

Theoretical isotherm equation for adsorption-induced structural transition on flexible metal-organic frameworks

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Flexible metal-organic frameworks (MOFs) exhibit an adsorption-induced structural transition known as "gate opening" or "breathing," resulting in an S-shaped adsorption isotherm. This unique feature of flexible MOFs offers significant advantages, such as a large working capacity, high selectivity, and intrinsic thermal management capability, positioning them as crucial candidates for revolutionizing adsorption separation processes. Therefore, the interest in the industrial applications of flexible MOFs is increasing, and the adsorption engineering for flexible MOFs is becoming important. However, despite the establishment of the theoretical background for adsorptioninduced structural transitions, no theoretical equation is available to describe S-shaped adsorption isotherms of flexible MOFs. Researchers rely on various empirical equations for process simulations that can lead to unreliable outcomes or may overlook insights into improving material performance owing to parameters without physical meaning. In this study, we derive a theoretical equation based on statistical mechanics that could be a standard for the structural transition type adsorption isotherms, as the Langmuir equation represents type I isotherms. The versatility of the derived equation is shown through four examples of flexible MOFs that exhibit gate opening and breathing. The consistency of the formula with existing theories, including the osmotic free energy analysis and intrinsic thermal management capabilities, is also discussed. The developed theoretical equation may lead to more reliable and insightful outcomes in adsorption separation processes, further advancing the direction of industrial applications of flexible MOFs.

metal-organic frameworks | adsorption-induced structural transition | adsorption isotherm equation | statistical mechanics

The 21st century is marked as the "age of gas" (1). Because of the depletion of petroleum, the demand for energy resources with economic and environmental-friendly alternatives, such as natural gas and biogas, is increasing. To achieve net zero emissions by 2050 (2), controlling of the gas is crucial. From this perspective, metal–organic frameworks (MOFs) (3, 4) have been at the forefront for the past two decades. MOFs have numerous applications owing to their high designability resulting from the innumerable combination of metal ions and organic ligands and are currently utilized by many start-up companies for practical uses (5).

Not only the design ability of the framework structure but also the structural flexibility are the remarkable features of MOFs, which are not found in conventional materials. This type of MOF, commonly referred to as flexible MOFs (6) or soft porous crystals (7), exhibits structural deformation induced by guest adsorption. Although certain flexible MOFs expand or contract their framework structure in proportion to the amount of guest molecules adsorbed, a remarkable feature of flexible MOFs is an adsorptioninduced phase transition, resulting in an S-shaped adsorption isotherm that cannot be classified by the existing IUPAC classification (8). Since this transition, known as "gate opening" or "breathing," occurs abruptly at a threshold pressure (the transition pressure, *P*^{tr}), a large working capacity can be induced with a pressure swing across *P*^{tr}. In addition, the flexibility allows for a gas-specific pore structure, resulting in exceptional selectivity. Flexible MOFs also have an intrinsic thermal management capability because the structural deformation is endothermic, which can suppress the negative effect of the adsorption heat (9, 10). These synergies can revolutionize adsorption separation processes (11). Therefore, the number of studies on the direction of industrial applications of flexible MOFs has been increasing (12-15). In the future, not only the adsorption science but also the adsorption engineering of flexible MOFs will become increasingly important.

The development of adsorption engineering is supported by basic theoretical equations, such as the Langmuir equation for type I isotherms and the

Significance

Flexible metal-organic frameworks (MOFs) are a class of materials that can undergo a structural transition called "gate opening" or "breathing" when adsorbing molecules, resulting in a unique S-shaped adsorption isotherm. The flexible MOFs have the potential advantage of being used in the separation of gas molecules due to their unique adsorption isotherm. However, a theoretical equation is required to model industrial applications using these materials, which is currently unavailable. In this study, we have formulated an equation based on statistical mechanics to describe the S-shaped adsorption isotherm on flexible MOFs, allowing researchers to predict how these materials will behave in adsorption separation processes. This equation enables the advancement of industrial applications of flexible MOFs.

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Brunauer-Emmett-Teller (BET) equation for type II isotherms. Although these equations include bold assumptions (for example, neglecting guest-guest interactions), they are robust and versatile because they are based on thermodynamics and can explain experimental results with good accuracy using a minimum number of parameters. This theoretical background enables engineers to safely interpolate and extrapolate data while conducting process simulations in which temperature, pressure, and the amount adsorbed vary extensively. However, a theoretical equation that describes the S-shaped adsorption isotherm for flexible MOFs is currently unavailable, although the theoretical framework for the adsorption-induced structural transition was first proposed in 2008 (16). Therefore, the current literature regarding adsorption process modeling for MOFs exhibiting the S-shaped isotherm relies on empirical equations proposed by individual researchers (17-25). Using such empirical formulas, which comprise parameters that lack physical meaning, not only undermines the reliability of the induced outcomes but also increases the possibility of overlooking insights into improving the performance of the material.

