# **Chapter 2**

# **Physical Adsorption**

The literature pertaining to the sorption of gases by solids is now so vast that it is impossible for any, except those who are specialists in the experimental technique, rightly to appraise the work, which has been done, or to understand the main theoretical problems which require elucidation. – J. E. Lennard-Jones,  $1932^{1}$ 

Adsorption is the phenomenon marked by an increase in density of a fluid near the surface, for our purposes, of a solid.<sup>\*</sup> In the case of gas adsorption, this happens when molecules of the gas occasion to the vicinity of the surface and undergo an interaction with it, temporarily departing from the gas phase. Molecules in this new condensed phase formed at the surface remain for a period of time, and then return to the gas phase. The duration of this stay depends on the nature of the adsorbing surface and the adsorptive gas, the number of gas molecules that strike the surface and their kinetic energy (or collectively, their temperature), and other factors (such as capillary forces, surface heterogeneities, etc.). Adsorption is by nature a surface phenomenon, governed by the unique properties of bulk materials that exist only at the surface due to bonding deficiencies.

<sup>&</sup>lt;sup>\*</sup> Adsorption may also occur at the surface of a liquid, or even between two solids.

The sorbent surface may be thought of as a two-dimensional potential energy landscape, dotted with wells of varying depths corresponding to adsorption sites (a simplified representation is shown in Figure 2.1). A single gas molecule incident on the surface collides in one of two fundamental ways: elastically, where no energy is exchanged, or inelastically, where the gas molecule may gain or lose energy. In the former case, the molecule is likely to reflect back into the gas phase, the system remaining unchanged. If the molecule lacks the energy to escape the surface potential well, it becomes adsorbed for some time and later returns to the gas phase. Inelastic collisions are likelier to lead to adsorption. Shallow potential wells in this energy landscape correspond to weak interactions, for example by van der Waals forces, and the trapped molecule may diffuse from well to well across the surface before acquiring the energy to return to the gas phase. In other cases, deeper wells may exist which correspond to stronger interactions, as in chemical bonding where an activation energy is overcome and electrons are transferred between the surface and the adsorbed



Figure 2.1. A potential energy landscape for adsorption of a diatomic molecule on a periodic two-dimensional surface. The depth of the energy well is shown in the z-axis.

molecule. This kind of well is harder to escape, the chemically bound molecule requiring a much greater increase in energy to return to the gas phase. In some systems, adsorption is accompanied by absorption, where the adsorbed species penetrates into the solid. This process is governed by the laws of diffusion, a much slower mechanism, and can be readily differentiated from adsorption by experimental means.

In the absence of chemical adsorption (chemisorption) and penetration into the bulk of the solid phase (absorption), only the weak physical adsorption (physisorption) case remains. The forces that bring about physisorption are predominantly the attractive "dispersion forces" (named so for their frequency dependent properties resembling optical dispersion) and short-range repulsive forces. In addition, electrostatic (Coulombic) forces are responsible for the adsorption of polar molecules, or by surfaces with a permanent dipole. Altogether, these forces are called "van der Waals forces," named after the Dutch physicist Johannes Diderik van der Waals.

## 2.1 Van der Waals Forces

An early and profoundly simple description of matter, the ideal law can be elegantly derived by myriad approaches, from kinetic theory to statistical mechanics. First stated by Émile Clapeyron in 1834, it combines Boyle's law (PV = constant) and Charles's law (stating the linear relationship between volume and temperature) and is commonly expressed in terms of Avogadro's number, n:

PV = nRT

Equation 2.1

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This simple equation describes the macroscopic state of a three-dimensional gas of non-interacting, volumeless point particles. The gas constant, *R*, is the fundamental link between microscopic energy and macroscopic temperature. While satisfactory for describing common gases at low pressures and high temperatures, it is ineffective for real gases over a wide temperature and pressure regime. A better approximation was determined by van der Waals, combining two important observations:<sup>2</sup> a) the volume excluded by the finite size of real gas particles must be subtracted, and b) an attractive force between molecules effects a decreased pressure. The suggestion of an excluded real gas volume was made earlier by Bernoulli and Herapath, and confirmed experimentally by Henri Victor Regnault, but the attractive interactions between molecules was the important contribution by van der Waals. The change in pressure due to intermolecular forces is taken to be proportional to the square of the molecular density, giving the van der Waals equation of state:

$$\left(P + a\frac{n^2}{V^2}\right)(V - n b) = n R T$$

Equation 2.2

At the time, van der Waals was adamant that no repulsive forces existed between what he reasoned were "hard sphere" gas particles. Interestingly, it was James Clerk Maxwell who completed and popularized van der Waals' (then obscure) work in *Nature*<sup>3</sup> and also who later correctly supposed that molecules do not in fact have a "hard sphere" nature. Nevertheless, the sum of the attractive and repulsive forces between atoms or molecules are now collectively referred to as "van der Waals forces." Forces

between any electrically neutral atoms or molecules (thereby excluding covalent, ionic, and hydrogen bonding) conventionally fall into this category. Together, these include: Keesom forces (between permanent multipoles), Debye forces (between a permanent multipole and an induced multipole), London dispersion forces (between two induced multipoles), and the Pauli repulsive force.

## 2.1.1 Intermolecular Potentials

In his time, the range of van der Waals' attractive interaction was predicted to be of molecular scale but the form of the potential as a function of distance, U(r), was unknown. There was unified acceptance that the attraction potential fell off with distance as  $r^{-\eta}$ , with  $\eta > 2$  (the value for that of gravitation), but the value of  $\eta$  was actively debated.

In parallel with the effort to determine this potential, a noteworthy advance in the general description of equation of state was the "virial expansion" by H. K. Onnes:<sup>4</sup>

$$\frac{PV}{nRT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \cdots$$

Equation 2.3

Perhaps most importantly, this description signified a realization of the unlikelihood that all gases could be accurately described by a simple closed form of equation. Additionally, the second virial coefficient, B(T), by its nature a first-neighbor term of interaction, sheds insight on the attractive potential between molecules. A major breakthrough followed, culminating in the theory now attributed to Sir John Edward Lennard-Jones, an English theoretical physicist. His description of the potential energy

between two interacting non-polar molecules used  $\eta = 6$  and a repulsive term of order 12:<sup>5, 6</sup>

$$U(r) = -\left(\frac{c_1}{r}\right)^6 + \left(\frac{c_2}{r}\right)^{12}$$

Equation 2.4

The result constitutes a balance between the longer range attractive van der Waals potential (of order  $r^{-6}$ ) with the short-range repulsive potential arising from electron orbital overlap (of order  $r^{-12}$ ), described by the Pauli exclusion principle, and is also referred to as a 6-12 potential. It approximates empirical data for simple systems with gratifying accuracy, and has the added advantage that it is computationally efficient since  $r^{-12}$  is easily calculated as  $r^{-6}$  squared, an important consideration in its time. A representative plot of this potential is shown in Figure 2.2.



Figure 2.2. The Lennard-Jones 6-12 potential, scaled in units of  $U_0$ , the depth of the well. The equilibrium distance between the interacting species is  $r = r_0$ .

At far distances ( $r >> r_0$ ), the magnitude of the interaction potential is negligible. If the species become spontaneously closer together (e.g., as the result of random collision), it is favorable for them to remain at a specific distance apart, namely  $r = r_0$ . At very short distance, the Pauli repulsion term dominates and the system is unfavorable.

A number of similar potential forms arose shortly afterward (using various forms for the Pauli repulsion term such as an exponential or other power of order near 12), and an early triumph of these models was accurately fitting the second virial coefficient of simple gases, such as helium for which the equilibrium He-He distance was calculated to be  $r_0 = 2.9$  Å in 1931. This value remains accurate within 2% today.

Coincidentally, Lennard-Jones' work was originally undertaken to attempt to explain a puzzling observation made during volumetric adsorption measurements of hydrogen on nickel,<sup>Z, §</sup> showing two distinct characteristic binding potentials associated with different temperature regimes. This would lead to the first explanation of the differentiable nature of adsorption at low and high temperature (now referred to separately as physisorption and chemisorption, respectively). As a result of its success, the Lennard-Jones inverse seventh-power force (from the inverse sixth-power potential) became the backbone of adsorption theory.

