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Temperature Dependence of Sorption

Seishi Shimizu* and Nobuyuki Matubayasi



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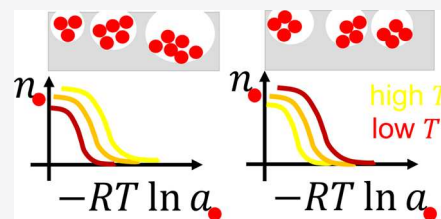
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ABSTRACT: Understanding how sorption depends on temperature on a molecular basis has been made difficult by the coexistence of isotherm models, each assuming a different sorption mechanism and the routine application of planar, multilayer sorption models (such as Brunauer–Emmett–Teller (BET) and Guggenheim–Anderson–de Boer (GAB)) beyond their premises. Furthermore, a common observation that adsorption isotherms measured at different temperatures fall onto a single “characteristic curve” when plotted against the adsorption potential has not been given a clear explanation, due to its ambiguous foundation. Extending our recent statistical thermodynamic fluctuation theory of sorption, we have generalized the classical isosteric theory of sorption into a statistical thermodynamic fluctuation theory and clarified how sorption depends on temperature. We have shown that a characteristic curve exists when sorbate number increment contributes purely energetically to the interface, whereas the correlation between sorbate number and entropy drives the temperature dependence of an isotherm. This theory rationalizes the opposite temperature dependence of water vapor sorption on activated carbons with uniform versus broad pore size distributions and can be applied to moisture sorption on starch gels. The adsorption potential is a convenient variable for sorption in its ability to unify sorbate–sorbate fluctuation and the isosteric thermodynamics of sorption.



INTRODUCTION

Understanding how sorption depends on temperature is an important question in basic and applied sciences alike.^{1–3} This paper aims to answer this question on a molecular scale via statistical thermodynamics.^{4–7} This question may seem simple yet has been made complicated. We have identified the three areas of difficulty in the previous attempts to answer this question.

Coexistence of Multiple Adsorption Models. Studying sorption was made complicated by the coexisting of 80+ different isotherm models, each assuming a different sorption mechanism including how it depends on temperature.^{8–14} Here, we demonstrate that temperature dependence has been explained differently from model to model and there are even disagreements within the same model as to which parameters are temperature-dependent.

- The Langmuir model¹⁵ contains two parameters, the Langmuir constant and the saturation loading.¹⁶ The Langmuir constant is linked to adsorption enthalpy via the van’t Hoff equation,¹⁷ and generally agreed to be temperature-dependent.^{1,3} However, an agreement has not been reached regarding when the saturation loading is temperature-independent^{18,19} or temperature-dependent.^{16,20,21}
- The models mathematically related to the Langmuir model, such as the Langmuir–Freundlich and Toth models,^{16,22} have been used to analyze the temperature dependence of adsorption, in which multiple different

assumptions on the temperature dependence of their parameters have been adopted.^{16,22}

- The Brunauer–Emmett–Teller (BET)^{23,24} and Guggenheim–Anderson–de Boer (GAB)^{25–27} models originally assumed monolayer adsorption to be temperature-independent, whereas adsorption onto second and subsequent adsorption layers depend on temperature. However, when applying the planar, multilayer GAB model to foods (which are not planar), the monolayer capacity is assumed to be temperature-independent²⁸ or being the only parameter that depends on temperature;²⁹ some authors consider all of the parameters temperature-dependent.³⁰ Thus, how the temperature dependence should be incorporated into the BET and GAB models has not been agreed upon.
- Iglesias, Chirife, and co-workers have demonstrated that moisture sorption isotherms of food can be expressed as the product of the two contributions, one dependent solely on temperature and another dependent solely on sorbate activity.^{29,31,32} They have attempted to justify this approach based on the fitting using the BET model and the Hailwood–Horrobin model.³³

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- The Dubinin–Astakhov³⁴ and Dubinin–Radushkevich^{34–38} models assume the isotherm to be a function of the “adsorption potential”, which fully accounts for the temperature dependence of sorption (see the [Adsorption Potential](#) subsection for details).

We have seen in the above that the study of temperature dependence has been model-dependent and that the model isotherms have been applied beyond their original assumptions and basic premises, leading to inconsistencies regarding the origin of the temperature dependence of sorption not only between different sorption models but also within the same model. Thus, the lack of consistency arising from the coexistence of many different sorption models must be overcome by a unified theory.

Adsorption Potential. Isotherms measured at different temperatures, when plotted against the “adsorption potential” instead of the sorbate activity, quite commonly fall onto a single “characteristic curve”.^{39–41} However, the theoretical foundation for this common observation, including the applicability and physical meaning of the adsorption potential,^{39,40} has been subjected to criticisms.^{41,42} First, considering an isotherm as a function of the adsorption potential violates Henry’s law.^{41,42} Second, there are at least three different definitions, each claiming to be the adsorption potential.⁴³ Consequently, Dubinin went so far as to say that “it became more and more obvious that the initial principles of the potential theory have no physical meaning for adsorption in micropores”.³⁷ A rigorous theoretical approach is required to clarify the physical basis of this common observation. Attempts have been made to clarify the theoretical foundation of the adsorption potential theory and of the isotherms based thereupon,^{36–41,44–46} yet the question has remained unresolved.

Thermodynamics of Adsorption. The thermodynamics of adsorption was founded mainly in the 1940s and 1950s, which have been summarized most systematically by Hill,^{47–50} Everett,^{51–53} and Dubinin and co-workers,^{34,36–38,54} with many subsequent applications.^{29,32,37,55} However, there are two different definitions for enthalpy, depending on the thermodynamic conditions.^{1,2,24,56} The “isosteric” enthalpy can be obtained from differentiating isotherms with respect to temperature under constant adsorbed quantity.^{1,2,24,56} The “calorimetric” enthalpy is accessible directly via calorimetry but its link to sorption isotherms is complex.^{1,2,24,56} The multiplicity of definitions regarding enthalpy, as well as the complex interrelationships, posed difficulties to understanding how isotherms change with temperature.^{56–58}

To clarify the mechanism of isotherm’s temperature dependence, the principles of statistical thermodynamics, with a few, generally acceptable assumptions, are necessary. The fluctuation sorption theory,^{4,5} an extension of the fluctuation solution theory^{59–65} to surfaces, is a rigorous theory applicable to any interfacial geometry; its only postulate is that the effect of an interface is confined within a finite distance.⁴ Taking full advantage of rigorous statistical thermodynamics,^{4,5} this paper will clarify the microscopic mechanism of temperature-dependent adsorption. To identify the microscopic mechanism for the existence of the characteristic curve, how sorption depends on temperature and sorbate activity must be explained from a molecular basis. To this end, we have generalized the classical isosteric thermodynamics of sorption into a statistical thermodynamic fluctuation theory. In

this framework, the existence of the characteristic curve, i.e., when sorption depends only on the adsorption potential, will be linked to a relationship between number–number and number–energy fluctuations, and the deviation therefrom can be attributed to the entropic contribution. A simple energetics of sorption will emerge from this linkage, clarifying why the characteristic curves are so common in adsorption phenomena.