The theoretical framework of the adsorption-induced structural transition was first proposed by Coudert et al. (16) The critical point of their approach was to consider the change in the osmotic free energy, $\Delta \Omega^{os}$, associated with the adsorptioninduced structural transition. Given a structural transition from a narrow-pore (NP) to large-pore (LP) structure, $\Delta\Omega^{os}$ can be disaggregated into two distinct contributions: ΔF^{host} , which represents the free-energy cost associated with the deformation of the framework structure from NP to LP, and $\Delta \Omega^{guest}$, which elucidates the difference in the stabilization of guest adsorption on NP and LP. Because the amount of gas adsorption increases with pressure, and this effect is greater for LP than that for NP, sufficient stabilization to balance the destabilization due to structural deformation will be obtained at a certain pressure Ptr, resulting in the adsorption-induced structural transition. This free-energy analysis has been substantially supported by several subsequent studies (26-35), including our previous studies (36-42), and has recently been further developed, such as the quantitative prediction of experimental values using full ab initio calculations with no adjustment parameters (43), and integration with classical density functional theory for adsorption (44, 45). However, this theoretical framework does not provide good information on the isotherm equation. In particular, the adsorption isotherm, N, can only be formulated via the conditional branch expression:

$$N(P, T) = \begin{cases} N_{\rm NP}(P, T) & (\Delta \Omega^{\rm os}(P, T) > 0) \\ N_{\rm LP}(P, T) & (\Delta \Omega^{\rm os}(P, T) < 0), \end{cases}$$
[1]

where *P* is the pressure, *T* is the temperature, and the adsorption isotherm on structure α (= NP, LP) is denoted $N_{\alpha}(P, T)$. This conditional expression is difficult to apply and differs from the experimental results: The observed sharp increase in the amount adsorbed is an S-shaped function with a small width rather than being completely discrete. Some studies (29, 46) have suggested that this small width reflects the dependence of the threshold pressure on the particle size and size distribution of the samples. Hence, empirical formulas were used in previous studies (17–25).

This study aims to derive a standard theoretical equation for the structural transition type adsorption isotherm, as well as the Langmuir and BET equations for type I and II isotherms, respectively. The rest of the paper is organized as follows: First, we show the most useful form of the derived isotherm equation and demonstrate the versatile manner in which it describes the adsorption-induced structural transition using the three examples of function fitting for flexible MOFs exhibiting gate opening and breathing. We then explain the formula induced from the analogous derivation for the Langmuir equation based on statistical mechanics. After establishing that the formula is consistent with the existing theory for intrinsic thermal management capabilities, we finally generalize the isothermal equation through the comparison with the free-energy analysis reported by Coudert et al. In discussion, three limitations of this equation are provided.

Results

Resultant Equation. First, for reference, the obtained adsorption isotherm equation is presented (and its derivation is discussed later). The equation for structural transition type adsorption isotherm (hereinafter, referred to as STA equation) can be written as

$$N(P) = \left\{1 - \sigma(P)\right\} L_{\rm NP}(P) + \sigma(P)L_{\rm LP}(P), \qquad [2]$$

where L_{α} is the Langmuir equation on the structure α (= LP, NP) defined with the parameters N_{α}^{∞} and K_{α} as

$$L_{\alpha}(P) = N_{\alpha}^{\infty} \frac{K_{\alpha}P}{1 + K_{\alpha}P}.$$
 [3]

In contrast, σ is an S-shaped function defined as

$$\sigma(P) = \frac{y^{\prime}}{1+y^{\prime}},$$
[4]

where *s* is a constant, and *y* is a function of *P* with parameters for the Langmuir equations of NP and LP and the structural transition pressure, P^{tr} :

$$y(P) = \left(\frac{1 + K_{\rm NP}P^{\rm tr}}{1 + K_{\rm NP}P}\right)^{N_{\rm NP}^{\rm cr}} \left(\frac{1 + K_{\rm LP}P}{1 + K_{\rm LP}P^{\rm tr}}\right)^{N_{\rm LP}^{\rm cc}}.$$
 [5]

Consequently, the STA equation at a constant temperature can be expressed with six parameters N_{NP}^{∞} , K_{NP} , N_{LP}^{∞} , K_{LP} , s, and P^{tr} .

