Chapter 2

Fundamentals of Physisorption

1. Background

Early work into determining a universal equation of state for all gases led to the development of the ideal gas law:

$$PV = nRT \tag{1}$$

This law, derived by Emile Clapeyron in 1834, brings together 3 linear gas relationships: Boyle's Law, Charles's Law and Avogadro's Law. The ideal gas law is simple, functional and fairly accurate at dilute conditions. However, at high pressures or low temperatures, the assumptions of the ideal gas law, namely that gases are composed of non-interacting point particles, break down. This shortcoming was addressed later in the 19th century by introducing nonlinear gas equations of state such as the van der Waals equation:

$$\left(P + \frac{n^2 a}{v^2}\right)(v - nb) = nRT \tag{2}$$

Introduced by Johannes Diderick van der Waals in 1873, this equation of state incorporates two gas-dependent parameters, *a,* and *b*, which account for the attractive interactions between gas molecules, and the finite volume of real gas molecules, respectively. Johannes van der Waals adamantly believed that gases collided as hard spheres and did not possess any other repulsive interactions. This is now known to be false.

Real gases exhibit both attractive and repulsive interactions that are strongly correlated with intermolecular spacing. For electrically neutral molecules, these forces (e.g. van der Waals) typically fall into one of 4 categories: Keesom Forces, Debye Forces, London Dispersion forces and Pauli repulsive forces. The first three result from some combination of permanent and/or induced multipole interactions while the Pauli repulsive force is a purely quantum effect.

The sum of the attractive and repulsive intermolecular interactions forms an "interaction potential." While early on it was generally agreed upon that van der Waals interactions fall off quickly with increasing intermolecular spacing, the precise function was unknown. A number of pair potentials were proposed including the commonly used Lennard-Jones Potential, V_{LJ}:

$$V_{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{3}$$

where r is the intermolecular separation and σ and ε are the Lennard-Jones parameters, specific to each gas. The Lennard-Jones potential balances the longer-range attractive interactions (that fall as r^{-6}) with the very short-range Pauli repulsion forces (arbitrarily modeled as falling with r^{-12}). While the r^{-6} dependence derives from the London dispersion force, the r^{-12} repulsive term has no physical basis. Thus while a useful heuristic, the Lennard-Jones potential is not rigorously accurate in describing potentials between two molecules. In physisorption, gas molecules interact with an adsorbent surface, which is generally considered to be much wider than the molecule itself. Patchwise, these interactions may be modeled as between a flat crystalline material and a small molecule, by generalizing the ideas of the Lennard-Jones potential into a new form called the Steele potential[1]:

$$\phi(x) = 2\pi\varepsilon_{sf}\rho_s\sigma^2\Delta\left[\frac{2}{5}\left(\frac{\sigma}{r}\right)^{10} - \left(\frac{\sigma}{r}\right)^{4} - \left(\frac{\sigma^4}{3\Delta(r+0.61\Delta)^3}\right)\right] \tag{4}$$

where ε_{sf} is the solid-fluid well-depth given by Berthelot mixing rules[2], ρ_s is the density of the solid, Δ is interplanar spacing of the crystalline material, and σ is a Lennard-Jones type distance parameter determined by Lorentz mixing rules[2].

In a dynamic view, gases may collide with a solid interface, either elastically or inelastically. Occasionally a gas molecule that collides inelastically will undergo an interaction with the surface, wherein it is briefly localized by the surface potential. This is the essence of physisorption at the microscale. The surface potential may vary over the surface due to impurities, defects, or overall structural features. In microporous materials, the surface potential heterogeneity is largely dictated by the pore-size distribution. Physisorptive systems typically have only shallow (weak) surface potentials that allow adsorbed molecules to explore multiple sites on the two-dimensional potential surface before reentering the gas phase. This is known as a mobile adsorption, as opposed to localized adsorption, which is typically associated with deeper potential wells and chemisorption.

From a fundamental thermodynamics perspective, adsorption compresses a 3-dimensional gas phase into a 2-dimensional adsorbed phase. This presents a significant drop in the molar entropy of the adsorptive species. The difference in molar entropy between the adsorbed and gas phases (at constant coverage) is called the isosteric entropy of adsorption (ΔS_{ads}). The gas-phase entropy (S_g) may be read from data tables. The adsorbed-phase entropy (S_a) depends on a number of factors including coverage.

In order to establish equilibrium, the isosteric entropy of adsorption must be offset by a comparable decrease in molar enthalpy upon adsorption. The difference between the adsorbed-phase enthalpy (H_a) and the gas-phase enthalpy (H_g) (at constant coverage) is called the isosteric enthalpy of adsorption (ΔH_{ads}). Physisorption is always exothermic, yielding a negative isosteric enthalpy of adsorption. By convention, the isosteric heat of adsorption (q_{st}) is defined as a positive quantity as follows

$$q_{st} \equiv -(H_a - H_g) \tag{5}$$

The isosteric heat of adsorption may be thought of as a proxy metric of the binding energy between the adsorbent and adsorbate that results from the interaction potential.