THEORY

Our aim for this section is twofold: to clarify the temperature dependence of sorption isotherms from a microscopic basis and to reveal the molecular interactions underlying the characteristic curve in the potential theory of adsorption (or adsorption potential theory). This section provides the theoretical foundation necessary to achieve our twofold aim. First, to clarify the molecular interactions underlying sorption, the statistical thermodynamic fluctuation theory^{4,5} will be extended to incorporate the temperature dependence of sorption. The sorbate number–number correlation and number–energy correlation will be the microscopic basis of how sorption isotherm changes with sorbate activity and temperature. Second, to understand the microscopic basis of the characteristic curve, a link between the potential theory and the statistical thermodynamic fluctuation theory must be established, which requires chemical thermodynamics.

Statistical Thermodynamic Fluctuation Theory. Number–Number Correlation Underlies the Activity Dependence of Adsorption. Let us consider the interface between phases I and II. Phase I is composed of the sorbent (molecular species 1) and phase II is of the sorbate (molecular species 2). The entire system, denoted by *, is composed of I and II, as well as the interface between them. The thermodynamic effect of the interface is the difference between the entire system (*, with the interface) and the reference systems (I + II, without the interface).^{1,3,4,66,67} The three systems are open to both species. We start from the following general thermodynamic relationship without any assumptions to deal with planar and nonplanar interfaces alike^{4,5,65}

$$F = \Omega^* - \Omega^I - \Omega^{II} \quad (1)$$

where the interfacial free energy F (which is conventionally expressed as a product of the interfacial tension and the surface area) is expressed in terms of the difference in the thermodynamic function ($\Omega = -PV$) between the entire system (*) and the two reference systems (I + II) under the conservation of volume.^{4,65} Instead of employing the concentration profile and the Gibbs dividing surface, we perform Legendre transformation, converting the thermodynamic function Ω (open to species 1 and 2) to $Y = \Omega + \mu_1 N_1$ (open to species 2 but closed to 1), as

$$F = Y^* - Y^I - Y^{II} - \mu_1 (N_1^* - N_1^I - N_1^{II}) \quad (2)$$

where μ_1 is the chemical potential of species 1.⁴ Here, we introduce the condition equivalent to the Gibbs dividing surface, $N_1^* - N_1^I - N_1^{II} = 0$ in eq 2. Note that this condition does not require an explicit consideration of the concentration profiles and is applicable to any interfaces regardless of surface geometry.⁴ Equation 2 now becomes

$$F = Y^* - Y^I - Y^{II} \quad (3a)$$

Equation 3a applies to any surface geometry and porosity. Using the corresponding partition functions for the semi-open systems, Γ^* , Γ^I , and Γ^{II} , eq 3a can be rewritten as

$$F = -kT \ln \frac{\Gamma^*}{\Gamma^I \Gamma^{II}} \quad (3b)$$

Equation 3b is our fundamental relationship. Differentiating eq 3b with respect to $\ln a_2$ (a_2 is the activity of sorbate), through elementary statistical thermodynamic calculus, yields the generalized Gibbs adsorption isotherm⁴

$$-\beta \left(\frac{\partial F}{\partial \ln a_2} \right)_T = \langle N_2^* \rangle - \langle N_2^I \rangle - \langle N_2^{II} \rangle \quad (4)$$

where $\langle \rangle$ denotes ensemble average. The only postulate that we need to introduce in our theory is that the effect of an interface is confined within a finite distance from the surface.⁴ Under this postulate, we have shown previously that the Gibbs adsorption isotherm can be expressed as^{4,68}

$$-\beta \left(\frac{\partial F}{\partial \ln a_2} \right)_T = \langle n_2^* \rangle - \langle n_2^I \rangle - \langle n_2^{II} \rangle \quad (5)$$

in terms of the difference in number between the interfacial subsystem, $\langle n_2^* \rangle$, and the reference subsystems I and II, $\langle n_2^I \rangle$ and $\langle n_2^{II} \rangle$, that have the volumes v^I and v^{II} .⁴ From eq 5, we have previously obtained the expression for the sorbate number–number correlation, again under the postulate of the finite-range nature of the interface, whose corollary is that the interfacial sorbate number does not correlate with the bulk sorbate number, leading to sorbate number–number correlation being confined within a finite distance range from the interface.⁴ Since the vapor-phase fluctuation is negligibly small, eq 5 leads to⁴

$$\left(\frac{\partial \langle n_2 \rangle}{\partial \ln a_2} \right)_T = \langle \delta n_2 \delta n_2 \rangle \quad (6)$$

where the asterisk has been omitted for simplicity and will be consistently so from now onward. Since $\delta n_2 = n_2 - \langle n_2 \rangle$, $\langle \delta n_2 \delta n_2 \rangle$ is the sorbate–sorbate number correlation in the presence of the interface.

Number–Energy Correlation Underlies the Temperature Dependence of Sorption. Here we show that understanding the temperature dependence of sorption is related to the number–energy correlation. Differentiating eq 4 with respect to β under constant fugacity yields

$$-\left(\frac{\partial \langle N_2 \rangle}{\partial \beta} \right)_{\lambda_2} = \langle N_2 U \rangle - \langle N_2 \rangle \langle U \rangle \quad (7)$$

where U is the potential energy of the system. This can be derived straightforwardly from the statistical thermodynamic expression for the mean number

$$\langle N_2 \rangle = \frac{\sum_{N_2 \geq 0} N_2 \lambda_2^{N_2} Q(T, V, N_1, N_2)}{\sum_{N_2 \geq 0} \lambda_2^{N_2} Q(T, V, N_1, N_2)} \quad (8)$$

where Q is the canonical partition function. Following our theory of number–number correlation summarized above, here, we introduce the same postulate again, that the effect of the interface is confined within a finite distance.⁵ Consequently, the bulk quantities do not correlate with the

quantities pertaining to the interfacial subsystem. Under this postulate, eq 8 can be rewritten using the number and energy (u) pertaining to the local interfacial subsystem as

$$-\left(\frac{\partial \langle n_2 \rangle}{\partial \beta} \right)_{\lambda_2} = \langle n_2 u \rangle - \langle n_2 \rangle \langle u \rangle \quad (9)$$