When considering the temperature dependence of the STA equation, $K_{\rm NP}$, $K_{\rm LP}$, and $P^{\rm tr}$ should be transformed into temperature-dependent forms. Since K_{α} is a Langmuir parameter, it can be written as

$$K_{\alpha}(T) = K_{\alpha}^{0} \exp\left(\frac{Q_{\alpha}}{RT}\right),$$
 [6]

where K_{α}^{0} is a constant, Q_{α} is the heat of adsorption, and *R* is the gas constant. In contrast, expressing the temperature dependency of P^{tr} in an explicit functional form is difficult. Nevertheless, Eq. 5 can be rewritten in the following simple equation using the changes in the internal energy and entropy of the host caused by the structural transition, ΔU_{host} and ΔS_{host} :

$$y(P, T) = \frac{(1 + K_{\rm LP}P)^{N_{\rm LP}^{\infty}}}{(1 + K_{\rm NP}P)^{N_{\rm NP}^{\infty}}} \exp\left(-\frac{\Delta U_{\rm host} - T\Delta S_{\rm host}}{RT}\right).$$
 [7]

In summary, the STA equation considering the temperature dependence can be written with nine parameters, comprising three Langmuir parameters for the NP structure (N_{NP}^{∞} , K_{NP}^{0} , Q_{NP}), those for the LP structure (N_{LP}^{∞} , K_{LP}^{0} , Q_{LP}), and three parameters regarding the S-shaped function (*s*, ΔU_{host} , ΔS_{host}).

	$ZIF\text{-}7\supsetCH_4$	$ELM-11 \supset CO_2$	MIL-53(Al) ⊃ Xe
$N_{\rm NP}^{\infty}$ [mol/kg]	1.267	-	3.448
$K_{\rm NP}^0$ [MPa ⁻¹]	2.112×10^{-4}	-	2180*
Q _{NP} [kJ/mol]	20.22	-	-
$N_{\rm LP}^{\infty}$ [mol/kg]	1.748	3.910	10.69
K_{LP}^{0} [MPa ⁻¹]	5.887×10^{-4}	6.769×10^{-6}	57.67*
Q _{LP} [kJ/mol]	23.04	39.05	-
s [kg/mol]	19.20	12.92	10.45
$\Delta U_{\rm host}$ [kJ/kg]	10.26	41.98	-
$\Delta S_{host} [J \cdot K^{-1} \cdot kg^{-1}]$	11.45	89.49	-
P ^{tr} [kPa]	-	-	0.8762
$\begin{aligned} & \mathcal{L}_{LP}^{0} [MPa^{-1}] \\ & \mathcal{Q}_{LP} [k]/mol] \\ & s [kg/mol] \\ & \Delta U_{host} [k]/kg] \\ & \Delta S_{host} [l\cdotK^{-1}\cdotkg^{-1}] \\ & \mathcal{P}^{tr} [kPa] \end{aligned}$	5.887 × 10 ⁻⁴ 23.04 19.20 10.26 11.45 -	6.769 × 10 ⁻⁶ 39.05 12.92 41.98 89.49 -	57.67* - 10.45 - - 0.8762

*These values are not K^0_{α} but K_{α} at 220 K.

Case Study. To verify the usefulness of the STA equation, we performed function fitting for three systems that exhibit typical adsorption-induced structural transitions, and the results are shown in Fig. 1 and Table 1. Notably, although a nonlinear least squares fitting is required to determine the parameters, the initial values can be estimated by a graphical approach, as shown *SI Appendix*, section S1.

Fig. 1*A* shows CH₄ adsorption on ZIF-7 (21). which exhibits the basic structural transition from an NP to an LP structure. Although a temperature difference of approximately 80 K is present, from 283 K to 362 K, the fitting is suitable for the position of the rise due to the structural transition and for the subtle differences in its sharpness. In addition, Fig. 1*B* shows CO₂ adsorption on ELM-11 (41), which exhibits a transition from a completely nonporous to a porous state. Here, $N_{NP}^{\infty} = 0$, the fitting can be achieved using a simplified function with six parameters given by Eqs. **8** and **9**:

$$N(P) = \frac{y^{s}}{1 + y^{s}} L_{\rm LP}(P), \qquad [8]$$

$$y(P, T) = (1 + K_{\rm LP}P)^{N_{\rm LP}^{\infty}} \exp\left(-\frac{\Delta U_{\rm host} - T\Delta S_{\rm host}}{RT}\right).$$
 [9]

ZIF-7 and ELM-11 exhibit gate opening, which is the transition from a state of low porosity to high porosity. However, the STA equation can also be applied to the breathing phenomenon, which is the transition from an LP to an NP state and back to the LP state. Fig. 1*C* shows Xe adsorption on MIL-53(Al) at 220 K (27), and both of the two rises can be well represented. Interestingly, the P^{tr} value obtained was 0.876 kPa, indicating that the transition pressure fitted as a parameter of the STA equation corresponds only to the first LP to NP transition, and the theory automatically determines pressure of the second NP to LP transition.