#### 2.1.2 Dispersion Forces

The  $-r^{-6}$  Lennard-Jones potential was derived from first-principles and first explained correctly by the German physicist Fritz London;<sup>9, 10</sup> hence, the attractive force that occurs between neutral, non-polar molecules is called the "London dispersion force." It is a weak, long-range, non-specific intermolecular interaction arising from the induced polarization between two species, resulting in the formation of instantaneous electrical multipole moments that attract each other. Arising by rapid, quantum induced fluctuations of the electron density within a molecule or atom (the reason they were coined as "dispersive" forces by London), the force is stronger between larger species due to those species' increased polarizability. The key to the correct explanation of dispersion forces is in quantum mechanics; without the uncertainty principle (and the fundamental quantum-mechanical property of zero-point energy), two spherically symmetric species with no permanent multipole could not influence a force on each other and would remain in their classical rest position. The subject of dispersion forces is important to many fields, and a thorough overview of their modern theory can be found elsewhere.<sup>11</sup>

The physisorption of nonpolar molecules or atoms on a nonpolar surface (as well as their liquefaction) occurs exclusively by dispersion forces. Dispersion forces are also essential for explaining the total attractive forces between multipolar molecules (e.g., H<sub>2</sub>) for which typical static models of intermolecular forces (e.g., Keesom or Debye forces) account for only a fraction of the actual attractive force. The existence of "noble liquids" (liquefied noble gases) is a fundamental verification of dispersion forces since there is no other attractive intermolecular force between noble gas atoms that could otherwise explain their condensation.

## 2.1.3 Modern Theory of Physical Adsorption

Despite their correct explanation over 80 years ago, dispersion forces are not well simulated by typical computational methods, such as density-functional theory which cannot accurately treat long-range interactions in weakly bound systems.<sup>12</sup> The firstprinciples methods that are dependable are computationally intensive and are often foregone for empirical potentials such as a Lennard-Jones potential as described in the previous section.<sup>13, 14</sup> For this reason, the ab-initio guidance of the design of physisorptive materials has been much less than that for chemisorptive materials, and was not a component of the work described in this thesis.

## 2.2 Gas-Solid Adsorption Models

A thermodynamic understanding of adsorption can be achieved by describing a simplified system, and a small subset of important models will be discussed. The constituent chemical species of the simplest system are a pure solid, indexed as *s*, and a single-component adsorptive gas, indexed as *a* in the adsorbed phase, *g* in the gas phase, or *x* if it is ambiguous. The system is held at fixed temperature and pressure. We start with the following description:

- (i) the adsorptive density,  $\rho_x$ , is zero within and up to the surface of a material,
- (ii) at the material surface and beyond,  $\rho_x$  is an unknown function of r, the distance from the surface, and
- (iii) at distance from the surface,  $\rho_x$  is equal to the bulk gas density,  $\rho_q$ .



Figure 2.3. A simplified representation of a gas-solid adsorption system (left) and a nonadsorbing reference system of the same volume (right). Adsorptive density (green) is plotted as a function of *r*.

A schematic of this system is shown in Figure 2.3 (left). The functional form of the densification at the sorbent surface, and the thickness of the adsorption layer are not precisely known. However, the adsorbed amount can be defined as the quantity existing in much higher density near the surface, and is easily discerned when compared to the reference case of a non-adsorptive container, shown in Figure 2.3 (right). We may assume that the gas pressure,  $P_g$ , is equal to the total hydrostatic pressure, P, of the system at equilibrium, which is consistent with ordinary experimental conditions.

#### 2.2.1 Monolayer Adsorption

The simplest representation of an adsorbed phase is as an ideal gas, constrained to a two-dimensional monolayer where there is no interaction between adsorbed molecules:

$$P_a A_a = n_a R T$$

Equation 2.5

Here,  $P_a$  is the spreading pressure of the adsorption layer and  $A_a$  is its area of coverage. In the system described, the surface area for adsorption is fixed, as well as the temperature. If we take the spreading pressure as proportional to that of the gas phase in equilibrium with it, we find that the amount adsorbed is a linear function of pressure:

$$n_a = \frac{P_a A_a}{R T} = \frac{c P A_a}{R T} = k_H P$$

Equation 2.6

This relationship, called Henry's law, is the simplest description of adsorption, and applies to systems at low relative occupancy. When occupancy increases, the relationship between the pressures of the adsorbed phase and the gas phase becomes unknown, and a more general treatment is necessary.

A first approximation of an imperfect two-dimensional gas may be made by adapting the van der Waals equation of state to two dimensions:

$$\left(P_a + a\frac{n_a^2}{A_a^2}\right)(A_a - n_a b) = n_a R T$$

Equation 2.7

For simplicity, it is convenient to define a fractional coverage of the surface available for adsorption,  $\theta$ , as the number of adsorbed molecules per surface site, a unitless fraction that can also be expressed in terms of relative surface area:

$$\theta = \frac{n_a}{n_{sites}} = A_{site} \frac{n_a}{A_a}$$

Equation 2.8

With this definition, and a more elegant description of the spreading pressure of the van der Waals two-dimensional phase, the Hill-de Boer equation is derived:

$$P = \frac{\theta}{k_H (1-\theta)} e^{\left(\frac{\theta}{(1-\theta)} - k_2 \theta\right)}$$

Equation 2.9

This equation has been shown to be accurate for certain systems, up to a maximum coverage of  $\theta = 0.5$ .<sup>15</sup> Ultimately though, treatment of the adsorbed phase without reference to its interaction with the surface encounters difficulties.

A more insightful approach is to treat adsorption and desorption as kinetic processes dependent on an interaction potential with the surface, also seen as an energy of adsorption. In dynamic equilibrium, the exchange of mass between the adsorption layer and the bulk gas phase can be treated by kinetic theory; at a fixed pressure, the rate of adsorption and desorption will be equal, resulting in an equilibrium monolayer coverage. This equilibrium can be described by the following scheme:

$$X_g + empty \ site \leftrightarrow X_a$$

The rate (where adsorption is taken to be an elementary reaction) is given by the (mathematical) product of the concentrations of the reactants,  $c_i$ , and a reaction constant, K(T):

$$r_{ads} = K_{ads} c_g c_{empty site}$$

Equation 2.10

Correspondingly, for the reverse (desorption) reaction:

 $r_{des} = K_{des} c_a$ 

Equation 2.11

We can assume that the number of adsorption sites is fixed, so the concentration of adsorbed molecules and empty adsorption sites is complementary. To satisfy equilibrium, we set Equations 2.10 and 2.11 equal and express them in terms of the fractional occupancy, recognized as equivalent to  $c_a$ :

$$r_{eq} = r_a = K_{ads} c_g (1 - \theta) = r_d = K_{des} \theta$$
$$\theta = \frac{K_{ads} c_g}{K_{des} + K_{ads} c_g} = \frac{\frac{K_{ads}}{K_{des}} c_g}{1 + \frac{K_{ads}}{K_{des}} c_g}$$

Equation 2.12

To express the temperature dependence of the reaction constants, we can use an Arrhenius-type equation:

$$K_i = \frac{A_i}{\sqrt{T}} \ e^{\left(\frac{-E_i}{RT}\right)}$$

Equation 2.13

The ratio of the adsorption and desorption constants is:

$$K = \frac{K_{ads}}{K_{des}} = \frac{A_{ads}}{A_{des}} e^{\left(\frac{E_g - E_a}{RT}\right)} = A e^{\left(\frac{-\Delta E}{RT}\right)}$$

If the gas phase is assumed to be ideal, its concentration is proportional to pressure, P. Secondly, if we assume that the energy of the adsorbed molecule,  $E_a$ , is the same at every site, and the change in energy upon adsorption,  $\Delta E$ , is independent of surface coverage, the result is Langmuir's isotherm equation:

$$\theta = \frac{KP}{1 + KP}$$

Equation 2.14

The Langmuir isotherm, in the context of its inherent assumptions, is applicable over the entire range of  $\theta$ . Plots of multiple Langmuir isotherms with varying energies of adsorption are shown in Figure 2.4 (right). In the limit of low pressure, the Langmuir isotherm is equivalent to Henry's law:

$$\lim_{P \to 0} \frac{KP}{1 + KP} = \frac{KP}{1} = KP$$

Equation 2.15

The plots in Figure 2.4 show the temperature and energy dependence of the Langmuir isotherm equation. With increasing temperature, the Henry's law region is marked by more gradual uptake, a similar trend as for decreasing energy of adsorption; both trends are consistent with experiment (in systems referred to as exhibiting type-I isotherms).