Equation 9 can be expressed in an equivalent manner as

$$kT^2 \left(\frac{\partial \ln \langle n_2 \rangle}{\partial T} \right)_{\lambda_2} = - \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \beta} \right)_{\lambda_2} = \frac{\langle \delta n_2 \delta u \rangle}{\langle n_2 \rangle} \quad (10)$$

Adsorption Thermodynamics. Adsorption Potential. Here, we present the isosteric thermodynamics in a form conducive for statistical thermodynamic generalization. First, the “adsorption potential” ϵ , originally introduced by Polanyi,^{1–3,39–41} is defined most commonly in the current literature as

$$\epsilon = -RT \ln a_2 \quad (11)$$

where R is the gas constant. When plotted against the adsorption potential, instead of a_2 , adsorption isotherms measured at different temperatures commonly fall onto the same curve.^{1–3,39–41} This experimental observation is expressed as

$$\frac{\langle n_2 \rangle}{n_1} = f(\epsilon) \quad (12)$$

where f is a function, namely, the characteristic curve. Note that the sorbed quantity per sorbent, $\langle n_2 \rangle / n_1$, has been used as the definition in eq 12. The lack of clarity regarding the theoretical basis of eq 12, together with the long-standing doubts about the physical meaning of eq 11,^{37,46,69} motivates us to construct a statistical thermodynamic generalization of the isosteric thermodynamics of sorption to clarify the existence of the characteristic curve on a molecular scale. To do so, as a first step, let us note that varying T and a_2 under constant ϵ does not change the isotherm because of eq 12. Consequently

$$\delta \epsilon = 0 = \frac{\partial \epsilon}{\partial T} \delta T + \frac{\partial \epsilon}{\partial a_2} \delta a_2 = \frac{\epsilon}{T} \delta T - \frac{RT}{a_2} \delta a_2 \quad (13a)$$

Applying the implicit function theorem^{70,71} on eq 13a yields

$$\left(\frac{\partial a_2}{\partial T} \right)_\epsilon = \frac{a_2 \epsilon}{RT^2} \quad (13b)$$

Noting the equivalence between constant ϵ and constant $\langle n_2 \rangle / n_1$ and using again the definition (eq 11), we obtain

$$\left(\frac{\partial \frac{\epsilon}{T}}{\partial \frac{1}{T}} \right)_{\langle n_2 \rangle / n_1} = \epsilon \quad (14)$$

This left-hand side of eq 14 is reminiscent of the procedure for obtaining the energy from the free energy (ϵ in this case). This derivative is also ϵ ; hence, eq 14 signifies the purely energetic nature of the adsorption potential, ϵ ,^{34,36–41,46,54} which is in agreement with the original assumption by Polanyi.^{1–3,39–41}

Relationship to the Isosteric Thermodynamics of Adsorption. Here, we generalize the above thermodynamic treatment of the adsorption potential when the characteristic curve, eq 12, is not observed. To do so, let us first link the

adsorption potential ϵ to the chemical potential of sorbate, μ_2 , and the standard chemical potential, μ_2^0

$$\mu_2 = \mu_2^0 + RT \ln a_2 = \mu_2^0 - \epsilon \quad (15)$$

Equation 15 makes it clear that the introduction of sorbate–interface interaction lowers the chemical potential by ϵ . The “interaction” here is defined in reference to the standard chemical potential, μ_2^0 , of the saturated vapor. Consequently

$$\epsilon = \mu_2^0 - \mu_2 \quad (16)$$

which signifies the free energy required to move a sorbate molecule to its saturated vapor standard state. Let us now generalize eq 14 to the cases when eq 12 does not apply, i.e., there is no characteristic curve. The following relationship always holds true

$$\epsilon = \left(\frac{\partial \epsilon}{\partial T} \right)_{\langle n_2 \rangle / n_1} + T \left(\frac{\partial \epsilon}{\partial T} \right)_{\langle n_2 \rangle / n_1} \quad (17)$$

Equation 14 is a special case of eq 17, in which $\left(\frac{\partial \epsilon}{\partial T} \right)_{\langle n_2 \rangle / n_1} = 0$,

whose significance can be made clear using the definition of ϵ in eq 16, which yields

$$\left(\frac{\partial \epsilon}{\partial T} \right)_{\langle n_2 \rangle / n_1} = \left(\frac{\partial [\mu_2^0 - \mu_2]}{\partial T} \right)_{\langle n_2 \rangle / n_1} = u_2^0 - u_2 \quad (18a)$$

$$-\left(\frac{\partial \epsilon}{\partial T} \right)_{\langle n_2 \rangle / n_1} = -\left(\frac{\partial [\mu_2^0 - \mu_2]}{\partial T} \right)_{\langle n_2 \rangle / n_1} = s_2^0 - s_2 \quad (18b)$$

where the isosteric energy and entropy (u_2 and s_2), as well as their standard (saturated vapor) counterparts with the superscript 0, are defined as

$$u_2 = \left(\frac{\partial \mu_2}{\partial T} \right)_{\langle n_2 \rangle / n_1}, \quad u_2^0 = \left(\frac{\partial \mu_2^0}{\partial T} \right)_{\langle n_2 \rangle / n_1} \quad (19a)$$

$$s_2 = -\left(\frac{\partial \mu_2}{\partial T} \right)_{\langle n_2 \rangle / n_1}, \quad s_2^0 = -\left(\frac{\partial \mu_2^0}{\partial T} \right)_{\langle n_2 \rangle / n_1} \quad (19b)$$

Thus, the temperature dependence of the adsorption potential, ϵ , has been linked to the isosteric thermodynamic quantities of sorbates.^{47–53} In the language of the isosteric thermodynamics of adsorption, the existence of the characteristic curve (eq 12), under which ϵ is purely energetic (eq 14), leads to $s_2^0 - s_2 = -\left(\frac{\partial \epsilon}{\partial T} \right)_{\langle n_2 \rangle / n_1} = 0$, i.e., the entropic contribution is negligible.