Difference from Empirical Equations. The STA equation has a form that smoothly connects the Langmuir isotherms for NP and LP structures using an S-shaped function. Owing to its simplicity, several empirical formulas with the same form were proposed (17-25). However, the S-shaped function used in empirical formulas varied widely, including the cumulative logistic distribution (17), cumulative log-logistic distribution (19, 20, 23, 25), error function (18, 21, 22), and arctangent (24). According to the STA equation, the S-shaped function should be a cumulative log-logistic distribution, as shown in Eq. 4, and the empirical formula by Hefti et al. (19) and its derivatives (20, 23, 25) were close to our theoretical equation. However, differences were observed, such as the simplicity of $y = P/P^{tr}$, consideration of temperature dependence for s, and the use of a parameter γ as the power of the cumulative log-logistic distribution (i.e., σ^{γ}), resulting in five parameters for the S-shaped function. While these empirical formulas may represent a single transition, they cannot express complex transitions such as the breathing phenomenon.

Formula Derivation. This section presents the derivation of the STA equation. While the Langmuir equation is derived by considering the balance between adsorption and desorption rates, another derivation based on statistical mechanics is available. In particular, this derivation considers the probability \mathcal{P} that *n* molecules are adsorbed in a system comprising N^{∞} adsorption sites with adsorption energies of -Q (Q > 0) placed in an environment with a chemical potential μ and temperature *T*, as



Fig. 1. Function fitting results for (*A*) CH₄ adsorption on ZIF-7, (*B*) CO₂ adsorption on ELM-11, and (*C*) Xe adsorption on MIL-53(Al). Experimental data of ZIF-7 and MIL-53(Al) are extracted from refs. 21 and 27, respectively, using a plot digitizer software application. Orange symbols, green-dashed, purple-dashed, and black solid lines are experimental data, *L*_{NP}, *L*_{LP}, and *N*, respectively.

illustrated in Fig. 2*A*. Considering all configurations, the grand partition function Ξ and grand potential Ω can be derived. The average amount adsorbed can be induced by the partial derivative of Ω to μ . Since μ is related to the gas pressure *P*, the adsorbed amount at a given *P* and *T*, i.e., the Langmuir equation, is derived as Eqs. **3** and **6**.

A similar statistical mechanics approach is employed in deriving the STA equation. In contrast to the Langmuir equation, which assumes an invariant host, counting the number of states of a deforming host is considered. This derivation assumes that the adsorption-induced structural transition arises from a balance between destabilization due to the structural changes in the host and stabilization owing to adsorption. Along a variable that characterizes the structural deformation, commonly referred to as the reaction coordinate x, the free energy of the system has a bimodal profile with two minima at low (x_{NP}) and high (x_{LP}) adsorption levels. Generally, the free energy is high at $x \neq x$ $x_{\rm NP}$, $x_{\rm LP}$, resulting in a significantly lower probability that the system will be in these states compared to NP and LP. Therefore, only NP and LP states were considered as possible states of the host. In addition, particularly for the equation derivation, the structural transitions are assumed to not occur simultaneously throughout the entire system but rather for domains of a certain size. While decisive evidence for the coexistence of NP and LP within crystallites is currently unavailable, molecular simulations of a large MIL-53 system consisting of millions of atoms have shown that the pressure-induced structural transition occurs for each domain (47). Our study on the molding of flexible MOFs has also revealed that the slacking of the gate opening

is due to the differences in the structural transition pressures for each domain caused by the external force (48). Moreover, the study on film formation of flexible MOFs showed that only the distant part from the substrate experienced structural transition, resulting in the coexistence of NP and LP (49). These findings and other computational analyses (50–52) suggest that the adsorption-induced structural transition is not a phenomenon that occurs cooperatively throughout the entire system, but rather a phenomenon that occurs within a limited range.

Based on the above, the model system devised shown schematically in Fig. 2*B*, is as follows. First, as the target system, a host framework with a unit quantity (e.g., 1 kg or 1 mol based on monomer units) is considered, and *M* domains are assumed to be present, which are the minimum units that undergo structural transition cooperatively. Consider that among these domains, M - m domains have NP structures, and *m* domains have LP structures, with a probability $\mathcal{P}^{\text{host}}(m)$. If the free energy of the host per domain is denoted by f_{α}^{host} ($\alpha = \text{NP}$, LP), $\mathcal{P}^{\text{host}}(m)$ can be expressed as

$$\mathcal{D}^{\text{host}}(m) \propto {}_{M}C_{m}e^{-\beta(M-m)f_{\text{NP}}^{\text{host}}}e^{-\beta m f_{\text{LP}}^{\text{host}}}$$
$$\propto {}_{M}C_{m}e^{-\beta m \Delta f^{\text{host}}}, \qquad [10]$$

where, ${}_{M}C_{m}$ is the binomial coefficient, corresponding to the number of combinations of selecting *m* domains from *M* for LP structures. $\beta = (k_{\rm B}T)^{-1}$, $k_{\rm B}$ is the Boltzmann constant, and $\Delta f^{\rm host} = f_{\rm LP}^{\rm host} - f_{\rm NP}^{\rm host}$. Then, the NP and LP domains are assumed to have $S_{\rm NP}$ and $S_{\rm LP}$ adsorption sites with