Figure 2.4. Langmuir isotherms showing the dependence of adsorption site occupancy with pressure, varying temperature (left) and energy of adsorption (right).

Although it enjoys quantitative success in characterizing adsorption in limited ranges of pressure for certain systems, conformity of experimental systems to the Langmuir equation is not predictable, and does not necessarily coincide with known properties of the system (such as expected homogeneity of adsorption sites, or known adsorbate-adsorbate interactions).<sup>16</sup> No system has been found which can be characterized by a single Langmuir equation with satisfactory accuracy across an arbitrary range of pressure and temperature.<sup>15</sup> Langmuir's model assumes: 1) the adsorption sites are identical, 2) the energy of adsorption is independent of site occupancy, and 3) both the two- and three-dimensional phases of the adsorptive are well approximated as ideal gases. Numerous methods have been suggested to modify the Langmuir model to generalize its assumptions for application to real systems.

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For heterogeneous surfaces with a distribution of adsorption sites of different characteristic energies, one possibility is to superimpose a set of Langmuir equations, each corresponding to a different type of site. This generalized-Langmuir equation can be written as:

$$\theta = \sum_{i} \alpha_{i} \left( \frac{K_{i} P}{1 + K_{i} P} \right)$$
$$\sum_{i} \alpha_{i} = 1$$

Equation 2.16

The weight of each component isotherm,  $\alpha_i$ , corresponds to the fraction of sites with the energy  $E_i$ . This form of Langmuir's equation is applicable across a wide range of experimental systems, and can lend insight into the heterogeneity of the adsorbent surface and the range of its characteristic binging energies. Its treatment of adsorption sites as belonging to a two-dimensional "monolayer" can be made completely general; the adsorption layer can be understood as any set of equally accessible sites within the adsorption volume, assuming the volume of gas remains constant as site occupancy increases (an assumption that is valid when  $\rho_a >> \rho_g$ ). The application of this equation for high-pressure adsorption in microporous materials is discussed in Section 2.4.6.

#### 2.2.2 Multilayer Adsorption

A practical shortcoming of Langmuir's model is in determining the surface area available for adsorption. Typically, fitting experimental adsorption data to a Langmuir equation results in an overestimation of the surface area.<sup>16</sup> The tendency of experimental isotherms toward a non-zero slope in the region beyond the "knee" indicates that adsorption occurs in two distinct phases: a primary phase, presumably adsorption on homogeneous adsorption sites at the sorbent surface, and a secondary phase corresponding to adsorption in layers beyond the surface of the adsorbent.

An adaptation of Langmuir's model can be made which accounts for multiple, distinct layers of adsorption. A characteristic of adsorption in a multilayer system is that each layer corresponds to a different effective surface, and thus a different energy of adsorption. The distinction between the multilayer class of systems and a generalizedmonolayer system (such as in Equation 2.16) lies in the description of the adsorbent surface; even a perfectly homogeneous surface is susceptible to a multiple layers of adsorption, an important consideration at temperatures and pressures near the saturation point. Brunauer, Emmett, and Teller successfully adapted the Langmuir model to multilayer adsorption by introducing a number of simplifying assumptions.<sup>17</sup> Most importantly, 1) the second, third, and i<sup>th</sup> layers have the same energy of adsorption, notably that of liquefaction, and 2) the number of layers as the pressure approaches the saturation pressure, P<sub>0</sub>, tends to infinity and the adsorbed phase becomes a liquid. Their equation, called the BET equation, can be derived by extending Equation 2.12 to i layers, where the rate of evaporation and condensation between adjacent layers is set equal. Their summation leads to a simple result:

$$\theta = \frac{c_{BET} \frac{P}{P_0}}{\left(1 - \frac{P}{P_0}\right) \left(1 - \frac{P}{P_0} + c_{BET} \frac{P}{P_0}\right)}$$

Equation 2.17

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If the Arrhenius pre-exponential factors  $A_1/A_2$  and  $A_2/A_1$  (from Equation 2.13) are approximately equal, a typical assumption, <sup>16</sup> the parameter  $c_{BET}$  can be written:

$$c_{BET} = e^{\frac{(\Delta E_1 - \Delta E_l)}{RT}}$$

Equation 2.18

The change in energy upon adsorption in any of the layers beyond the surface layer is taken as the energy of liquefaction, and the difference in the exponent in Equation 2.18 is referred to as the net molar energy of adsorption. Strictly within BET theory, no allowance is made for adsorbate-adsorbate interactions or different adsorption energies at the surface, assumptions that prevent the BET model from being applied to general systems and across large pressure ranges of adsorption.

The BET equation was specifically developed for characterizing adsorption in a gassolid system near the saturation point of the adsorptive gas for the practical purpose of determining the surface area of the solid adsorbent. Despite its narrow set of defining assumptions, its applicability to experimental systems is remarkably widespread. As a result, it is the most widely applied of all adsorption models, even for systems with known insufficiencies to meet the required assumptions. Nitrogen adsorption at 77 K up to  $P_0$  = 101 kPa has become an essential characterization technique for porous materials, and the BET model is commonly applied to determine the surface available for adsorption, called the BET surface area. Even for microporous adsorbents where the BET assumptions are highly inadequate, this is the most common method for determination of specific surface area, and its deficiencies are typically assumed to be similar between comparable materials. The BET surface area of a material can be determined by fitting experimental adsorption data to Equation 2.17 and determining the monolayer capacity,  $n_{sites}$ . Typically, N<sub>2</sub> adsorption data are plotted in the form of the linearized-BET equation, a rearrangement of Equation 2.17:

$$\frac{n_a}{n_{sites}} = \frac{c_{BET} \frac{P}{P_0}}{\left(1 - \frac{P}{P_0}\right) \left(1 - \frac{P}{P_0} + c_{BET} \frac{P}{P_0}\right)}$$
$$B_{BET} = \frac{\frac{P}{P_0}}{n_a \left(1 - \frac{P}{P_0}\right)} = \frac{\left(1 - \frac{P}{P_0} - c_{BET} \frac{P}{P_0}\right)}{c_{BET} n_{sites}} = \frac{1}{c_{BET} n_{sites}} + \frac{c_{BET} - 1}{c_{BET} n_{sites}} \frac{P}{P_0}$$

Equation 2.19

The BET variable,  $B_{BET}$ , is plotted as a function of  $P/P_0$  and if the data are satisfyingly linear, the slope and intercept are used to determine  $n_{sites}$  which is proportional to the surface area as stated in Equation 2.8 (using  $A_{sites} = 16.2 \text{ Å}^2$ )<sup>16</sup>. In practice, the linearity of the BET plot of a nitrogen isotherm at 77 K may be limited to a small range of partial pressure. An accepted strategy is to fit the low-pressure data up to and including a point referred to as "point B," the end of the characteristic knee and the start of the linear region in a Type II isotherm.<sup>15, 16</sup>

## 2.2.3 Pore-Filling Models

The Langmuir model, and its successive adaptations, were developed in reference to an idealized surface which did not have any considerations for microstructure, such as the presence of narrow micropores, which significantly change the justifiability of the assumptions of monolayer and multilayer adsorption. While numerous advances have been made in adsorption theory since the BET model, a notable contribution was by Dubinin and collaborators to develop a pore-filling theory of adsorption. Their success at overcoming the inadequacies of layer theories at explaining nitrogen adsorption in highly microporous media, especially activated carbons, is highly relevant. The Dubinin-Radushkevich (DR) equation, describing the fractional pore occupancy  $\theta_{pore}$ , is stated as:

$$\theta_{pore} = \frac{W}{W_0} = e^{\left(-B\left(\frac{T}{\beta}\right)^2 \log^2\left(\frac{P}{P_0}\right)\right)}$$

Equation 2.20

The DR equation can be used for determining DR micropore volume,  $W_0$ , in an analogous way as the Langmuir or BET equation for determining surface area. Its similarities to BET analyses are discussed in Appendix D.

## 2.2.4 Gibbs Surface Excess

Measurements of adsorption near or above the critical point, either by volumetric (successive gas expansions into an accurately known volume containing the adsorbent) or gravimetric (gas expansions into an enclosed microbalance containing the adsorbent) methods, have the simple shortcoming that they cannot directly determine the adsorbed amount. This is readily apparent at high pressures where it is observed that the measured uptake amount increases up to a maximum and then decreases with increasing pressure. This is fundamentally inconsistent with the Langmuir model of adsorption, which predicts a monotonically increasing adsorption quantity as a function of pressure. The reason for the discrepancy can be traced to the finite volume of the adsorbed phase, shown in Figure 2.3. The "free gas" volume displaced by the adsorbed phase would have contained an amount of gas given by the bulk gas density even in the absence of adsorption. Therefore, this amount is necessarily excluded from the measured adsorption amount since the gas density, measured remotely, must be subtracted from in the entire void volume, such that adsorption is zero in the "reference state" which does not have any adsorption surface.

