited relative to the full data set considered here (boxes, Figure 4a). Although the curves were qualitatively similar, there were no notable trends in either the adsorption potential of the sharp

Scaling of Dubinin-type curves by an appropriate energy parameter can generalize the curves into a master curve, as noted by Yamazaki et al.²⁵ and others.³⁸ The UAT suggests that use of the critical temperature will provide the desired characteristic energy scaling parameter, with critical pressure as the reference pressure. Although the proportionality between T_C and the initial heat of adsorption (as proposed by Ding et al.³⁶) implies this is equivalent treatment, use of T_C requires no experimental measurement. Consideration of the reduced adsorption potential (Equation 11) provides convergence over a considerably expanded temperature and pressure range (Figure 4b), relative to the same data set considered at absolute conditions (Figure 4a). Although not fully coincident, the characteristic curves consistently trend with the T_R of measurement. Below and close to T_C , there is considerable convergence of the curves for the various adsorbates, temperatures, and pressures. The convergence demonstrates the applicability of the UAT to provide the critical energy scaling parameter, T_C , and suggests the forces that lead to the abrupt change in capacity are nearly the same for the multiple gases below T_C . Above T_R of ~ 1.6 , the curves diverge but continue to trend with T_R .

Energetics of Adsorption at UAT Reduced Conditions

The Clausius-Clapeyron equation has been used extensively for films adsorbed on porous and non-porous adsorbents to determine the isosteric heat of the film as a function of coverage or sorbent loading. For GO-MOFs,^{25, 33} this has been extended to relationships between P_{GO} and T for individual gases (i.e. Equation 5). . A rationale for applying the Clausius-Clapeyron relation to adsorbed films is provided in the Supporting Information. Extending the Clausius-Clapeyron

analysis to the complete data set, shows that each gas follows this relationship over the extended temperature and pressure range (Figure 5a), demonstrating that ΔH_{GO} is not a strong function of temperature, as one would expect. Values for ΔH_{GO} for the expanded data set are similar to those reported previously²⁵ (Table S1 in Supporting Information). Prediction of P_{GO} from T (or vice versa) will require individual experimental measurements of each gas, as no trends in ΔH_{GO} with adsorbate emerge with this method.

Use of the UAT to calculate the heats of GO at reduced conditions for all nine gases at reduced conditions leads to a single value of ΔH_{GO}^R of 0.075 kJ/mol/K (Equation 6, Figure 5b) with an R^2 of 0.792, which seems to be a reasonable fit given three sources of data and inherent difference in methodology. The largest divergence in this data occurs at $T_R \sim 1.0$ for N_2 and O_2 at 137 K (enlarged in Figure 5b')--returning to the Yamazaki et al. paper, the N_2 and O_2 isotherms at these (generally low) temperatures lack an abrupt GO transition, and thus in hindsight it is not surprising they would deviate from trends concerning the GO transition. Consideration of the individually calculated heats of GO versus T_c shows good linearity ($R^2=0.815$) for all nine gases (Equation 8, Figure 5c). The convergence of the data demonstrates that the heat of adsorption at reduced conditions is relatively independent of the adsorbate, which is the underlying premise of the UAT as explained by Kim et al.²⁷ and discussed in the theory section above. Thus, the convergence of ΔH_{GO}^R at comparable reduced conditions validates the extension of UAT to flexible structures such as Cu(db).

Consideration of the individual ΔH_{GO} values versus T_c (Figure 5c) leads to a ΔH_{EXP} of 2.4 kJ/mol and an α of 0.079 kJ/mol/K (Equation 8). The goodness of fit of the linear trend line ($R^2=0.815$) supports the applicability of this simple treatment. The α and ΔH_{GO}^R terms differ by only ~5%,