Representing Equilibrium Conditions at the Interface. Let us take solid sorbents for simplicity. According to the Gibbs phase rule, the subsystem composed of the adsorbate + interface is a two-phase system containing two components, leading to 2 degrees of freedom. Two intensive variables, such as (T, μ_2) or (T, ϵ) , can be chosen as the independent variables. In the theory of sorption, $\langle n_2 \rangle / n_1$ is also an intensive quantity within our treatments, which is a function of (T, μ_2) or (T, ϵ) . Consequently, the change of $\langle n_2 \rangle / n_1$ is linked to

$$d \left(\frac{\langle n_2 \rangle}{n_1} \right)_{v, n_1, \mu_2} = \left(\frac{\partial \left(\frac{\langle n_2 \rangle}{n_1} \right)}{\partial T} \right)_{v, n_1, \mu_2} dT + \left(\frac{\partial \left(\frac{\langle n_2 \rangle}{n_1} \right)}{\partial \mu_2} \right)_{v, n_1, T} d\mu_2 \quad (20)$$

Two out of $(T, \mu_2, \langle n_2 \rangle / n_1)$ can be adopted as independent variables for sorption equilibria, and this property will be exploited in the following developments through variable transformations. It should be noted that n_1 is constant throughout our treatments, and n_1 will be omitted from the list of fixed variables in partial differentiation.

RESULTS AND DISCUSSION

Fluctuation Theory of Temperature-Dependent Sorption. Relationship between Number–Number and Number–Energy Correlations. Statistical thermodynamics makes it possible to quantify molecular interactions underlying an isotherm.⁴ In the Theory section, we have shown that sorbate–sorbate interaction (that is, by definition, mediated by the presence of the interface), characterized by number–number and number–enthalpy correlations, determines how an isotherm varies with activity and temperature. Before clarifying the consequence of the existence of the characteristic curve (eq 12) on number–number and number–energy correlations, let us first establish a general relationship between these two correlations, using ϵ as a variable. The sorbate number–number correlation (eq 6) can be expressed as

$$\frac{\langle \delta n_2 \delta n_2 \rangle}{\langle n_2 \rangle} = \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \ln a_2} \right)_T = -kT \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \epsilon} \right)_T \quad (21)$$

which leads to a simple relationship valid for any T . The number–energy correlation, eq 10, can be expressed using ϵ via the change of variables as

$$\begin{aligned} -\frac{\langle \delta n_2 \delta u \rangle}{\langle n_2 \rangle} &= \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \beta} \right)_{\lambda_2} \\ &= \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \beta} \right)_\epsilon + \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \epsilon} \right)_\beta \left(\frac{\partial \epsilon}{\partial \beta} \right)_{\lambda_2} \end{aligned} \quad (22)$$

Note that $\lambda_2 = e^{-\beta \epsilon} e^{\beta \mu_2^0}$. For the first term of the right-hand side, applying the chain rule, as well as eq 18b, it can be rewritten as

$$\begin{aligned} \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \beta} \right)_\epsilon &= -\left(\frac{\partial \ln \langle n_2 \rangle}{\partial \epsilon} \right)_\beta \left(\frac{\partial \epsilon}{\partial \beta} \right)_{\ln \langle n_2 \rangle} \\ &= -kT^2 (s_2^0 - s_2) \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \epsilon} \right)_\beta \end{aligned} \quad (23)$$

The second term of the right-hand side of eq 22 can be simplified via

$$\left(\frac{\partial \epsilon}{\partial \beta} \right)_{\lambda_2} = -\left(\frac{\partial \lambda_2}{\partial \beta} \right)_\epsilon \left(\frac{\partial \epsilon}{\partial \lambda_2} \right)_\beta = \frac{u_2^0 - \epsilon}{\beta} \quad (24a)$$

where u_2^0 is the partial molar energy of saturated vapor. Equation 24a has been derived using the definition of fugacity λ_2

$$\begin{aligned} \left(\frac{\partial \lambda_2}{\partial \beta}\right)_\epsilon &= \left(\frac{\partial}{\partial \beta} e^{\beta(-\epsilon + \mu_2^0)}\right)_\epsilon = \left[-\epsilon + \mu_2^0 + \beta \left(\frac{\partial \mu_2^0}{\partial \beta}\right)\right] \lambda_2 \\ &= (u_2^0 - \epsilon) \lambda_2 \end{aligned} \quad (24b)$$

$$\left(\frac{\partial \lambda_2}{\partial \epsilon}\right)_\beta = \left(\frac{\partial}{\partial \epsilon} e^{\beta(\mu_2^0 - \epsilon)}\right)_\beta = -\beta \lambda_2 \quad (24c)$$

Combining all of the above, we obtain the following result for number–energy correlation

$$-\frac{\langle \delta n_2 \delta u \rangle}{\langle n_2 \rangle} = kT [u_2^0 - \epsilon - T(s_2^0 - s_2)] \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \epsilon}\right)_\beta \quad (25a)$$

Using eq 16, eq 25a can be simplified as

$$-\frac{\langle \delta n_2 \delta u \rangle}{\langle n_2 \rangle} = kT u_2 \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \epsilon}\right)_\beta \quad (25b)$$

Comparing eq 25b with eq 21, we obtain the following relationship between number–number and number–energy correlations

$$\langle \delta n_2 \delta u \rangle = u_2 \langle \delta n_2 \delta n_2 \rangle \quad (26)$$

We emphasize that this linkage between number–energy and number–number correlations originates from the representation of the vapor–interface equilibrium condition with T and ϵ as the independent variables. Note that $s_2^0 - s_2 = 0$ leads to $\left(\frac{\partial \ln \langle n_2 \rangle}{\partial \beta}\right)_\epsilon = 0$ via eq 23, signifying the existence of the characteristic curve. Taken together with our argument in the Theory section, the existence of the characteristic curve has been proven to be equivalent to $s_2^0 - s_2 = 0$.

Isosteric and Partial Molar Energies. In simple terms, eq 26 means that an increase of sorbate number by δn_2 is accompanied by the increment of energy by $\delta u = u_2 \delta n_2$. Here we show that the isosteric energy u_2 is actually the same as the partial molar energy of the sorbate in the interface. To do so, let us start from the expressions for the number–number and number–energy fluctuations, as

$$\left(\frac{\partial \langle n_2 \rangle_{\{T, v, \mu_2\}}}{\partial \mu_2}\right)_{v, T} = \beta \frac{\langle \delta n_2 \delta n_2 \rangle}{\langle n_2 \rangle} \quad (27a)$$

$$\left(\frac{\partial \langle u \rangle_{\{T, v, \mu_2\}}}{\partial \mu_2}\right)_{v, T} = \beta \frac{\langle \delta u \delta n_2 \rangle}{\langle n_2 \rangle} \quad (27b)$$

Combining eqs 27a and 27b yields

$$\frac{\langle \delta u \delta n_2 \rangle}{\langle \delta n_2 \delta n_2 \rangle} = \frac{\left(\frac{\partial \langle u \rangle_{\{T, v, \mu_2\}}}{\partial \mu_2}\right)_{v, T}}{\left(\frac{\partial \langle n_2 \rangle_{\{T, v, \mu_2\}}}{\partial \mu_2}\right)_{v, T}} = \frac{\langle \delta \langle u \rangle_{\{T, v, \mu_2\}} \rangle}{\langle \delta \langle n_2 \rangle_{\{T, v, \mu_2\}} \rangle} \quad (28a)$$

Comparing eq 28a with eq 26 leads to

$$u_2 = \frac{\langle \delta \langle u \rangle_{\{T, v, \mu_2\}} \rangle}{\langle \delta \langle n_2 \rangle_{\{T, v, \mu_2\}} \rangle} \quad (28b)$$

The isosteric energy u_2 is proven to be the partial molar energy of the sorbate through statistical thermodynamics.