In the landmark paper of early thermodynamics, On the Equilibrium of *Heterogeneous Substances*,<sup>18</sup> Josiah Willard Gibbs gave a simple geometrical explanation of the excess quantity adsorbed at the interface between two bulk phases, summarized for the gas-solid case in Figure 2.5. The absolute adsorbed amount, shown in purple, is subdivided into two constituents: *reference* molecules shown in light blue, existing within the adsorbed layer but corresponding to the density of the bulk gas far

from the surface, and *excess* molecules shown in dark blue, the measured quantity of adsorption. The Gibbs definition of excess adsorption,  $n_e$ , as a function of absolute adsorption,  $n_a$ , is:

$$n_e = n_a - V_{ads} \,\rho(P,T)$$

Equation 2.21

Any measurement of gas density far from the surface cannot account for the existence of the reference molecules near the surface; these would be present in the reference system. The excess quantity, the amount in the densified layer that is in excess of the bulk gas density, is the experimentally accessible value. It is simple to show that the excess uptake is approximately equal to the absolute quantity at low pressures. As the bulk gas density increases, the difference between excess and absolute adsorption increases. A state may be reached at high pressure,  $P_3$  in Figure 2.5, where the increase in adsorption density is equal to the increase in bulk gas density, and thus the excess quantity reaches a maximum. This point is referred to as the Gibbs excess maximum. Beyond this pressure, the excess quantity may plateau or decline, a phenomenon readily apparent in the high-pressure data presented in this thesis.



Figure 2.5. The Gibbs excess adsorption is plotted as a function of pressure (center). A microscopic representation of the excess (light blue), reference (dark blue), and absolute (combined) quantities is shown at five pressures,  $P_1$ - $P_5$ . The bulk gas density (gray) is a function of the pressure, and depicted as a regular pattern for clarity. The volume of the adsorbed phase, unknown experimentally, is shown in purple (top).

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## 2.3 Adsorption Thermodynamics

## 2.3.1 Gibbs Free Energy

Adsorption is a spontaneous process and must therefore be characterized by a decrease in the total free energy of the system. When a gas molecule (or atom) is adsorbed on a surface, it transitions from the free gas (with three degrees of translational freedom) to the adsorbed film (with two degrees of translational freedom) and therefore loses translational entropy. Unless the adsorbed state is characterized by a very large additional entropy (perhaps from vibrations), it follows that adsorption must always be exothermic ( $\Delta H_{ads} < 0$ ) since:

$$\Delta G_{ads} = \Delta H_{ads} - T \Delta S_{ads} < 0$$
$$\Delta H_{ads} = H_a - H_g$$

Equation 2.22

We refer to the Gibbs free energy, *G*, since it governs thermodynamic systems at constant temperature and pressure, the variables held constant during equilibrium gas adsorption measurements. The chemical potential in each phase is defined as:

$$\mu_a = \left(\frac{\partial G_a}{\partial n_a}\right)_{T,P}$$
$$\mu_g = \left(\frac{\partial G_g}{\partial n_g}\right)_{T,P}$$

Equation 2.23

We have assumed that the thermodynamic properties of the solid surface remain unchanged upon adsorption, an approximation that serves us well for this purpose. Let us assume that the system is held in a constant temperature bath, and we have instantaneously adjusted the pressure of the system at a location remote to the adsorbent surface by adding  $dn_g$  molecules of gas. The adsorbed phase and the bulk gas phase are not in equilibrium, and will proceed to transfer matter in the direction of lower free energy, resulting in adsorption. When equilibrium is reached, the chemical potential of the gas phase and the adsorbed phase are equal, since:

$$dG = (\mu_a - \mu_g)dn_a = 0$$
$$\mu_a = \mu_g$$

Equation 2.24

Determining the change in chemical potential, or the Gibbs free energy, of the adsorptive species as the system evolves toward equilibrium is essential to a fundamental understanding of adsorptive systems for energy storage or other engineering applications. We develop this understanding through the experimentally accessible components of the Gibbs free energy:  $\Delta H_{ads}$  and  $\Delta S_{ads}$ .

#### 2.3.2 Entropy of Adsorption

We take the total derivative of both sides of Equation 2.24, and rearrange to arrive at the classic Clausius-Clapeyron relation:

$$-s_a dT + v_a dP = -s_g dT + v_g dP$$
$$\frac{dP}{dT} = \frac{(s_g - s_a)}{(v_g - v_a)}$$

Equation 2.25

where:

$$s_i = \left(\frac{\partial S}{\partial n_i}\right)_{T,P} \quad v_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P}$$

The specific volume of the free gas is usually much greater than that of the adsorbed gas, and a robust<sup>19</sup> approximation simplifies the relation:

$$v_g - v_a \approx v_g$$

Equation 2.26

$$\frac{dP}{dT} = \frac{\left(s_g - s_a\right)}{v_g} = -\left(s_a - s_g\right)\rho_g$$

We rearrange to derive the common equation for change in entropy upon adsorption:

$$\Delta S_{ads}(n_a) = -\left(\frac{dP}{dT}\right)_{n_a} \rho_g^{-1}$$

Equation 2.27

## 2.3.3 Enthalpy of Adsorption

At equilibrium, the corresponding change in enthalpy upon adsorption is:

$$\Delta H_{ads}(n_a) = T \Delta S_{ads} = -T \left(\frac{dP}{dT}\right)_{n_a} \rho_g^{-1}$$

Equation 2.28

We refer to this as the "common" enthalpy of adsorption. To simplify further, we must specify the equation of state of the bulk gas phase. The ideal gas law is commonly used, a suitable equation of state in limited temperature and pressure regimes for typical gases (the limitations of which are investigated in Section 2.4.1). For an ideal gas:

$$\rho_g = \frac{n_g}{V_g} = \frac{P}{R T}$$

$$\Delta H_{ads}(n_a) = -T \left(\frac{dP}{dT}\right)_{n_a} \frac{RT}{P} = -\frac{RT^2}{P} \left(\frac{dP}{dT}\right)_{n_a}$$

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This is often rearranged in the van't Hoff form:

$$\Delta H_{ads}(n_a) = R\left(\frac{d\ln P}{d\left(\frac{1}{T}\right)}\right)_{n_a}$$

Equation 2.30

The isosteric heat of adsorption, a commonly reported thermodynamic quantity, is given a positive value:<sup>\*</sup>

$$q_{st}(n_a) = -\Delta H_{ads}(n_a) = -R\left(\frac{d\ln P}{d\left(\frac{1}{T}\right)}\right)_{n_a} > 0$$

Equation 2.31

For adsorption at temperatures or pressures outside the ideal gas regime, the density of the bulk gas phase is not easily simplified, and we use the more general relationship:

$$q_{st}(n_a) = T \left(\frac{dP}{dT}\right)_{n_a} \rho_g^{-1}$$

Equation 2.32

If the excess adsorption,  $n_e$ , is substituted for the absolute quantity in the equations above, the result is called the "isoexcess heat of adsorption":

$$q_{st}(n_e) = T\left(\frac{dP}{dT}\right)_{n_e} \rho_g^{-1}$$

<sup>&</sup>lt;sup>\*</sup> It is typical to report the "isosteric enthalpy of adsorption" in this way as well, and for our purpose, "increasing enthalpy" refers to the increase in magnitude of the enthalpy, or most specifically, the increase in the heat of adsorption.