suggesting ΔH_{EXP}^R is small for Cu(db) (see Equation 9). Elsewhere, using an alternate methodology to fit both adsorption and desorption isotherms to the osmotic potential,²⁰ the free energy of expansion was determined to be 4 kJ/mol (± 0.5 kJ/mol) using the 298K data subset, but with a quite large uncertainty and spread for different adsorbates (i.e. reported values were 3-4.5 kJ/mol for N₂; 3.6-5.1 kJ/mol for CH₄; 3.4-4.3 kJ/mol for O₂; < 6 kJ/mol for CO₂).² The large uncertainty in this previous report was attributed to the inability to pinpoint the P_{GO} (and P_{GC}) transition pressures, presumably for CH₄ and CO₂ for which the adsorption-desorption hysteresis was quite minor (see data labeled ‘0.98’ and ‘1.6’ in Figure 2). The increased size of the data set considered here perhaps helps to minimize this uncertainty, and only the adsorption branch is considered for reasons mentioned above. Furthermore, our method alleviates fitting the adsorption isotherms to the Langmuir model (or equivalent), which introduces additional uncertainty and assumptions. The authors of the prior analysis noted a striking convergence for the calculated free energies found for the four gases, which is perhaps less striking when the broad range of the reported values is considered. The convergence of the expanded data set using the UAT shows better convergence, and the origin of the convergence is now clear: energies should converge when considered at appropriate reduced conditions. The analysis is also considerably simpler than other proposed methods, such as Rietveld refinement of XRD patterns, molecular modeling,²⁰ and/or an additional experiment using thermogravimetry and calorimetry.⁴¹ Although the UAT will not replace the other complex methods, it allows for a preliminary calculation/estimate with a limited number of experimental isotherms to be used to determine a reduced ΔH_{GO}^R , which can be used to extrapolate a $P_{GO}(T)$ relationship for other gases.

Figure 5: Clausius-Clapeyron analysis of the GO conditions in terms of (a) absolute temperature and pressure and (b) reduced conditions, which lead to (c) a linear trend of heat of gate opening with critical temperature, which allows calculation of the heat of expansion. Symbols and color-coding are defined in Figure 3. The lower right figure is an enlargement of the (b) in the region shown, outliers to the general trend (shown in gray) lacked a sharp GO transition, with gases and temperatures (in K) indicated.

Conclusions

Understanding the thermodynamics of GO can provide a means to understand trends in uptake for different gases and the temperature-dependence of P_{GO} . Adsorption capacities for various gases at different temperatures and pressures provide insights into the gas-surface potential and the mechanism for interaction. To date, no methodology has emerged to predict the capacity of adsorption to GO-MOFs, and proposed means to predict P_{GO} from T (or vice versa) still require measurements of the same adsorbate at other conditions. Here, we consider experimental adsorption data from multiple laboratories in the context of the approximate UAT, in which temperature and pressure of adsorption are reduced by the critical values. Trends in adsorption capacity are found for classical gas molecules when considered versus reduced temperature; outliers include H_2 (which has been previously attributed to quantum effects²⁷), and molecules that seem to have particularly strong interactions with the structure (i.e. large and/or polar molecules). Despite the outliers and the approximate nature of the UAT, plotting both saturation capacity and Dubinin-type ‘characteristic curves’ via the UAT reduced analysis provides a broader temperature- and pressure- convergence than previous analysis of experimental trends. The trends are, in fact, surprising in view of the chemical heterogeneity of the Cu(db), combined with the complexities brought about by the GO process, relative to the original application of the UAT theory to activated carbons.²⁶ The UAT is a useful “lens” to consider the shape of the adsorption isotherm, the P_{GO} , and ultimate capacities of multiple gases to the same adsorbent at multiple temperature and pressures. An extension of the Clausius-Clapeyron analysis to adsorption in porous media provides a means to obtain both the heat of adsorption and the heat of expansion of the GO structure, confirms that these parameters can be treated as separable, and provides a means to extrapolate the $P_{GO}(T)$ relationship from one adsorbate to another. The

influence adsorption temperature has on adsorption capacity and P_{GO} will determine whether GO-MOFs are viable for gas separations and/or storage at desirable operating conditions.