Fig. 2. Schematics of models considered for formula derivation: (A) the Langmuir model and (B) our model for the STA equation.

adsorption energies of $-Q_{\rm NP}$ and $-Q_{\rm LP}$ ($Q_{\alpha} > 0$), respectively, while ignoring the intermolecular interactions between adsorbed molecules. The total number of adsorption sites in the system is $(M - m)S_{\rm NP}$ for NP structures and $mS_{\rm LP}$ for LP structures. In this case, the probability $\mathcal{P}^{\rm guest}(n_{\rm NP}, n_{\rm LP} \mid m)$ that the number of adsorbed molecules on each state is $n_{\rm NP}$ and $n_{\rm LP}$ under the environment of chemical potential μ and temperature T is

$$\mathcal{P}^{\text{guess}}(n_{\text{NP}}, n_{\text{LP}} \mid m) = {}_{(M-m)S_{\text{NP}}} C_{n_{\text{NP}}} e^{\beta(Q_{\text{NP}}+\mu)n_{\text{NP}}} {}_{mS_{\text{LP}}} C_{n_{\text{LP}}} e^{\beta(Q_{\text{LP}}+\mu)n_{\text{LP}}}.$$
[11]

The partition function O of the system can be induced by taking the sum over all combinations of $(m, n_{\text{NP}}, n_{\text{LP}})$:

$$\mathcal{O} = \sum_{m=0}^{M} \sum_{n_{\rm NP}=0}^{(M-m)S_{\rm NP}} \sum_{n_{\rm LP}=0}^{mS_{\rm LP}} \mathcal{P}^{\rm host}(m) \mathcal{P}^{\rm guest}(n_{\rm NP}, n_{\rm LP} \mid m) \\ = \left[\left\{ 1 + e^{\beta(Q_{\rm NP}+\mu)} \right\}^{S_{\rm NP}} + e^{-\beta\Delta f^{\rm host}} \left\{ 1 + e^{\beta(Q_{\rm LP}+\mu)} \right\}^{S_{\rm LP}} \right]^{M} .$$
[12]

More detailed formula transformations are provided in *SI* Appendix, section S2. To obtain the average adsorbed amount N, the logarithm of the partition function, i.e., the free energy, should be differentiated with respect to μ . Although some intricate formula transformations are required (*SI Appendix*, section S3), the final formula is

$$N = k_{\rm B} T \left(\frac{\partial \ln \mathcal{O}}{\partial \mu}\right)_T = \left(1 - \frac{Y}{1+Y}\right) L_{\rm NP} + \frac{Y}{1+Y} L_{\rm LP},$$
[13]

where

$$Y = \frac{(1 + K_{\rm LP}P)^{S_{\rm LP}}}{(1 + K_{\rm NP}P)^{S_{\rm NP}}} \exp\left(-\frac{\Delta f^{\rm host}}{k_{\rm B}T}\right).$$
 [14]

 L_{α} and K_{α} are the Langmuir adsorption isotherm defined by Eq. **3** and its parameter defined by Eq. **6** in structure α , respectively. S_{α} and Δf^{host} in Eq. **14** are the values per domain as their definitions; however, expressing them per unit of host would be more convenient. Therefore, multiplying the number of domains per unit of host M with $MS_{\alpha} = N_{\alpha}^{\infty}$ and $M\Delta f^{\text{host}} = \Delta F^{\text{host}}$, and replacing k_{B} to R for easier-to-use units, Eq. **14** can be rewritten as

$$Y = \left\{ \frac{(1 + K_{\rm LP}P)^{N_{\rm LP}^{\infty}}}{(1 + K_{\rm NP}P)^{N_{\rm NP}^{\infty}}} \exp\left(-\frac{\Delta F^{\rm host}}{RT}\right) \right\}^{\frac{1}{M}} \equiv y^{\rm s}.$$
 [15]

Inserting Eq. 15 into Eq. 13 yields the STA equation presented above.

Isosteric Heat of Adsorption and Intrinsic Thermal Management Capabilities. The isosteric heat of adsorption, Q_{st} , can be obtained using the Clausius–Clapeyron equation:

$$Q_{\rm st} = -\left(\frac{\partial\ln P}{\partial\beta}\right)_N.$$
 [16]

By substituting Eq. 2 into Eq. 16, we derived the theoretical equation of the isosteric heat of adsorption on the adsorption-induced structural transition. After numerous equation transfor-

mations shown in *SI Appendix*, section S4, the following equation is finally obtained:

 $Q_{\rm st} = \frac{AQ_{\rm NP} + BQ_{\rm LP} + CQ_{\rm net}}{A + B + C},$

and

$$Q_{\text{net}} = \frac{Q_{\text{LP}}L_{\text{LP}} - Q_{\text{NP}}L_{\text{NP}} - \Delta U_{\text{host}}}{L_{\text{LP}} - L_{\text{NP}}},$$
 [18]

[17]

$$\begin{cases}
A = (1 - \sigma) \frac{L_{\rm NP}}{1 + K_{\rm NP}P} \\
B = \sigma \frac{L_{\rm LP}}{1 + K_{\rm LP}P} \\
C = s\sigma (1 - \sigma) (L_{\rm LP} - L_{\rm NP})^2.
\end{cases}$$
[19]

Since A, B, and C include the S-shaped function, their attributes dramatically change as the pressure changes; namely, A is dominant when $P < P^{tr}$, B is dominant when $P > P^{tr}$, whereas C is dominant when $P \simeq P^{\text{tr}}$. Therefore, plotting Q_{st} (Eq. 17) against N (Eq. 2) of CH₄ adsorption on ZIF-7, as an example, results in the curve with three plateaus, as shown in Fig. 3. While the $Q_{\rm st}$ values before and after the structural transition match $Q_{\rm NP}$ and Q_{LP} , respectively, Q_{st} during the structural transition shows a slight deviation from the Q_{net} value at $P = P^{tr}$. This is because the majority of C also depends on the s value. For example, changing only the *s* value for ZIF-7 \supset CH₄ from 19.2 to 200, the transitions between the plateaus became steeper, and $Q_{\rm st}$ during the structural transition approached Q_{net} . Note that Q_{net} (Eq. 18) represents the intrinsic thermal management capabilities (9, 10) where the exothermic heat due to guest adsorption is partially offset by the endothermic heat of structural deformation and is the same as the equation derived in the previous study (10).

General Form of the STA Equation. In this section, we generalize the STA equation by comparing the free-energy analysis reported by Coudert et al. According to Coudert et al. (16), the osmotic free energy of the system, ω^{os} , can be expressed as

$$\omega^{\rm os}(\mu, T, x) = f^{\rm host}(T, x) + PV - \int_{-\infty}^{\mu} N(\mu, T, x) d\mu.$$
 [20]



Fig. 3. Isosteric heat of adsorption (Eq. **17**) calculated using the parameters for $ZIF-7 \supset CH_4$ listed in Table 1 (blue solid line). The red dashed line represents the *s* dependence of Q_{st} , which was obtained by changing *s* of $ZIF-7 \supset CH_4$ from 19.2 to 200.

Based on the fact that $\omega^{os}(\mu, T, x)$ exhibits a bimodal profile where it takes a minimum at x_{NP} and x_{LP} , the free energy difference between both states

$$\Delta \omega^{\rm os}(\mu, T) = \omega^{\rm os}(\mu, T, x_{\rm LP}) - \omega^{\rm os}(\mu, T, x_{\rm NP})$$
$$= \Delta f^{\rm host}(T) + P\Delta V - \int_{-\infty}^{\mu} \Delta N(\mu, T) d\mu,$$
[21]

becomes zero at a certain chemical potential $\mu = \mu^{tr}(T)$. Here, the $P\Delta V$ term is negligible compared to the others. Therefore, their analysis considers that NP and LP states switch at this threshold value. However, relying on statistical mechanics, the average number of adsorbed molecules should be calculated as an ensemble average:

$$N(\mu, T) = \frac{\int N(\mu, T, x) e^{-\beta \omega^{\text{os}}(\mu, T, x)} dx}{\int e^{-\beta \omega^{\text{os}}(\mu, T, x)} dx}.$$
 [22]

Although all *x* should be considered in principle, if the contribution of $x \neq x_{NP}$, x_{LP} is sufficiently small, it can be approximated as

$$N(\mu, T) \simeq \frac{N_{\rm NP}(\mu, T)e^{-\beta\omega_{\rm NP}^{\rm os}(\mu, T)} + N_{\rm LP}(\mu, T)e^{-\beta\omega_{\rm LP}^{\rm os}(\mu, T)}}{e^{-\beta\omega_{\rm NP}^{\rm os}(\mu, T)} + e^{-\beta\omega_{\rm LP}^{\rm os}(\mu, T)}}$$