It is common to include the ideal gas assumption in the isoexcess method since the assumptions are valid in similar regimes of temperature and pressure, giving:

$$q_{st}(n_e) = -R\left(\frac{d\ln P}{d\left(\frac{1}{T}\right)}\right)_{n_e}$$

Equation 2.34

For cases where the adsorptive is in a regime far from ideality, it is sometimes necessary to use a better approximation for the change in molar volume specified in Equation 2.26. For example, gaseous methane at high pressures and near-ambient temperatures (near-critical) has a molar volume approaching that of liquid methane. Therefore, a more general equation must be used, and here we suggest to approximate the molar volume of the adsorbed phase as that of the adsorptive liquid at 0.1 MPa,  $v_{liq}$ :

$$v_g - v_a \approx v_g - v_{liq}$$

Equation 2.35

$$\frac{dP}{dT} = \frac{\left(s_g - s_a\right)}{v_g} = -\frac{\left(s_a - s_g\right)}{\left(v_g - v_{liq}\right)}$$

This gives the following equations for the isosteric and isoexcess heat of adsorption:

$$q_{st}(n_a) = T\left(\frac{dP}{dT}\right)_{n_a} \left(v_g - v_{liq}\right)$$

Equation 2.36

$$q_{st}(n_e) = T\left(\frac{dP}{dT}\right)_{n_e} \left(\nu_g - \nu_{liq}\right)$$

In summary:

Assumptions:	Isosteric Method	Isoexcess Method ( $n_a \approx n_e$ )
Ideal Gas $v_g \gg v_a$	$\Delta S_{ads}(n_a) = \frac{R}{T} \left( \frac{d \ln P}{d \left( \frac{1}{T} \right)} \right)_{n_a}$ $q_{st}(n_a) = -R \left( \frac{d \ln P}{d \left( \frac{1}{T} \right)} \right)_{n_a}$ Eq. 2.31	$\Delta S_{ads}(n_e) = \frac{R}{T} \left( \frac{d \ln P}{d \left( \frac{1}{T} \right)} \right)_{n_e}$ $q_{st}(n_e) = -R \left( \frac{d \ln P}{d \left( \frac{1}{T} \right)} \right)_{n_e}$ Eq. 2.34
Non-ideal Gas $v_g \gg v_a$	$\Delta S_{ads}(n_a) = -\left(\frac{dP}{dT}\right)_{n_a} \rho_g^{-1}$ $q_{st}(n_a) = T\left(\frac{dP}{dT}\right)_{n_a} \rho_g^{-1}$ Eq. 2.32	$\Delta S_{ads}(n_e) = -\left(\frac{dP}{dT}\right)_{n_e} \rho_g^{-1}$ $q_{st}(n_e) = T\left(\frac{dP}{dT}\right)_{n_e} \rho_g^{-1}$ Eq. 2.33
Non-ideal Gas $v_a pprox v_{liq}$	$\Delta S_{ads}(n_a) = -\left(\frac{dP}{dT}\right)_{n_a} \left(v_g - v_{liq}\right)$ $q_{st}(n_a) = T\left(\frac{dP}{dT}\right)_{n_a} \left(v_g - v_{liq}\right)$ Eq. 2.36	$\Delta S_{ads}(n_e) = -\left(\frac{dP}{dT}\right)_{n_e} \left(v_g - v_{liq}\right)$ $q_{st}(n_e) = T\left(\frac{dP}{dT}\right)_{n_e} \left(v_g - v_{liq}\right)$ Eq. 2.37

The Henry's law value of the isosteric enthalpy of adsorption,  $-\Delta H_0$ , is calculated by extrapolation of the adsorption enthalpy to zero uptake:

$$-\Delta H_0 = \lim_{n \to 0} \left( -\Delta H_{ads}(n) \right)$$

A common technique for determining the enthalpy of adsorption in the ideal gas approximation is to plot  $\ln P$  as a function of  $T^{-1}$ , a van't Hoff plot, and to find the slope of the line along each isostere (corresponding to a fixed value of *n*). If the data are linear in a certain range of  $T^{-1}$ , the enthalpy of adsorption is determined to be temperature independent in that range, corresponding to the average temperature:

$$T_{avg} = \frac{2}{\left(\frac{1}{T_{max}} + \frac{1}{T_{min}}\right)}$$

Equation 2.39

If the slope is nonlinear, a subset of the data between two temperatures,  $T_1$  and  $T_2$ , is found where the slope is approximately linear. A difference of 10 K is considered to be acceptable for most purposes.<sup>15</sup> Inside this "window," the average temperature is:

$$T_{window} = \frac{2}{\left(\frac{1}{T_1} + \frac{1}{T_2}\right)}$$

Equation 2.40

With a series of windows, a temperature dependence of the data can be determined within the range of temperatures collected.

## 2.4 Thermodynamic Calculations from Experimental Data

Simplicity and accuracy are desired in solving the thermodynamic relations derived in Section 2.3 for calculating the entropy and enthalpy of adsorption from experimental data. The limitations of the two most commonly applied simplifications, the ideal gas and isoexcess assumptions, are discussed in Sections 2.4.1-2.

The primary obstacles to a completely assumptionless derivation of the thermodynamic quantities of interest are twofold. Most importantly, both the isosteric and isoexcess treatments require tabulations of the equilibrium pressure, or ln *P*, at fixed values of uptake,  $n_a$  or  $n_e$ . Experimentally, it is possible to control P and measure the amount adsorbed, but exceedingly difficult to fix the adsorbed quantity and measure the equilibrium pressure. Therefore, a fitting equation is often used to interpolate the measured values. The interpolation of adsorption data is very sensitive to the fitting method chosen, and small deviations from the true value cause significant errors in thermodynamic calculations.<sup>20-22</sup> Sections 2.4.3-6 discuss the use of the data with and without a fitting equation, and compare the results across three types of model-independent fitting equations in an effort to determine the most accurate methodology for calculating thermodynamic quantities of adsorption.

Secondly, the determination of the absolute quantity of adsorption requires a model which defines the volume of the adsorbed phase as a function of pressure and temperature in the system. Numerous methods have been suggested to define it, and a successful model is presented in Section 2.5. The data used for the comparisons is methane adsorption on superactivated carbon MSC-30, a standard carbon material whose properties are thoroughly discussed in Chapters 4-6. It is a well characterized material with traditional sorbent properties and a large surface area (giving a large signal to noise ratio in measurements of its adsorption uptake). The data set consists of 13 isotherms between 238-521 K, and spans pressures between 0.05-9 MPa, as shown in Figure 2.6.



Figure 2.6. Equilibrium adsorption isotherms of methane on MSC-30 between 238-521 K, the test data for thermodynamic calculations of adsorption.

#### 2.4.1 Ideal Gas Assumption

The ideal gas law is defined by two main approximations: that the gas molecules do not interact or have inherent volume. In the limit of zero pressure, all gases tend toward ideality since they are dilute enough that interactions are improbable and the total volume of the system is approximately unchanged by including the molecules in it. For hydrogen, the ideal gas law holds approximately true for a large pressure and temperature regime around ambient; for example, the error in density is only 6% even at 10 MPa and 298 K (see Figure 2.7a). However, at low temperatures and high pressures that are desired in many adsorption applications, non-ideality of the gas phase is strikingly apparent for most common gases. Figure 2.7b shows the density of methane as a function of pressure at various temperatures of interest for storage applications. The very significant non-ideality of both hydrogen and methane is apparent at room temperature and elevated pressures. In addition, each gas shows significant non-ideality in their respective low temperature regimes of interest for storage applications, even at low pressures. This is an issue for most adsorptive gases since the latent heat of physical adsorption is very close to that of liquefaction.

The van der Waals equation of state predicts a density for hydrogen and methane that is generally an acceptable approximation of the true density at pressures up to 10 MPa, as shown in Figure 2.8. For hydrogen at 77 K, the error in density is less than 0.4% between 0-5 MPa, an acceptable figure for isosteric heat calculations, and much improved compared to the 4.5% error in the ideal gas density. Ultimately, real gases exhibit properties that cannot be accurately modeled in our pressure and temperature regime of interest by any simple means. The most accurate pure fluid model available at this time is the 32-term modified Benedict-Webb-Rubin (mBWR) equation of state.<sup>23</sup> For this work, we refer to the mBWR model, as implemented by the REFPROP standard reference database,<sup>24</sup> as the "real gas" equation of state.



Figure 2.7. A comparison of ideal gas density (dotted lines) to (a) hydrogen and (b) methane at various temperatures, and pressures up to 100 MPa.



Figure 2.8. A comparison of the ideal gas, van der Waals (vdW) gas, and real (mBWR) gas density of methane and hydrogen at 298 K between 0-100 MPa.