ACKNOWLEDGEMENTS

This work was supported, in part, by the U.S. Department of Energy, Energy Efficiency and Renewable Energy program, Award DE-FG36-08GO18139. This paper has benefited from reviewers' comments, for which we are grateful.

Supporting Information Available:

Supporting Information Available: PXRD, TGA, and H₂ isotherms for Cu(db). Derivations of equations. Grouping in capacities at similar reduced conditions. Plots of capacities with trends in T and T_R. Calculation of heats of adsorption. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References:

1. Férey, G. Hybrid porous solids: past, present, future. *Chem. Soc. Rev.* **2008**, *37*, 191-214.
2. Kitaura, R.; Seki, K.; Akiyama, G.; Kitagawa, S. Porous coordination-polymer crystals with gated channels specific for supercritical gases. *Angew Chem Int Ed Engl* **2003**, *42*, 428-31.
3. Sircar, S.; Wu, H.; Li, J.; Lueking, A. D. Effect of time, temperature, and kinetics on the hysteretic adsorption-desorption of H₂, Ar, and N₂ in the metal-organic framework Zn₂(bpdca)(bpee). *Langmuir : the ACS journal of surfaces and colloids* **2011**, *27*, 14169-79.
4. Zhao, X.; Xiao, B.; Fletcher, A. J.; Thomas, K. M.; Bradshaw, D.; Rosseinsky, M. J. Hysteretic adsorption and desorption of hydrogen by nanoporous metal-organic frameworks. *Science* **2004**, *306*, 1012-5.
5. Sircar, S.; Lueking, A. D. A Growth-Limited Shrinking Core Model to Describe Adsorption Rates in Gate-Opening Metal Organic Frameworks. *Langmuir : the ACS journal of surfaces and colloids* **Submitted 2014**.
6. Kondo, A.; Noguchi, H.; Ohnishi, S.; Kajiro, H.; Tohdoh, A.; Hattori, Y.; Xu, W. C.; Tanaka, H.; Kanoh, H.; Kaneko, K. Novel expansion/shrinkage modulation of 2D layered MOF triggered by clathrate formation with CO₂ molecules. *Nano Lett* **2006**, *6*, 2581-2584.