= $\frac{1}{1 + e^{-\beta\Delta\omega^{\rm os}(\mu, T)}}N_{\rm NP}(\mu, T)$
+ $\frac{e^{-\beta\Delta\omega^{\rm os}(\mu, T)}}{1 + e^{-\beta\Delta\omega^{\rm os}(\mu, T)}}N_{\rm LP}(\mu, T),$ [23]

where we denote $N_{\alpha}(\mu, T) \equiv N(\mu, T, x_{\alpha})$ and $\omega_{\alpha}^{os}(\mu, T) \equiv \omega^{os}(\mu, T, x_{\alpha})$. The value of $\Delta \omega^{os}$ to be considered is the amount of the free energy change observed in the system. Namely, it must be the value per domain, i.e., the portion where a cooperative structural transition occurs, rather than the value per 1 mol monomer unit or 1 mol unit cell defined for convenience. Thus, when the osmotic free energy change per unit host is denoted as $\Delta \Omega^{os}$, since the domain size relative to the unit host is $s, \Delta \omega^{os}$ should be $s\Delta \Omega^{os}$. To clarify the influence of the domain size on Eq. 23, consider a slightly higher chemical potential (pressure) than the threshold value making $\Delta \omega^{os}$ zero. At this chemical potential, $\Delta \omega^{os}(\mu^{tr} + \Delta \mu) = s\Delta \Omega^{os}(\mu^{tr} + \Delta \mu) < 0$, but the magnitude of this value varies depending on *s*. For instance, if *s* is large, the exponential value in the right-hand side of Eq. 23



Fig. 4. Dependence of the shape of the STA equation on the parameter s.



Fig. 5. Function fitting results for CO₂ adsorption on MIL-53(Al). In (*A*), the Langmuir equation was used as $N_{\text{NP}}(P,T)$ and $N_{\text{LP}}(P,T)$, while the Sips equation was used in (*B*). Details on the Sips version of STA equation are provided in *SI Appendix*, section S5.

becomes significantly large, causing the first term to approach zero. Conversely, if *s* is small, the first and second terms become comparable, albeit with slight differences in magnitude. That is, as *s* increases, the contribution of the first and second terms of the right-hand side changes abruptly to μ . The conventional free-energy analysis assumed that $s \rightarrow \infty$, which corresponds to the treatment of the thermodynamic limit. However, if the domain size has a finite value for which thermodynamic limits should not be applied, the presence ratio of NP and LP states changes smoothly depending on the *s* value, as shown in Fig. 4. In summary, one obtains the generalized STA equation:

$$N(P, T) = \{1 - \sigma(P, T)\} N_{\rm NP}(P, T) + \sigma(P, T) N_{\rm LP}(P, T)$$

$$\sigma(P, T) = \frac{\gamma^{\varsigma}}{1 + \gamma^{\varsigma}}$$

$$\gamma(P, T) = \exp\left\{-\frac{\Delta\Omega^{\rm os}(P, T)}{RT}\right\}$$

$$\Delta\Omega^{\rm os}(P, T) = \Delta F^{\rm host}(T) - \int_{0}^{P} \Delta N(P, T) V_{\rm m} dP,$$

[24]

where $V_{\rm m} = (\partial \mu / \partial P)_T$. In particular, Eqs. 2–7 are specific cases of applying the Langmuir equation to $N_{\alpha}(P, T)$. In contrast, these equations can implement any arbitrary isotherm equation suitable for the pore size and properties of the target flexible MOF, such as the Freundlich, Toth, BET, and Sips equations. This will aid in augmenting the fitting accuracy, as shown in Fig. 5.

Discussion

Based on statistical mechanics, we derived the isotherm equation for the adsorption-induced structural transition on flexible MOFs. The obtained formula, the STA equation, could reproduce the adsorption isotherms and their temperature dependence observed in various flexible MOFs, including those exhibiting gate-opening and breathing behaviors. In addition, we demonstrated the relationship between the STA equation and the existing theory, the osmotic free energy analysis and intrinsic thermal management capabilities as well as the generalized form of the STA equation. Our equation is applicable to all types of soft porous crystals, not only flexible MOFs, as long as they show an adsorption-induced phase transition between two stable structures.

Finally, we remark on three limitations of this study.

First, we assumed that domains of a certain size undergo structural transitions without interacting with neighboring domains. However, considering the interfacial energy based on whether neighboring unit cells, which are smaller than domains, are in different states is more fundamental to physics. In other words, while our study modeled the domain size as a parameter, the domain size should be determined by a balance between the entropic term of the free energy and the disadvantage stemming from the resulting interfacial energy. Therefore, modeling equations based on the interfacial energy associated with the coexistence of NP and LP states would be more physically favorable. The interfacial energy between adjacent cells would be studied using an analogical approach to the well-known Ising model typically applied to ferromagnetism. In fact, a MOF with rotatable moieties has been successfully analyzed based on similar considerations (53, 54).