Condition for the Existence of the Characteristic Curve. When the sorption isotherms, measured at different temperatures, fall onto a single characteristic curve, eq 12 is satisfied. Under this condition, eq 14 holds true, which is equivalent to $s_2^0 - s_2 = 0$ in eq 18b, leading, via eq 25a, to

$$\langle \delta n_2 \delta u \rangle = (u_2^0 - \epsilon) \langle \delta n_2 \delta n_2 \rangle \quad (29)$$

and eq 28a becomes

$$\delta u = (u_2^0 - \epsilon) \delta n_2 \quad (30)$$

Thus, the characteristic curve is observed when transferring a sorbate molecule from the saturated vapor reference state to interact with the interface reduces the energy simply by the adsorption potential, ϵ .

Temperature Dependence of Sorption Isotherms. *Adsorption Potential Facilitates the Analysis.* The temperature dependence of an isotherm is often invoked for validating the basic assumptions of an isotherm model. However, there are multiple ways to plot isotherms from different temperatures: sorbate activity, a_2 , sorbate pressure, P_2 , and adsorption potential, ϵ , have been used as variables.^{1–3} Here, we show that choosing adsorption potential as the variable facilitates the analysis of the temperature dependence of sorption isotherms. The temperature dependence of the isotherm under constant ϵ can be linked to correlations using the following change of variables⁷¹

$$\left(\frac{\partial \ln \langle n_2 \rangle}{\partial \beta}\right)_\epsilon = \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \beta}\right)_{\lambda_2} + \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \lambda_2}\right)_\beta \left(\frac{\partial \lambda_2}{\partial \beta}\right)_\epsilon \quad (31)$$

The first term on the right-hand side, via eq 10, is related to the number–energy correlation. The second term of eq 31, with the definition $\lambda_2 = e^{\beta(\mu_2^0 - \epsilon)}$, yields

$$\left(\frac{\partial \lambda_2}{\partial \beta}\right)_\epsilon = \left(\mu_2^0 - \epsilon + \beta \left(\frac{\partial \mu_2^0}{\partial \beta}\right)\right) \lambda_2 = (u_2^0 - \epsilon) \lambda_2 \quad (32a)$$

Using eq 32a, we obtain

$$\begin{aligned} \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \lambda_2}\right)_\beta \left(\frac{\partial \lambda_2}{\partial \beta}\right)_\epsilon &= (u_2^0 - \epsilon) \lambda_2 \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \lambda_2}\right)_\beta \\ &= -kT (u_2^0 - \epsilon) \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \epsilon}\right)_\beta \end{aligned} \quad (32b)$$

It should be noted that μ_2^0 is a function only of the temperature. Therefore, combining eqs 31, 32b, 21, and 22 yields

$$\begin{aligned} kT^2 \left(\frac{\partial \ln \langle n_2 \rangle}{\partial T}\right)_\epsilon &= -\left(\frac{\partial \ln \langle n_2 \rangle}{\partial \beta}\right)_\epsilon \\ &= \frac{\langle \delta n_2 \delta u \rangle}{\langle n_2 \rangle} - (u_2^0 - \epsilon) \frac{\langle \delta n_2 \delta n_2 \rangle}{\langle n_2 \rangle} \end{aligned} \quad (33)$$

Since number–number and number–energy correlations are linked via eq 26, with the help of eq 16, we obtain

$$kT^2 \left(\frac{\partial \ln \langle n_2 \rangle}{\partial T} \right)_\epsilon = - \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \beta} \right)_\epsilon = T(s_2 - s_2^0) \frac{\langle \delta n_2 \delta n_2 \rangle}{\langle n_2 \rangle} \quad (34)$$

Thus, adopting the adsorption potential ϵ as the variable facilitates the analysis of the temperature dependence of an isotherm. The key is the increment of entropy, δs , which accompanies the introduction of a sorbate, as

$$\delta s \equiv (s_2 - s_2^0) \delta n_2 \quad (35)$$

Note that δs is defined relative to the saturated vapor, which is different from the definition of δu . The temperature dependence of an isotherm is driven via eq 34 by

$$\langle \delta n_2 \delta s \rangle = (s_2 - s_2^0) \langle \delta n_2 \delta n_2 \rangle \quad (36)$$

The linkage between number–entropy and number–number correlations comes again from the representation of the vapor–interface equilibrium condition with T and ϵ as the independent variables. Here, the isosteric entropy, s_2 , defined by eq 19b is also the partial molar entropy of sorbates under isochoric condition, which is a direct consequence of our proof that the isosteric energy, u_2 , is the isochoric partial molar energy (see eq 28b). Thus, eq 34 signifies that a larger number–entropy correlation leads to a greater variation of $\ln \langle n_2 \rangle$ with temperature. When there is no entropy change, there is no temperature dependence of an isotherm plotted against ϵ , leading to the existence of the characteristic curve.

Sorbate Activity and Partial Pressure Perspectives for the Analysis of Temperature Dependence. We saw that simplicity and clarity are attained using the adsorption potential as a variable, while sorbate activity or pressure may also be used as a variable to describe adsorption. As derived in Appendix A, taking a_2 or P_2 as the variable requires the consideration of $u_2 - u_2^0$ or $u_2 - h_2^{\text{cal}}$, respectively. When a_2 is the variable, the deviation from the "characteristic curve" (when a_2 is chosen as the abscissa) is caused by the energetic contribution. The choice of P_2 as the variable does not lead to a clear-cut interpretation because of the factor $u_2 - h_2^{\text{cal}}$. The adoption of ϵ as the variable has offered a clear link to $s_2 - s_2^0$, the entropy difference between the interface and the saturated vapor, as the cause of temperature dependence. When $s_2 - s_2^0 = 0$, it leads straightway to the existence of the characteristic curve and the lack of temperature-dependent sorption when plotted against ϵ .