7. Liu, Y.; Her, J. H.; Dailly, A.; Ramirez-Cuesta, A. J.; Neumann, D. A.; Brown, C. M. Reversible structural transition in MIL-53 with large temperature hysteresis. *Journal of the American Chemical Society* **2008**, *130*, 11813-8.
8. Ferey, G.; Latroche, M.; Serre, C.; Millange, F.; Loiseau, T.; Percheron-Guegan, A. Hydrogen adsorption in the nanoporous metal-benzenedicarboxylate $M(OH)(O_2C-C_6H_4-CO_2)$ ($M = Al^{3+}, Cr^{3+}$), MIL-53. *Chem. Commun.* **2003**, 2976-2977.
9. Serre, C.; Millange, F.; Thouvenot, C.; Nogues, M.; Marsolier, G.; Louer, D.; Ferey, G. Very large breathing effect in the first nanoporous chromium(III)-based solids: MIL-53 or $Cr-III(OH)center dot\{O_2C-C_6H_4-CO_2\}center dot\{HO_2C-C_6H_4-CO_2H\}(x)center dot H_2O$. *Journal of the American Chemical Society* **2002**, *124*, 13519-13526.
10. Mendt, M.; Jee, B.; Stock, N.; Ahnfeldt, T.; Hartmann, M.; Himsl, D.; Poppl, A. Structural Phase Transitions and Thermal Hysteresis in the Metal–Organic Framework Compound MIL-53 As Studied by Electron Spin Resonance Spectroscopy. *The Journal of Physical Chemistry C* **2010**, *114*, 19443-19451.
11. Bourrelly, S.; Moulin, B.; Rivera, A.; Maurin, G.; Devautour-Vinot, S.; Serre, C.; Devic, T.; Horcajada, P.; Vimont, A.; Clet, G.; Daturi, M.; Lavalley, J. C.; Loera-Serna, S.; Denoyel, R.; Llewellyn, P. L.; Ferey, G. Explanation of the adsorption of polar vapors in the highly flexible metal organic framework MIL-53(Cr). *Journal of the American Chemical Society* **2010**, *132*, 9488-98.
12. Li, D.; Kaneko, K. Hydrogen bond-regulated microporous nature of copper complex-assembled microcrystals. *Chem Phys Lett* **2001**, *335*, 50-56.
13. Culp, J. T.; Smith, M. R.; Bittner, E.; Bockrath, B. Hysteresis in the physisorption of CO_2 and N_2 in a flexible pillared layer nickel cyanide. *Journal of the American Chemical Society* **2008**, *130*, 12427-34.
14. Noa, K. E.; Lueking, A. D.; Cole, M. W. Imbibition Transition: Gas Intercalation Between Graphene and a Solid Surface. *J Low Temp Phys* **2011**, *163*, 26-33.
15. Ancilotto, F.; Cole, M. W.; Grosman, A.; Hernandez, E. S.; Toigo, F. Expansion or Contraction of Slit Pores Due to Gas Uptake. *J Low Temp Phys* **2011**, *163*, 284-301.
16. Neimark, A. V.; Coudert, F.-X.; Boutin, A.; Fuchs, A. H. Stress-Based Model for the Breathing of Metal–Organic Frameworks. *The Journal of Physical Chemistry Letters* **2009**, *1*, 445-449.
17. Neimark, A. V.; Coudert, F. X.; Triguero, C.; Boutin, A.; Fuchs, A. H.; Beurroies, I.; Denoyel, R. Structural transitions in MIL-53 (Cr): view from outside and inside. *Langmuir : the ACS journal of surfaces and colloids* **2011**, *27*, 4734-41.
18. Coudert, F. X.; Boutin, A.; Fuchs, A. H.; Neimark, A. V. Adsorption Deformation and Structural Transitions in Metal–Organic Frameworks: From the Unit Cell to the Crystal. *The Journal of Physical Chemistry Letters* **2013**, *4*, 3198-3205.
19. Coudert, F. X.; Boutin, A.; Jeffroy, M.; Mellot-Draznieks, C.; Fuchs, A. H. Thermodynamic methods and models to study flexible metal-organic frameworks. *Chemphyschem : a European journal of chemical physics and physical chemistry* **2011**, *12*, 247-58.
20. Coudert, F. X.; Jeffroy, M.; Fuchs, A. H.; Boutin, A.; Mellot-Draznieks, C. Thermodynamics of guest-induced structural transitions in hybrid organic-inorganic frameworks. *Journal of the American Chemical Society* **2008**, *130*, 14294-302.
21. Coudert, F. X.; Mellot-Draznieks, C.; Fuchs, A. H.; Boutin, A. Prediction of breathing and gate-opening transitions upon binary mixture adsorption in metal-organic frameworks. *Journal of the American Chemical Society* **2009**, *131*, 11329-31.
22. Salles, F.; Ghoufi, A.; Maurin, G.; Bell, R. G.; Mellot-Draznieks, C.; Ferey, G. Molecular Dynamics Simulations of Breathing MOFs: Structural Transformations of MIL-53(Cr) upon Thermal Activation and CO_2 Adsorption. *Angew Chem Int Edit* **2008**, *47*, 8487-8491.
23. Grosch, J. S.; Paesani, F. Molecular-Level Characterization of the Breathing Behavior of the Jungle-Gym-type DMOF-1 Metal-Organic Framework. *Journal of the American Chemical Society* **2012**, *134*, 4207-4215.