#### 2.4.2 Isoexcess Assumption

For thermodynamic or other calculations from experimental adsorption data at sufficiently low pressures, such as in determining BET surface area, the measured (excess) quantity of adsorption (from Equation 2.21) suffices for approximating the total adsorption amount. However, this assumption quickly becomes invalid even at relatively modest pressures and especially at low temperatures where the gas density is high compared to the density of the adsorbed layer. <sup>20, 21</sup>

Nevertheless, the simplest approach to thermodynamic calculations using experimental isotherm data is to proceed with the measured excess uptake quantity,  $n_e$ , in place of the absolute adsorption quantity,  $n_a$ . Since the volume of adsorption is fundamentally unknown, a model is required to determine the absolute adsorption amount, a task that is beyond the scope of many adsorption studies. This shortcut is valid in the low coverage limit since, from Equation 2.21, if the pressure of the gas approaches zero:

$$\lim_{P \to 0} (n_a) = \lim_{P \to 0} (n_e + \rho_g V_{ads}) = n_e + 0 = n_e$$

Equation 2.41

This approach can therefore be effective for approximating the "Henry's law" value of the isosteric enthalpy of adsorption. However, it leads to significant errors in determining the dependence of the enthalpy on uptake (discussed further in Section 2.4.3-5) and any isoexcess enthalpy of adsorption values calculated at coverages higher than  $n_e/n_{max} = 0.5$  should only be accepted with great caution.

#### 2.4.3 Calculations Without Fitting

Controlling the pressure of experimental measurements is possible, but it proves very difficult to perform experiments at specific fixed quantities of uptake. By coincidence, such as in a large data set like the one used in this comparison, it may happen that numerous data points lie at similar values of excess adsorption, and analysis of the isosteric enthalpy of adsorption may be performed without fitting. The van't Hoff plot of these coincidentally aligned points is shown in Figure 2.9.



Figure 2.9. The van't Hoff plot of the (unfitted) methane uptake data at particular values of excess adsorption on MSC-30. The dashed colored lines, from blue to orange, indicate the temperatures of the isotherms from 238-521 K, respectively.



Figure 2.10. The average isoexcess enthalpy of adsorption calculated over the entire temperature range of data shown in Figure 2.9, 238-521 K.

Since the experimental quantity is excess adsorption, the isoexcess method must be used; the resulting isoexcess enthalpy of adsorption is shown in Figure 2.10. This method is severely limited since it relies on the statistical probability of two data points lying on the same isostere in the van't Hoff plot. This likelihood is dramatically less at high uptake where only low temperature data are available, and requires intense experimental effort to be accurate. The "fixed" values of  $n_e$  are necessarily approximated (in this case, ±0.05 mmol g<sup>-1</sup>) and the absolute adsorbed amount is not used, resulting in a significant, unphysical divergence at high values of uptake. Nonetheless, without any fitting equation or model, we achieve an acceptable determination of the Henry's law value of the enthalpy of methane adsorption on MSC-30 (as an average over the entire temperature range): 15 kJ mol<sup>-1</sup> at  $T_{avg} = 310$  K.

#### 2.4.4 Linear Interpolation

A primitive method for fitting the experimental adsorption data is by linear interpolation. This method does not require any fitting equation and is the simplest approach to determining values of *P* at specific fixed values of  $n_e$  to be used in the isoexcess method. The MSC-30 data set fitted by linear interpolation and the resulting van't Hoff plot is shown in Figure 2.11. The data are often apparently linear for analysis across the entire range of  $n_e$ , but are limited to the values of  $n_e$  where there are multiple measured points (favoring the measurements at low uptake and low temperature). Additionally, at high values of  $n_e$  the isoexcess approximation becomes invalid, or  $n_e \neq$  $n_a$ , and errors become larger as  $n_e$  increases.

To calculate the enthalpy of adsorption, the isoexcess method is used because the absolute adsorption is unknown; the results are shown in Figure 2.12. The average enthalpy of adsorption over the entire data set (where  $T_{avg} = 310$  K) is plotted at the top. The temperature dependent results are plotted at top, middle, and bottom, using windows of sizes 3, 5, and 7 temperatures, respectively. The colors from blue to orange represent the average temperatures of each window, from low to high. Two observations may be made: there is no significant trend of the temperature dependence of the data, and increasing the window size has the effect of decreasing outliers but not elucidating any further insight into the thermodynamics of adsorption in this system. As before, the enthalpy of adsorption diverges at high values of uptake where the isoexcess approximation is invalid ( $n_e > 10$ ) and cannot be regarded as accurate.



Figure 2.11. Linear interpolation of the experimental (excess) uptake data of methane on MSC-30 (top), and the corresponding van't Hoff plot showing the relative linearity of the data even using this primitive fitting technique (bottom). The colored lines, from blue to orange, indicate the temperatures of the measurements from 238-521 K, respectively.



Figure 2.12. Isoexcess enthalpy of adsorption of methane on MSC-30, using linear interpolation fits and 3- (top), 5- (middle), and 7- (bottom) temperature windows. A calculation over all data (a single 13-temperature window) is also shown (dashed black).

#### 2.4.5 Virial Type Fitting Equation

Numerous equations have been suggested to fit experimental adsorption data for thermodynamic calculations. The most common is to fit the data with a model-independent virial-type equation<sup>25</sup> and proceed with the Gibbs excess quantities,  $n_e$ , as directly fitted. The advantages to this method are that the number of fitting parameters is easily adjusted to suit the data. The fitting equation has the form:

$$\ln\left(\frac{P}{n_e}\right) = \frac{1}{T}\sum_i a_i n_e^{i} + \sum_i b_i n_e^{i}$$

Equation 2.42

The parameters  $a_i$  and  $b_i$  are temperature independent, and optimized by a least squares fitting algorithm. The experimental data of methane adsorption on MSC-30 are shown in Figure 2.13, fitted using first, third, and fifth order terms (with 4, 8, and 12 independent parameters, respectively). It can be observed that the data are very poorly fitted beyond the Gibbs excess maximum and cannot be used. In addition, as the number of fitting parameters is increased, a well-known limitation of polynomial fitting occurs: a curvature is introduced between data points. However, the isoexcess method is never employed beyond the Gibbs excess maximum, and an analogous plot of optimized fits of only selected data is shown in Figure 2.14. The data are well approximated even for i = 1, but some improvement is gained for i = 3. There is no significant improvement by adding parameters to i = 5. The data are well fitted at low temperatures up to ~4 MPa and at all pressures for isotherms at and above 340 K.

The enthalpy of adsorption is calculated by the isoexcess method, using:

$$-\Delta H_{ads}(n_e) = -R\left(\frac{d\ln P}{d\left(\frac{1}{T}\right)}\right)_{n_e} = \sum_i a_i n_e^{it}$$

Equation 2.43

The functional form of the enthalpy is that of an *i*<sup>th</sup> order polynomial. Therefore, if only first order parameters are used, the enthalpy will be a straight line (as shown in Figure 2.15). This is acceptable for some purposes, but allows little potential insight to the true dependence of the enthalpy on uptake. A fit using higher order terms may be preferred for that reason. Nevertheless, in this comparison, third order terms do not lend any significant contribution to the analysis (see Figure 2.16). The Henry's law value of the enthalpy calculated in Equation 2.43 is:

$$-\Delta H_0 = \lim_{n \to 0} \left( \sum_i a_i n_e^i \right) = a_0$$

Equation 2.44

The fits of select data give values of the Henry's law enthalpy in the range of 13.5-17.5 kJ mol<sup>-1</sup>. Since the parameters are constant with temperature, it is not possible to determine the temperature dependence of the isoexcess enthalpy with a single fitting equation, and it is often assumed to be negligible. If a moving window method is employed, a temperature dependence is accessible, but does not yield any significant trends in this case (for windows of 3 temperatures, with i = 1 or i = 3) as shown in Figures 2.15-16. All calculations show an increasing isoexcess enthalpy of adsorption except for small windows of isotherms using only first order fits, and overall, this fitting methodology is unsatisfactory for analyzing methane adsorption on MSC-30.



Figure 2.13. First- (top), third- (middle), and fifth-order (bottom) virial-equation fits of methane adsorption uptake on MSC-30 between 238-521 K, fitting the *complete* data set including the uptake beyond the Gibbs excess maximum.



Figure 2.14. First- (top), third- (middle), and fifth-order (bottom) virial-equation fits of methane adsorption uptake on MSC-30 between 238-521 K, fitting *only the data below the Gibbs excess maximum*.