Over time an adsorbed molecule may explore many adsorption sites, but due to energetic constraints, the most favorable sites (with the largest isosteric heats) will have the highest average occupation. For conventional adsorbents, the highest isosteric heat values are observed at the lowest coverage. As coverage is increased, the most favorable adsorption sites become saturated. This leads to a decreasing isosteric heat (an average quantity) with increasing coverage.

2. History of Adsorption

Simple adsorptive applications have been employed since at least 1550 BC, when records indicate that the Egyptians made use of charcoals to adsorb putrid gases expelled during human dissection.[3] Scientific adsorptive experiments are more recent. Scheele in 1773, followed by Fontana in 1777, were the first scientists to measure the uptake of gases by porous solids.[3] Saussure built upon this work, and in 1814 determined that adsorption was exothermic in nature.[3] A theoretical understanding of adsorption followed far behind experiments. It wasn't until 1888 that Bemmelen made the first known attempt at fitting adsorption data, introducing a fitting equation now known as the "Freundlich Equation."[3] More precise terminology soon followed when Bois-Reymond and Kayser introduced the term "adsorption" into standard scientific lexiconography.[3]

By the 20th century, the field of adsorption was full steam ahead. 1903 saw the discovery of selective adsorption (Twsett)[4]. In 1909 McBain introduced the term "absorption" to differentiate bulk uptake from the surface phenomenon of "adsorption."[5] Within the next few decades physisorption had been cast into a number of rigorous theoretical frameworks, namely Eucken-Polanyi Theory (1914)[6], the Langmuir Isotherm (1918)[7], BET Theory (1935-1939)[8,9,10] and Dubinin Theory (1946)[11].

3. Adsorption Theory

Apart from limited calorimetric work, the "adsorption isotherm" forms the fundamental basis of adsorption measurement and theory. Constant-temperature isotherms may be measured in a number a ways but ultimately yield the same information: Gibbs excess adsorption as a function of pressure. A simple model for adsorption may be drawn up as follows (Figure 1).

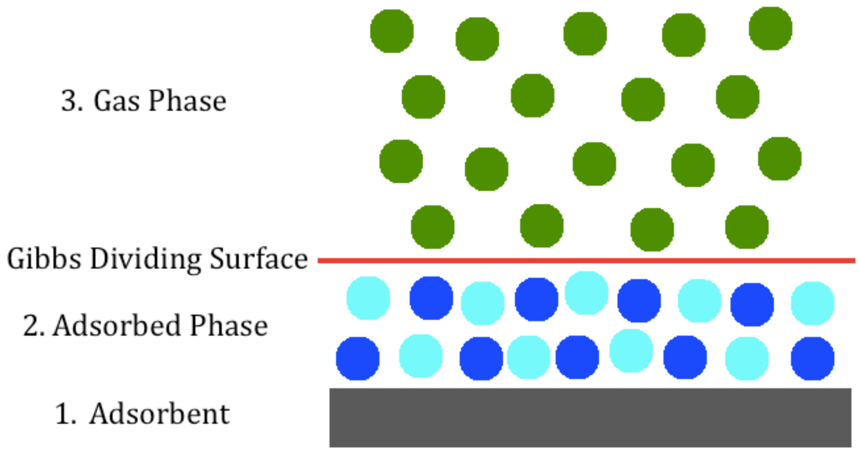

Figure 1. Cartoon depiction of adsorption. The gray rectangle represents the adsorbent

surface. All blue molecules represent absolute adsorption molecules. The dark blue circles represent excess adsorption molecules. The red line indicates a dividing surface. The green circles represent the gas-phase molecules.

Here section 1 represents the solid adsorbent surface, section 2 represents the adsorbed phase (densified molecules near the interface), and section 3 represents the molecules that remain unaffected by the adsorbent and remain free in the gas phase. The quantity of absolute adsorption (n_a) comprises all of the molecules in the adsorbed phase. The volume of the adsorbed phase (V_{ads}), however, is not rigorously established. Thus absolute adsorption cannot be directly measured via experiment. Instead Gibbs worked around this problem by defining excess adsorption (n_e) as follows:

$$n_e = n_a - V_{ads}\rho(P,T) \tag{6}$$

Gibbs excess adsorption differs from absolute adsorption by an amount equal to the volume of the adsorption layer multiplied by the density of the free gas phase ($\rho(P,T)$). Here the volume of the adsorbed phase is defined as the volume between the adsorbent surface and a dividing surface. The quantity of Gibbs excess adsorption measures the amount of adsorbate in the vicinity of the adsorbent surface that is in excess of the free gas phase density. For this reason, the Gibbs excess adsorption is directly measurable by volumetric or gravimetric methods without need for assumptions about the volume of the adsorbed layer. Absolute adsorption, however, cannot be easily and directly measured. Instead it is often crudely assumed that absolute adsorption equals excess adsorption. This assumption is only valid when the gas phase is dilute, and quickly breaks down at high pressures and low temperatures. Thus in this thesis, we instead use a robust fitting method (presented in Chapter 3) to back out reasonable values of the absolute adsorption.