Second, the adsorption-induced structural transition typically exhibits hysteresis in adsorption and desorption. In particular, experimentally observed steps are transitions from metastable states, and thus fitting the STA equation, which is derived based on the equilibrium theory, to experimental data is not strictly accurate. However, as shown in Fig. 1, the formula can represent the adsorption branch including its temperature dependence, as well as the desorption branch (SI Appendix, section S6), with sufficient precision for engineering use. The reason for this successful approximation is related to the good linearity between the logarithm of the structural transition pressure and the inverse temperature, and many experimental and computational examples have been reported not only for the equilibrium transition pressure but also for the gate opening and closing pressures (11, 37, 55). This empirical linearity allows us to treat Q_{net} (Eq. 18) as a constant with almost negligible temperature dependence and tune $Q_{\rm net}$ by varying the $\Delta U_{
m host}$ value according to the branch provided. Numaguchi et al. concluded from their simulation study on a stacked-layer MOF that the slope of the $\ln P^{\text{tr}}$ versus T^{-1} plot decreases in the order of using the desorption branch, equilibrium branch, and adsorption branch as P^{tr} (37). This implies that the ΔU_{host} value obtained from fitting the adsorption and desorption branches are larger and smaller than the true value at the equilibrium point, respectively. The authors also observed that the desorption branch is much closer to equilibrium behavior than the adsorption branch, which indicates that the $\Delta U_{\rm host}$ value obtained from the desorption branch can be taken as the equilibrium value, at least for the stacked-layer MOF considered in their study. Therefore, it would be useful to extend Eq. 7 to handle isotherms with hysteresis as

$$y(P, T) = \frac{(1 + K_{\rm LP}P)^{N_{\rm LP}^{\infty}}}{(1 + K_{\rm NP}P)^{N_{\rm NP}^{\infty}}} \times \exp\left(-\frac{\Delta U_{\rm host} + \phi\Omega_{\rm add} - T\Delta S_{\rm host}}{RT}\right).$$
 [25]

where Ω_{add} is an additional stabilization factor required to overcome the transition state from NP to LP, and ϕ is a binary variable depending on the branch considered (0: desorption branch, 1: adsorption branch). For example, in this expression, the values for ELM-11 \supset CO₂ are $\Delta U_{host} = 39.91$ kJ/kg and $\Omega_{add} = 2.07$ kJ/kg (*SI Appendix*, section S6). However, it should be noted again that this is an approximate analysis that forcefully applies an equation derived from equilibrium theory to a kinetic phenomenon. To properly address hysteresis phenomena, it is desirable to derive advanced theoretical equations that incorporate kinetic factors into the model constructed in this study.

The final remark concerns the parameters obtained. Since the formula is based on statistical mechanics, the parameters obtained by function fitting have physical meanings. However, they are not necessarily highly accurate. This is because the data we have on the adsorption behavior of the LP structure are limited to the range after the structural transition, that is, the part closer to the saturated; in particular, accurately estimating the Langmuir constant K_{LP} and Q_{LP} obtained from its temperature dependence is difficult. In many cases, QLP would be underestimated. However, as evident from Eq. 18, the temperature dependence of the structural transition pressure is determined by the difference between Q_{LP} and ΔU_{host} . Even if Q_{LP} is underestimated, the fitting will work well with the underestimated value of ΔU_{host} . The values obtained by function fitting for ELM-11 \supset CO₂ are Q_{LP} = 39.05 kJ/mol-CO₂, ΔU_{host} = 39.91 kJ/kg, and ΔS_{host} = 89.49 J·K⁻¹·kg⁻¹, whereas the more reliable values obtained by utilizing molecular simulation and free energy analysis are $Q_{LP} = 40.8 \text{ kJ/mol-CO}_2$,

 $\Delta U_{\text{host}} = 55.7 \text{ kJ/kg}$, and $\Delta S_{\text{host}} = 120 \text{ J} \cdot \text{K}^{-1} \cdot \text{kg}^{-1}$ (10). Despite these limitations, the STA equation remains a valuable tool for organizing and inter/extrapolating adsorption data of flexible MOFs. This allows us to perform numerical simulations, such as those used for adsorption separation processes, which should accelerate the use of flexible MOFs in industrial applications.

Materials and Methods

Details on Adsorption Measurements. Pre-ELM-11 was obtained from Tokyo Chemical Industry Co. The pre-ELM-11 was transformed into ELM-11 by heating at 373 K for 10 h under vacuum (<0.1 mPa), and the CO₂ adsorption isotherms on ELM-11 were measured at 268, 283, and 298 K using the BELSORP-max instrument (MicrotracBel Co.) and a cryostat equipped with a two-stage Gifford-McMahon refrigerator. The cell temperature was kept within ±0.01 K during the adsorption measurements.

MIL-53(AI) was obtained from SyncMOF Inc. The CO₂ adsorption isotherms on MIL-53(AI) were measured at 195, 223, and 273 K using the BELSORP-max instrument (MicrotracBel Co.) and a cryostat equipped with a two-stage Gifford–McMahon refrigerator. The cell temperature was kept within \pm 0.01 K during the adsorption measurements. Prior to each measurement, MIL-53(AI) was activated by heating it at 473 K for 12 h under a vacuum.

Data, **Materials**, **and Software Availability**. All study data are included in the article and/or *SI Appendix*.

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