Application to Water Vapor Sorption on Porous Carbons. The origin of temperature-dependent sorption, when plotted against the adsorption potential, was attributed to the partial molar entropy of sorbates at the interface. Such a simplification of the question, via statistical thermodynamics, will be beneficial in interpreting challenging sorption behaviors, as will be demonstrated below. We take water vapor adsorption on carbons as our examples: (i) on a bamboo-derived activated carbon, B-AC, by Horikawa et al.⁷² with a broad distribution of pore sizes (Figure 1a) and pitch-based activated carbon fiber, ACF, by Ohba et al.⁷³ which contains slit pores with uniform width (Figure 2a), both plotted against the adsorption potential. B-AC is reported to exhibit pore size distribution ranging broadly from the microporous to mesoporous regions with the microporous peak at around 0.7 nm and another broad distribution ranging between 1 and 3 nm.⁷² ACF, on the other hand, has been reported to have considerably uniform slit pores with a width

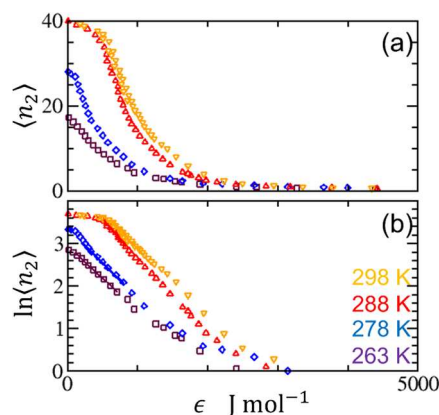


Figure 1. (a) Water vapor adsorption $\langle n_2 \rangle$ on a bamboo-derived activated carbon, B-AC, using the data by Horikawa et al.⁷² measured at 263, 278, 288, and 298 K, plotted against the adsorption potential, ϵ . B-AC is reported to have a broad distribution of pore sizes. (b) Replotting of (a) in terms of $\ln \langle n_2 \rangle$. The gradient was calculated from fitting (solid lines).

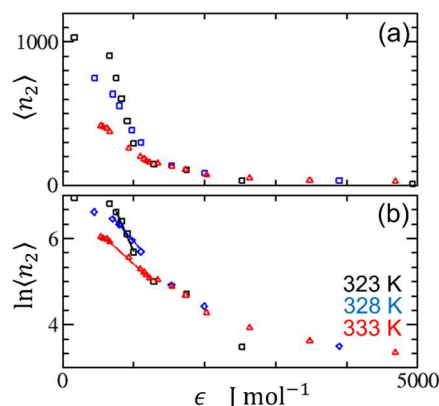


Figure 2. (a) Water vapor adsorption $\langle n_2 \rangle$ on pitch-based activated carbon fiber, ACF, using the data by Ohba et al.⁷³ measured at 323, 328, and 333 K, plotted against the adsorption potential, ϵ . ACF is reported to be with uniform pore width. (b) Replotting of (a) in terms of $\ln \langle n_2 \rangle$. The gradient was calculated from fitting (solid lines).

around 1.1 nm.^{73,74} These two examples exhibit an opposite temperature dependence:⁷⁵ adsorption increases with temperature on B-AC⁷² and decreases on ACF.⁷³ Figures 1b and 2b shows the plots of $\ln \langle n_2 \rangle$ against ϵ for both adsorbents; note that the log plot makes low $\langle n_2 \rangle$ datapoints look more scattered. Since the gradient of a plot of $\ln \langle n_2 \rangle$ against ϵ is $\left(\frac{\partial \ln \langle n_2 \rangle}{\partial \epsilon} \right)_T = -\beta \frac{\langle \delta n_2 \delta n_2 \rangle}{\langle n_2 \rangle} (\equiv -\beta(N_{22} + 1))$ via eq 21, the excess cluster number (i.e., N_{22} , the excess number of sorbates around a probe sorbate, plus 1 including the probe sorbate), $N_{22} + 1$, for ACF has been calculated using eq 21 and Figures 1b and 2b as 10.2 (323 K), 5.2 (328 K), and 4.2 (333 K), whereas for B-AC, the values are 3.3 (263 K), 4.0 (278 K), 4.5 (288 K), and 4.0 (298 K). Our result for ACF at 323 K is close to the estimation based on isosteric enthalpy and simulation, 9.0, by Ohba et al.⁷³ The smaller $N_{22} + 1$ for B-AC is consistent with the report of a peak around a smaller pore size (ca. 0.7 nm) in the pore size distribution.⁷² Note that the excess cluster number depends only weakly with temperature for B-AC (with a broad pore size distribution), whereas the excess cluster number for ACF (with a narrow pore width distribution) decreases significantly with temperature rise.

The difference in the temperature dependence of isotherm and excess cluster number can be rationalized based on the fluctuation theory. However, in experiments, the temperature is not changed in small increments to allow differentiation with respect to it.⁵⁸ Our analysis here will be qualitative. Under constant $\langle n_2 \rangle$, the change $(\delta\epsilon)_{\langle n_2 \rangle}$ is positive for B-AC (Figure 1), negative for ACF (Figure 2). The positive (negative) $(\delta\epsilon)_{\langle n_2 \rangle}$ indicates the positive (negative) entropy difference, $s_2 - s_2^0$, from the saturated vapor. (The signs here are justified by eq 18b). Hence, according to eq 36, the number–entropy correlation is positive for B-AC, negative for ACF. A positive entropy–sorbate number correlation for B-AC is consistent with a broad pore size distribution with a sharp peak in distribution in the microporous region.⁷² While water can form large clusters in mesopores, micropores restrict water cluster size. The water molecules in the micropores are expected to contribute to a positive number–entropy correlation because the addition of water into a micropore already filled with water is possible only by breaking the hydrogen bonding. Moreover, a broad pore size distribution leads to an increasing number of arrangements for the additional water. This rationalizes the positive number–entropy correlation for B-AC. For ACF with the slit-like pores of uniform width, the growth of the water cluster is possible only along the slit pore,⁷³ because the additional water molecule can form hydrogen bonding with the cluster. Consequently, $s_2 - s_2^0$ is negative, which rationalizes the negative number–entropy correlation. Previously, the decrease of water sorption on ACF as the increase of temperature was attributed to the reduction of water cluster stability,⁷³ which is in line with our calculation of excess cluster number. Thus, entropy–number correlation, via eq 34, governs the temperature dependence of sorption, through the entropic cost of introducing another adsorbate.