The first attempts to fit physisorption isotherms came as early as 1888 when Bemmelen introduced what is now known as the "Freundlich Equation"[12,3]:

$$\frac{n}{m} = KP^{\frac{1}{\eta}} \qquad (7)$$

where n is the uptake, m is the mass of the adsorbent, P is equilibrium pressure, and K and η are adsorbent-specific parameters. This equation is only empirical and does not purport to capture or contain the physics of adsorption. Nonetheless, it displays key behaviors that are common to fit functions for type 1 isotherms. At low pressures, uptake increases linearly with pressure per Henry's Law:

$$n = K_H P \qquad (8)$$

where K_H is the Henry's Law constant. Henry's Law was first formulated by William Henry in 1803 and can be derived from ideal gas assumptions. If we assume that the adsorbed phase takes the form of a two-dimensional ideal gas following

$$P_a A_a = nRT \qquad (9)$$

where P_a and A_a are the spreading pressure and surface area, respectively, and also assume that the equilibrium spreading pressure is proportional to the equilibrium bulk gas pressure, then

$$n = \frac{P_a A_a}{RT} = \frac{cPA_a}{RT} = K_H P \qquad (10)$$

Accordingly, the low-pressure regime of an isotherm where uptake is proportional to applied gas pressure is commonly referred to as the Henry's Law regime. At higher pressures, the adsorption isotherm saturates as all of the available adsorption sites are filled. This correlation, however, is not exact as unlike absolute adsorption, experimentally measured excess adsorption data behaves in a non-monotonic fashion at high pressures. Nonetheless, most type

1 adsorption fit functions subsume both the Henry's Law regime behavior and the saturation regime behavior.

The Langmuir isotherm, derived by Irving Langmuir in 1918[7], provides a fundamental model for gas adsorption that incorporates both the Henry's Law regime the saturation regime behavior. Here the adsorbed phase is assumed to exist as a monolayer of adsorbate directly above the adsorbent surface. Langmuir's model makes a number of simplifying assumptions as follows:

1. The adsorbent surface is perfectly flat.
2. The gas adsorbs into an immobile state.
3. There is a finite number of adsorption sites that can each by filled by no more than one adsorbate molecule.
4. All adsorption sites are energetically identical.
5. Adsorbate molecules do not interact.

With these simplifying assumptions in hand, the Langmuir adsorption isotherm may be derived from kinetic theory, statistical mechanics, or from a phenomological perspective, and takes the form:

$$\theta = \frac{KP}{1+KP} \tag{11}$$

where θ is fractional occupancy and K is an equilibrium constant given by an Arrhenius-type equation (Equation 12):

$$K_i = \frac{A_i}{\sqrt{T}} e^{\frac{-E_i}{RT}} \tag{12}$$

where A_i is a prefactor and E_i is an energy of the i^{th} isotherm.

Unfortunately, the five simplifying assumptions above are almost never entirely satisfied and the Langmuir isotherm cannot be applied over broad ranges of conditions. Many of the drawbacks of the Langmuir isotherm may be overcome by fitting excess adsorption data with a weighted superposition of Langmuir isotherms (see Chapter 3).

In particular, the Langmuir model breaks down when multilayer adsorption is possible, as found in larger micropores, mesopores, and macropores. In 1938 Stephen Brunauer, Paul Emmett, and Edward Teller extended the Langmuir model to consider multilayer adsorption.[8] They realized that in multilayer adsorption, molecules do not successively fill one complete monolayer after another. Rather, fragments of multilayer stacks of varying sizes dot the adsorbent surface. Each layer is in dynamic equilibrium with the layers above and below it, much in the same way that the Langmuir model assumes a dynamic equilibrium between the adsorbed monolayer and the gas phase above it. The Brunauer, Emmett, Teller, or BET method has been elaborated on in detail in literature[13,14] and will not be rederived here. Rather, the results and key insights are elucidated from the BET equation:

$$\frac{1}{n\left[\left(\frac{P_o}{P}\right)-1\right]} = \frac{C-1}{n_{max}C}\left(\frac{P}{P_o}\right) + \frac{1}{n_{max}C} \qquad (13)$$

where n is uptake, P is equilibrium pressure, P_o is saturation pressure, n_{max} is maximum possible uptake, and C is the BET constant. BET Theory assumes that infinite layers may be adsorbed successively on a surface. Moreover, these layers do not interact with one another and each follow the Langmuir model. Two additional assumptions are made:

1. The E_1 parameter is the isosteric heat between the adsorbent and first adsorbed layer.
2. All higher layers have an E_L parameter equal to the heat of liquefaction of the adsorbate.