24. Zhang, L. L.; Hu, Z. Q.; Jiang, J. W. Sorption-Induced Structural Transition of Zeolitic Imidazolate Framework-8: A Hybrid Molecular Simulation Study. *Journal of the American Chemical Society* **2013**, *135*, 3722-3728.
25. Yamazaki, T.; Takahashi, Y.; Yoshida, D. Adsorption of several gases on flexible metal organic framework [Cu(dhbc)2(4,4'-bpy)]·H₂O. *Journal of colloid and interface science* **2011**, *362*, 463-9.
26. Quinn, D. F. Supercritical adsorption of 'permanent' gases under corresponding states on various carbons. *Carbon* **2002**, *40*, 2767-2773.
27. Kim, H. Y.; Lueking, A. D.; Gatica, S. M.; Johnson, J. K.; Cole, M. W. A corresponding states principle for physisorption and deviations for quantum fluids. *Mol Phys* **2008**, *106*, 1579-1585.
28. Cole, M. W.; Gatica, S. M.; Kim, H.-Y.; Lueking, A. D.; Sircar, S. Gas Adsorption in Novel Environments, Including Effects of Pore Relaxation. *J Low Temp Phys* **2012**, *166*, 231-241.
29. Jain, P.; Fonseca, D. A.; Schaible, E.; Lueking, A. D. Hydrogen uptake of platinum-doped graphite nanoribers and stochastic analysis of hydrogen spillover. *J Phys Chem C* **2007**, *111*, 1788-1800.
30. Sircar, S.; Wang, C. Y.; Lueking, A. D. Design of high pressure differential volumetric adsorption measurements with increased accuracy. *Adsorption* **2013**, *19*, 1211-1234.
31. Berry, R. S.; Rice, S. A.; Ross, J., *Physical Chemistry*; Oxford University Press: New York, 2000.
32. Bruch, L. W.; Cole, M. W.; Zaremba, E., *Physical Adsorption: Forces and Phenomena*; Dover Publications: Mineola, N.Y., 2007.
33. Noguchi, H.; Kondoh, A.; Hattori, Y.; Kanoh, H.; Kajiro, H.; Kaneko, K. Clathrate-formation mediated adsorption of methane on Cu-complex crystals. *J. Phys. Chem. B* **2005**, *109*, 13851-3.
34. Dubinin, M. M. The Potential Theory of Adsorption of Gases and Vapors for Adsorbents with Energetically Nonuniform Surfaces. *Chem. Rev.* **1960**, *60*, 235-241.
35. Polanyi, M. Theories of the Adsorption of Gases. A General Survey and Some Additional Remarks. *Trans. Faraday Soc.* **1932**, *28*, 316.
36. Ding, T. F.; Ozawa, S.; Yamazaki, T.; Watanuki, I.; Ogino, Y. A Generalized Treatment of Adsorption of Methane onto Various Zeolites. *Langmuir : the ACS journal of surfaces and colloids* **1988**, *4*, 392-396.
37. Sircar, S.; Myers, A. L. Characteristic Adsorption-Isotherm for Adsorption of Vapors on Heterogeneous Adsorbents. *Aiche J* **1986**, *32*, 650-656.
38. Wood, G. O. Affinity coefficients of the Polanyi/Dubinin adsorption isotherm equations - A review with compilations and correlations. *Carbon* **2001**, *39*, 343-356.
39. Roquerol, F.; Rouquerol, J.; Sing, K., *Adsorption by powders and solids: principles, methodology, and applications*. Academic Press: London: San Diego, CA, 1999; pp 110-112.
40. Yang, R. T., *Gas Separation by Adsorption Processes*; Butterworth: Boston, 1987.
41. Devautour-Vinot, S.; Maurin, G.; Henn, F.; Serre, C.; Devic, T.; Ferey, G. Estimation of the breathing energy of flexible MOFs by combining TGA and DSC techniques. *Chem. Commun.* **2009**, 2733-2735.
42. Yamazaki, T.; Takahashi, Y.; Yoshida, D. Adsorption of several gases on flexible metal organic framework [Cu(dhbc)2(4,4'-bpy)]·H₂O. *J. Colloid Interface Sci.* **2011**, *362*, 463-469.