Figure 2.15. Isoexcess enthalpy of adsorption, using first-order virial equation fits and 3temperature windows. Also shown is the result for a first-order virial equation fit using the entire data set, a 13-temperature (13T) single window. The calculated enthalpies are compared to those for a generalized-Langmuir fit (given in Section 2.5).



Figure 2.16. Isoexcess enthalpy of adsorption, using third-order virial equation fits and 3temperature windows. Also shown is the result for a third-order virial equation fit using the entire data set, a 13-temperature (13T) single window. The calculated enthalpies are compared to those for a generalized-Langmuir fit (given in Section 2.5).

### 2.4.6 Generalized-Langmuir Fitting Equation

A major limitation of the virial-type equation is that it does not accurately interpolate the data at high adsorption uptake in the near- or supercritical regime where the maximum in Gibbs excess is a prominent feature of the data. Another approach is to incorporate the Gibbs definition (Equation 2.21) of adsorption into the fitting equation, which can be done in a model-independent way.

An effective strategy is to choose a functional form for  $n_a$  that is monotonically increasing with pressure, consistent with the physical nature of adsorption.<sup>20</sup> The Langmuir isotherm is one example, although others have been suggested (e.g., Langmuir-Freundlich,<sup>21</sup> Unilan,<sup>22</sup> and Toth<sup>26</sup> equations). If an arbitrary number of Langmuir isotherms are superpositioned, referred to as a generalized-Langmuir equation, the number of independent fitting parameters can be easily tuned to suit the data. Langmuir was the first to generalize his equation for a heterogeneous surface consisting of numerous different adsorption sites of different characteristic energies.<sup>27</sup> Implementing the generalized-Langmuir model (Equation 2.16) in a model-independent way, absolute adsorption takes the form:

$$n_{a}(P,T) = c_{n} \sum_{i} \alpha_{i} \left( \frac{K_{i} P}{1 + K_{i} P} \right)$$
$$\sum_{i} \alpha_{i} = 1$$

Equation 2.45

The volume of adsorption in the Gibbs equation also has a pressure dependence that is fundamentally unknown, but which is generally accepted to be monotonically increasing in most systems. It too can be approximated by a generalized-Langmuir equation, simplifying the final equation and keeping the number of parameters low:

$$V_{ads}(P,T) = c_V \sum_i \alpha_i \left(\frac{K_i P}{1 + K_i P}\right)$$

Equation 2.46

The excess adsorption data are then fitted to:

$$n_e(P,T) = c_n \sum_i \alpha_i \left(\frac{K_i P}{1 + K_i P}\right) - \left(c_V \sum_i \alpha_i \left(\frac{K_i P}{1 + K_i P}\right)\right) \rho(P,T)$$
$$n_e(P,T) = \left(c_n - c_V \rho(P,T)\right) \left(\sum_i \alpha_i \left(\frac{K_i P}{1 + K_i P}\right)\right)$$

Equation 2.47

The  $K_i$  are equivalent to the equilibrium constants of adsorption in the classical Langmuir model, but are not required to have physical meaning for this purpose. They can be taken as constant with pressure, but having a dependence on temperature similar to Equation 2.13:

$$K_i = \frac{C_i}{\sqrt{T}} e^{\frac{E_i}{RT}}$$

Equation 2.48

The fitting parameters ( $c_n$ ,  $c_v$ ,  $\alpha_i$ ,  $C_i$ , and  $E_i$ ) are constants. If the ideal gas law applies to the pressure and temperature regime of interest, the equation simplifies:

$$n_e(P,T) = \left(c_n - c_V \frac{P}{RT}\right) \left(\sum_i \alpha_i \left(\frac{K_i P}{1 + K_i P}\right)\right)$$



Figure 2.17. Double-Langmuir fit of methane uptake on MSC-30 using the ideal gas law.

The experimental data fitted by a double-Langmuir isotherm (i = 2) with the ideal gas assumption are shown in Figure 2.17. For all but the highest pressures, the data are well approximated by this method. The curvature of the interpolation between points, even near or at the Gibbs excess maximum, is representative of the physical nature of the system, and the extrapolation to high pressures shows much improved behavior compared to the previous fitting methods. A limitation of the ideal gas assumption is that the excess uptake isotherms cannot cross at high pressure, the lowest temperature data decreasing proportionally with pressure. This is not consistent with experimental results where it frequently occurs that low temperature data falls significantly below higher temperature data at the same pressure. This phenomenon is entirely due to nonideal gas interactions from a nonlinear change in gas density, and can be accounted for by using the more general form of the excess adsorption (Equation 2.47). Data fitted using 1, 2, and 3 superimposed Langmuir isotherms (with 4, 7, and 10 independent parameters, respectively) and using the mBWR gas density are shown in Figure 2.18.



Figure 2.18. Single- (top), double- (middle), and triple- (bottom) Langmuir equation fits of methane adsorption uptake on MSC-30 between 238-521 K.

The double-Langmuir fit is satisfactory for thermodynamic calculations, and is the preferred method in this study. The triple-Langmuir fit is not significantly improved to justify the addition of 3 independent fitting parameters. The extrapolation of the data to high pressures shows behavior consistent with other experimental results of hydrogen and methane adsorption at low temperature.

## 2.5 Generalized-Langmuir High-Pressure Adsorption Model

To understand the true thermodynamic quantities of adsorption from experimentally measured adsorption data, a model is necessary to determine the absolute adsorption amount as a function of pressure. The necessary variable that remains unknown is the volume of the adsorption layer and numerous methods have been suggested to estimate it. Typical methods include fixing the volume of adsorption as the total pore volume of the sorbent material,<sup>20</sup> using a volume proportional to the surface area (assuming fixed thickness),<sup>28</sup> or deriving the volume by assuming the adsorbed layer is at liquid density.<sup>29</sup> Some approaches are specific to graphite-like carbon materials, such as the Ono-Kondo model.<sup>30, 31</sup> The most general approach is to let the adsorption volume be an independent parameter of the fitting equation of choice, equivalent to the parameter  $c_V$  in the model-independent treatment above.

The generalized-Langmuir equation<sup>20</sup> (as shown in Section 2.4.6) and numerous others (e.g., Langmuir-Freundlich,<sup>21</sup> Unilan,<sup>22</sup> and Toth<sup>26</sup> equations) have been shown to be suitable fitting equations for determining absolute adsorption from excess uptake isotherms since they are monotonically increasing and contain a relatively small number

of fitting parameters to achieve a satisfactory fit to the experimental data. We consider the following fitting equation for Gibbs excess adsorption as a function of pressure, identical in form to the model-independent equation above (Equation 2.47):

$$n_e(P,T) = \left(n_{max} - V_{max} \,\rho(P,T)\right) \left(\sum_i \alpha_i \,\left(\frac{K_i \,P}{1 + K_i \,P}\right)\right)$$
$$K_i = \frac{A_i}{\sqrt{T}} e^{\frac{E_i}{RT}} \qquad \sum_i \alpha_i = 1$$

The minimum number of independent parameters is desired, and we find that i = 2 yields satisfying results across a number of materials in supercritical adsorption studies of both methane and hydrogen (where the regime beyond the excess maximum is well-characterized), giving the reduced equation:

$$n_e(P,T) = \left(n_{max} - V_{max}\,\rho(P,T)\right) \left((1-\alpha)\,\left(\frac{K_1\,P}{1+K_1\,P}\right) + \alpha\,\left(\frac{K_2\,P}{1+K_2\,P}\right)\right)$$

Equation 2.51

Equation 2.50

We have found that the assumption that the total adsorption volume scales proportionally with site occupancy is robust, and this fitting equation has been shown to be successful for both carbonaceous (see Chapter 6) and MOF materials.<sup>20</sup> We refer to this method as the double-Langmuir method, and if the absolute quantity of adsorption is held constant, it yields the true isosteric quantities of adsorption. The absolute quantity, from the Gibbs definition, is:

$$n_a(P,T) = n_{max} \left( (1-\alpha) \left( \frac{K_1 P}{1+K_1 P} \right) + \alpha \left( \frac{K_2 P}{1+K_2 P} \right) \right)$$

The fractional site occupancy, also called the surface coverage, is:

$$\theta(P,T) = (1-\alpha) \left(\frac{K_1 P}{1+K_1 P}\right) + \alpha \left(\frac{K_2 P}{1+K_2 P}\right)$$

Equation 2.53

Least squares fits of methane uptake on MSC-30 to the double-Langmuir equation are shown in Figure 2.19, the fitted excess adsorption (left) and calculated absolute adsorption (right) at all temperatures measured. The goodness of fit is satisfactory across the entire range of temperature and pressure, with a residual sum of squares less than 0.04 mmol g<sup>-1</sup> per data point. The optimal fitting parameters for MSC-30 are given in Table 5.2, and their relation to the materials properties is discussed in Section 5.2.3.