Note, at large ϵ (or low a_2), the adsorption isotherms $\langle n_2 \rangle$ seem to merge onto the characteristic curve, even though the errors inherent in the small values of $\langle n_2 \rangle$ makes it difficult to be conclusive. (ACF, for example, has been treated to reduce the surface functional groups significantly.⁷³) If it is the case, it follows that the adsorption potential ϵ in this region, which corresponds to the adsorption of water around the residual functional groups,⁷⁶ is predominantly energetic, while the entropic contribution is small, as has been shown above as the condition for the existence of the characteristic curve.

Temperature Dependence in the GAB Model.

Temperature dependence of moisture sorption is an important question in food science, for which the GAB model is routinely used^{8,14,28} beyond its original model assumptions of planar multilayer adsorption.^{4,5} Using the GAB model purely as a fitting equation,^{4,5} here, we apply our theory to elucidate the mechanism of temperature-dependent sorption. As an example, we have chosen the water moisture sorption isotherm of potato starch gel, measured at 303, 318, and 333 K, reported by McMinn et al.⁷⁷ The GAB model^{25–27}

$$\langle n_2 \rangle = \frac{n_m K C a_2}{(1 - K a_2)[1 + (C - 1)K a_2]} \quad (37)$$

where the parameters n_m , K , and C , varying with temperature, were used to fit the isotherms.⁷⁷ Combining eqs 21 and 37, we obtain

$$\begin{aligned} \frac{\langle \delta n_2 \delta n_2 \rangle}{\langle n_2 \rangle} &= \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \ln a_2} \right)_T \\ &= 1 + \frac{K a_2}{1 - K a_2} - \frac{(C - 1)K a_2}{1 + (C - 1)K a_2} \end{aligned} \quad (38)$$

The temperature dependence of the parameters K and C were assumed to be related to the enthalpy-related parameters, ΔH_K and ΔH_C , via $K = K_0 \exp(\beta \Delta H_K)$ and $C = C_0 \exp(\beta \Delta H_C)$, with K_0 and C_0 being the temperature-independent constants.⁷⁷ These relationships are based purely on the assumptions of the GAB model. Combining eqs 37 and 38, with $a_2 = \exp(-\beta\epsilon)$, yields

$$\begin{aligned} \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \beta} \right)_\epsilon &= -\frac{K a_2 (\epsilon - \Delta H_K)}{1 - K a_2} \\ &+ a_2 \frac{(C - 1)K (\epsilon - \Delta H_K) - CK \Delta H_C}{1 + (C - 1)K a_2} - \epsilon \\ &+ \Delta H_C + \Delta H_K - kT^2 \frac{b}{a + bT} \end{aligned} \quad (39)$$

with $n_m = a + bT$. Through eq 34, $T(s_2 - s_2^0)$ can be calculated from eqs 38 and 39, via

$$T(s_2 - s_2^0) = -\frac{\left(\frac{\partial \ln \langle n_2 \rangle}{\partial \beta} \right)_\epsilon}{\frac{\langle \delta n_2 \delta n_2 \rangle}{\langle n_2 \rangle}} \quad (40)$$

Figure 3 shows the temperature dependence of the isotherm, $\langle n_2 \rangle$ and $\ln \langle n_2 \rangle$, plotted against the adsorption potential, ϵ .

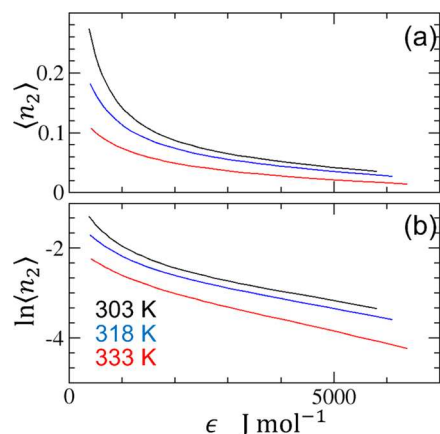


Figure 3. (a) Water vapor adsorption $\langle n_2 \rangle$ on a potato starch gel modeled using the GAB model (eq 37) at 303, 318, and 333 K,⁷⁷ plotted against the adsorption potential, ϵ . The parameters for eq 37 were reported by McMinn et al. (i.e., $n_m = 0.0559$, $C = 13.1$, $K = 0.929$ at 303 K, $n_m = 0.0505$, $C = 10.7$, $K = 0.85$ at 318 K, and $n_m = 0.0355$, $C = 6.26$, $K = 0.767$ at 333 K, with $\text{kg} (\text{kg dry solid})^{-1}$ for the units of n_m).⁷⁷ (b) Replotting of (a) in terms of $\ln \langle n_2 \rangle$.

Figure 4 shows the calculation of $T(s_2 - s_2^0)$ via eq 40. Remembering from the Theory section that $\epsilon = (u_2^0 - u_2) + T(s_2 - s_2^0)$ and that ϵ signifies the transfer of a sorbate from interface to the saturated vapor, the free energy change of a sorbate accompanying sorption, $\mu_2 - \mu_2^0 (= -\epsilon)$, is made up of compensating contributions from a large negative energy change $(u_2 - u_2^0)$ and a large negative entropy change $T(s_2 - s_2^0)$. At low a_2 (namely, high $\epsilon = -RT \ln a_2$, i.e., $\epsilon > 4000 \text{ J}$

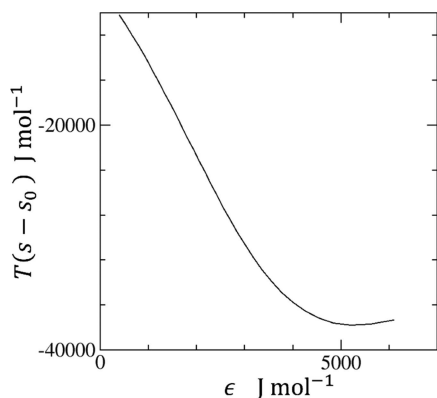


Figure 4. Entropic contribution, $T(s - s_0)$, accompanying the transfer of a sorbate from saturated vapor to the potato starch gel interface, calculated at 318 K via eqs 38–40 and plotted against the adsorption potential, ϵ . The parameters used were reported by McMinn et al.⁷⁷ In addition to the parameters mentioned here, $\Delta H_C = 20.0$, $\Delta H_K = 5.32$ kJ mol⁻¹, $a = 0.2636$, and $b = -0.0007$ kg (kg dry solid)⁻¹.

mol⁻¹), $T(s_2 - s_2^0)$ changes little. This large negative and near-constant $T(s_2 - s_2^0)$ signifies the restriction of the water molecule, which is reminiscent of the “bound water” hypothesis that has been invoked in biophysics and food science.^{78–80} While the increase (i.e., becoming less negative) of $T(s_2 - s_2^0)$ at higher a_2 (i.e., lower ϵ) shows that water molecules are less restricted. This is reminiscent of the oft-used previous speculation of the “free water”,^{78–80} yet our theory can provide quantitative measures on the state of sorbates directly from their isotherms. Thus, the fluctuation theory sheds light on the state of sorbates based on the temperature dependence of sorption isotherms beyond the assumptions made by sorption models.