Figure 2.19. Double-Langmuir equation fits of methane adsorption uptake on MSC-30 between 238-521 K, showing calculated excess uptake (left) and calculated absolute uptake (right) as solid lines, and the measured excess uptake data as filled diamonds (left and right).

To derive the isosteric enthalpy from the generalized Langmuir equation, the derivative of pressure with respect to temperature is decomposed as follows:

$$\left(\frac{\partial P}{\partial T}\right)_{n_{a}} = \left(\frac{\partial \theta}{\partial P}\right)_{n_{a}}^{-1} \sum_{i} \left(\frac{\partial \theta}{\partial K_{i}}\right)_{n_{a}} \left(\frac{\partial K_{i}}{\partial T}\right)_{n_{a}}$$

Equation 2.54

From Equations 2.50-53, the respective components of the derivative are given by:

$$\begin{split} \left(\frac{\partial\theta}{\partial P}\right)_{n_{a}} &= \left(\frac{\partial}{\partial P}\right)_{n_{a}} \left((1-\alpha)\left(\frac{K_{1}P}{1+K_{1}P}\right) + \alpha\left(\frac{K_{2}P}{1+K_{2}P}\right)\right) \right) \\ &= \left((1-\alpha)\left(\frac{K_{1}}{(1+K_{1}P)^{2}}\right) + \alpha\left(\frac{K_{2}}{(1+K_{2}P)^{2}}\right)\right) = X^{-1} \\ &\left(\frac{\partial\theta}{\partial K_{1}}\right)_{n_{a}} = (1-\alpha)\left(\frac{P}{(1+K_{1}P)^{2}}\right) = Y_{1} \\ &\left(\frac{\partial\theta}{\partial K_{2}}\right)_{n_{a}} = \alpha\left(\frac{P}{(1+K_{2}P)^{2}}\right) = Y_{2} \\ &\left(\frac{\partial K_{i}}{\partial T}\right)_{n_{a}} = \left(\frac{\partial}{\partial T}\right)_{n_{a}} \left(\frac{A_{i}}{\sqrt{T}}e^{\frac{E_{i}}{RT}}\right) = -\frac{\frac{1}{2}\frac{RT+E_{i}}{RT^{2}}\frac{A_{i}}{\sqrt{T}}e^{\frac{E_{i}}{RT}} = -Z_{i} \end{split}$$

These are combined to find the isosteric enthalpy of adsorption, in Equations 2.31-37. When a double-site Langmuir isotherm (i = 2) is used, this can be written as:

$$-\left(\frac{\partial P}{\partial T}\right)_{n_a} = X \left(Y_1 Z_1 + Y_2 Z_2\right)$$

Equation 2.55

The isosteric enthalpy of adsorption of methane on MSC-30 is shown in Figure 2.20, using the ideal gas law to approximate the density in the gas phase. The results are consistent with reported results for numerous sorbent systems and show a physically insightful dependence of the isosteric enthalpy on both uptake and temperature. The Henry's law value is between 14.5-15.5 kJ mol<sup>-1</sup>, consistent with the isoexcess results

calculated without a fitting equation (the best approximate of the Henry's law value), and the enthalpy declines with uptake to 14 kJ mol<sup>-1</sup>. Due to the ideal gas dependence of the density with pressure, the enthalpy reaches a plateau at high values of uptake.

When the real gas data is used, the calculation of isosteric enthalpy changes significantly at high pressures, as shown in Figure 2.21. Non-ideality of methane in the gas phase is substantial under these conditions and must be taken into account for the most accurate description of adsorption thermodynamics in MSC-30, and was also necessary when extended to other systems. The tendency of the isosteric heat to a constant value at high uptake<sup>32</sup> is commonly reported as evidence of proper calculation procedures<sup>20, 21</sup>; however a plateau was not observed when ideal gas assumptions were



Figure 2.20. Isosteric enthalpy of adsorption, using a double-Langmuir fit with the ideal gas assumption (Equation 2.31).



Figure 2.21. Isosteric enthalpy of adsorption, using double-Langmuir fits: (left) with the ideal gas assumption (Equation 2.31), and (right) with the real gas density (Equation 2.32), both employing the typical molar volume assumption.



Figure 2.22. Isosteric enthalpy of adsorption, using double-Langmuir fits and real gas density: (left) with the typical molar volume assumption (Equation 2.32), and (right) with the suggested liquid methane approximation (Equation 2.36).

omitted from the calculations in this study. We suggest that a general exception be made for adsorption in the significantly non-ideal gas regime where there is no reason to suggest that the isosteric enthalpy of adsorption would persist to a plateau value.

Secondly, the change in molar volume on adsorption must also be carefully considered at high pressure for certain adsorptives, where the molar volume in the gas phase approaches that of its liquid. This is not the case across a wide temperature and pressure regime for hydrogen, for example, but is highly relevant to methane even at temperatures near ambient. For methane adsorption on MSC-30 in this study, the usual approximation, treating the adsorbed phase volume as negligible compared to that of the gas phase, holds in the low pressure limit but becomes invalid beyond 1 MPa. The difference in isosteric heat calculated with or without the approximation is >1% beyond 1 MPa, as shown in Figure 2.22. To approximate the molar volume of the adsorbed phase, we suggest to use that of liquid methane (see Equations 2.36-37), a fixed value that can be easily determined and which is seen as a reasonable approximation in numerous gas-solid adsorption systems. Specifically for methane, we use  $v_a = v_{liq} = 38$ mL mol<sup>-1</sup>, the value for pure methane at 111.5 K and 0.1 MPa. For our data of methane on MSC-30, the difference between the molar volume of the gas and the adsorbed phases becomes significant at all temperatures since  $v_a$  is 5-30% the magnitude of  $v_q$  at 10 MPa. The variation of the liquid molar volume with temperature and pressure was considered; the density along the vaporization line is ~20%, and so can be considered a negligible complication within the error of the proposed assumption. A fixed molar volume of the adsorbed phase was used throughout all temperatures and pressures.

## 2.6 Conclusions

In summary, the method used to determine the uptake and temperature dependence of the isosteric (or isoexcess) enthalpy of adsorption of methane on MSC-30 had a significant effect on the results. The virial-type fitting method has the advantage that with few parameters, one can fit experimental isotherm data over a large range of P and T in many systems. The best fits to Equation 2.42 are found for systems with a weakly temperature dependent isosteric heat. For high temperatures (near the critical temperature and above) and up to modest pressures, this equation often suffices with only 2-4 parameters (i = 0-1). However, application of this fitting procedure to moderately high (defined as near-critical) pressures or low temperatures (where a Gibbs excess maximum is encountered) lends substantial error to the interpolated results even with the addition of many parameters. In every case implementing the isoexcess assumption, the enthalpy diverged at high uptake where the assumption is fundamentally invalid. It is simple to show that since  $n_e < n_a$ , the slope of the excess isosteres in the van't Hoff plot will be more negative than that of the correct absolute isosteres (since the pressure necessary to achieve a given state of uptake will be underestimated), effecting a perceived increase in the calculated enthalpy of adsorption. Pitfalls such as these are commonly ignored, or the data beyond moderate quantities of surface coverage are discarded. In any case, the isosteric enthalpy is not accessible for high pressures using this method, and quantities calculated using excess uptake data must be referred to as "isoexcess" quantities to distinguish them from true isosteric values based on absolute adsorption.<sup>33</sup>

A double-Langmuir-type equation with a built-in definition of Gibbs surface excess was a suitable fitting equation of methane uptake on MSC-30 in the model-independent case, and could also be used as a model to determine the absolute quantity of adsorption and to perform a true isosteric enthalpy analysis. In both the isoexcess and absolute results, the enthalpy of adsorption showed physically justifiable characteristics, and gave a Henry's law value closest to that for a model-free analysis of the low-pressure data. All simplifying approximations within the derivation of the isosteric enthalpy of adsorption were found to be extremely limited in validity for methane adsorption within a pressure and temperature range close to ambient. Therefore, real gas equation of state data must be used and a simple approximation of the finite molar volume of the adsorbed phase was proposed.

## 2.7 References

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