CONCLUSIONS

Sorption isotherms exhibit temperature dependence when plotted against sorbate activity. However, the isotherms from different temperatures very commonly fall onto a single “characteristic curve” when plotted against the adsorption potential.^{39–41} Ambiguity surrounding the theoretical foundation of the potential theory has long prevented a clear identification of the underlying mechanism.

To overcome this difficulty, the classical isosteric thermodynamics of sorption has been reformulated within a general framework of the statistical thermodynamic fluctuation theory in combination with an assumption regarding the finite-ranged nature of the interface.⁴ In this framework, the molecular energetics underlying the existence of the characteristic curve is the linkage between sorbate number–number and number–energy correlations, i.e., each incoming adsorbate brings in its partial molar energy without any entropic contributions. The characteristic curve thus guarantees the purely energetic behavior of sorbates at the interface.

When sorption at different temperatures does not fall onto a characteristic curve, each incoming sorbate brings in entropy also, giving rise to number–entropy correlation, which makes sorption temperature-dependent. Our theory was able to rationalize why activated carbons with uniform pore sizes exhibit the opposite temperature dependence of water vapor sorption from those with a broad pore size distribution and to reveal the state of water sorbed on a starch gel. The theory

presented here is based on the principles of statistical thermodynamics and independent of model assumptions.

Appendix A: Choice of a_2 or P_2 as the Variable for Sorption Isotherm

Here, we show that a_2 or P_2 (partial pressure of sorbates), when chosen as the variable, leads to a complicated picture for the temperature dependence of the isotherm.

Sorbate Activity, a_2 . The change of variables in partial differentiation yields

$$\left(\frac{\partial \ln \langle n_2 \rangle}{\partial \beta}\right)_{a_2} = \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \beta}\right)_{\lambda_2} + \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \lambda_2}\right)_{\beta} \left(\frac{\partial \lambda_2}{\partial \beta}\right)_{a_2} \quad (\text{A.1})$$

Using the definition of fugacity,⁸¹ $\left(\frac{\partial \lambda_2}{\partial \beta}\right)_{a_2}$ can be evaluated as

$$\left(\frac{\partial \lambda_2}{\partial \beta}\right)_{a_2} = \left(\frac{\partial}{\partial \beta} a_2 e^{\beta \mu_2^0}\right)_{a_2} = u_2^0 \lambda_2 \quad (\text{A.2})$$

Consequently, the second term of eq A.1 becomes

$$\left(\frac{\partial \ln \langle n_2 \rangle}{\partial \lambda_2}\right)_{\beta} \left(\frac{\partial \lambda_2}{\partial \beta}\right)_{a_2} = \frac{u_2^0}{\beta} \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \mu_2}\right)_{\beta} = u_2^0 \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \ln a_2}\right)_{\beta} \quad (\text{A.3})$$

Combining eqs A.1 and A.3 with the definitions of number–number and number–energy correlations (eqs 6 and 10), we obtain

$$\begin{aligned} kT^2 \left(\frac{\partial \ln \langle n_2 \rangle}{\partial T}\right)_{a_2} &= - \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \beta}\right)_{a_2} \\ &= \frac{\langle \delta n_2 \delta u \rangle}{\langle n_2 \rangle} - u_2^0 \frac{\langle \delta n_2 \delta n_2 \rangle}{\langle n_2 \rangle} \end{aligned} \quad (\text{A.4})$$

Through the relationship between number–number and number–energy correlations (eq 26), eq A.3 can be rewritten as

$$kT^2 \left(\frac{\partial \ln \langle n_2 \rangle}{\partial T}\right)_{a_2} = - \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \beta}\right)_{a_2} = (u_2 - u_2^0) \frac{\langle \delta n_2 \delta n_2 \rangle}{\langle n_2 \rangle} \quad (\text{A.5})$$

Sorbate Partial Pressure, P_2 . The change of variables in partial differentiation yields

$$\left(\frac{\partial \ln \langle n_2 \rangle}{\partial \beta}\right)_{P_2} = \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \beta}\right)_{\lambda_2} + \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \lambda_2}\right)_{\beta} \left(\frac{\partial \lambda_2}{\partial \beta}\right)_{P_2} \quad (\text{A.6})$$

Using the definition of fugacity,⁸¹ $\left(\frac{\partial \lambda_2}{\partial \beta}\right)_{P_2}$ can be evaluated as

$$\left(\frac{\partial \lambda_2}{\partial \beta}\right)_{P_2} = \left(\frac{\partial e^{\beta \mu_2}}{\partial \beta}\right)_{P_2} = \left(\mu_2 + \beta \left(\frac{\partial \mu_2}{\partial \beta}\right)_{P_2}\right) \lambda_2 = h_2^{(\text{cal})} \lambda_2 \quad (\text{A.7})$$

where we have introduced the partial molar entropy and enthalpy, which are referred to as the “calorimetric” quantities in the adsorption literature, as

$$h_2^{(\text{cal})} = \left(\frac{\partial \mu_2}{\partial T}\right)_{P_2}, \quad s_2^{(\text{cal})} = - \left(\frac{\partial \mu_2}{\partial T}\right)_{P_2} \quad (\text{A.8})$$

Combining eqs A.6 and A.7 with the definitions of number–number and number–energy correlations (eqs 6 and 10), we obtain

$$kT^2 \left(\frac{\partial \ln \langle n_2 \rangle}{\partial T} \right)_P = - \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \beta} \right)_P = \frac{\langle \delta n_2 \delta u \rangle}{\langle n_2 \rangle} - h_2^{(\text{cal})} \frac{\langle \delta n_2 \delta n_2 \rangle}{\langle n_2 \rangle} \quad (\text{A.9})$$

Combining eq A.9 with the relationship between the two correlations (eq 26), we obtain

$$kT^2 \left(\frac{\partial \ln \langle n_2 \rangle}{\partial T} \right)_P = - \left(\frac{\partial \ln \langle n_2 \rangle}{\partial \beta} \right)_P = (u_2 - h_2^{(\text{cal})}) \frac{\langle \delta n_2 \delta n_2 \rangle}{\langle n_2 \rangle} \quad (\text{A.10})$$

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Notes

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