BET theory has proven particularly useful at measuring the specific surface areas of porous carbons. For high quality surface area determinations, nitrogen, argon, carbon dioxide, and krypton have been used. In particular, a plot of $\frac{1}{n\left[\left(\frac{P_o}{P}\right)-1\right]}$ vs $\left(\frac{P}{P_o}\right)$ should yield a straight line in the relative pressure range of $0.05 < \left(\frac{P}{P_o}\right) < 0.3$. Using linear regression, the slope and y-intercept of this line are determined. The parameters n_{max} and C are determined by:

$$n_{max} = \frac{1}{(slope + intercept)} \tag{14}$$

$$C = \left(\frac{slope}{intercept}\right) + 1 \tag{15}$$

The surface area may then be determined from n_{max}, using the established cross-sectional area of the probe molecule.

While the Langmuir isotherm rapidly gained popularity and contributed to Irving Langmuir's 1932 Nobel Prize, it competed with Polanyi's theory of adsorption, which has now earned its place in annals of science history. Whereas Langmuir conceptualized adsorption as a monolayer effect localized at the adsorbent surface, Polanyi's approach was more amenable holistic pore filling with longer-range effects. Polanyi reasoned that the density of adsorptive molecules near a surface diminishes with distance from the attractive surface, much the way the atmosphere of a planet thins out at high altitudes. For adsorption this requires a longer-range interaction potential, now called the Polanyi Adsorption Potential[6].

Polanyi recognized that at equilibrium, the chemical potential (μ) of the adsorbed phase at an arbitrary distance, x, from the interface and a corresponding pressure P_x, must equal the chemical potential of the gas phase at an infinite distance and corresponding bulk pressure, *P*.

$$\mu(x, P_x) = \mu(\infty, P) \tag{16}$$

$$\int_{\mu(\infty,P)}^{\mu(x,P_x)} d\mu = \mu(x, P_x) - \mu(\infty, P) = 0 \tag{17}$$

Moreover,

$$d\mu = -SdT + VdP + dU \tag{18}$$

where *S* is entropy, *V* is volume and *U* is the potential energy. Constant temperature (isothermal) conditions yield

$$d\mu = VdP + dU \tag{19}$$

$$\int_{\mu(\infty,P)}^{\mu(x,P_x)} d\mu = \int_{P}^{P_x} VdP \ + U(x) - U(\infty) = 0 \tag{20}$$

where *U(x)* is the potential energy at a distance *x* from the surface and *U(∞)* is the potential energy at an infinite distance, which Polanyi took to be zero:

$$-U(x) = \int_{P}^{P_x} VdP \tag{21}$$

By substituting in the ideal gas law

$$-U(x) = \int_{P}^{P_x} \frac{RT}{P} dP \tag{22}$$

or

$$U(x) = RTln\left(\frac{P_x}{P}\right) \equiv A \tag{23}$$

where *A* is the Polanyi potential. While the Polanyi potential went unappreciated for many years, it was given new life in 1946 when Dubinin and Radushkevich introduced the "theory of the volume filling of micropores (TVFM)".[11,15,16] In this theory the Polanyi potential is the negative of the work done by the sorption system:

$$A = -\Delta G \tag{24}$$

This insight extended the Polanyi potential to broad thermodynamic analysis, codified in the Dubinin-Radushkevich equation:

$$n = n_{max}\, e^{\left(\frac{A}{\beta E_o}\right)^2} \tag{25}$$

where n is the uptake, n_{max} is the maximum possible uptake, β is the affinity coefficient, and E_o is the standard characteristic energy. Other modified and more generalized forms were later introduced, such as the Dubinin-Astakhov equation[17]

$$n = n_{max}\, e^{\left(\frac{A}{\beta E_o}\right)^\chi} \tag{26}$$

where χ is an adsorbent-specific heterogeneity parameter.

If uptake is plotted as a function of the Polanyi potential, the Dubinin-Radushkevich equation[15] yields a single characteristic curve for each gas-adsorbent system. In theory the characteristic curve may be used to predict uptake over a wide range of temperatures and pressures, and its accuracy has been generally confirmed by experiment.[18,19] Moreover, plotting $\ln(n)$ as a function of $-\left(\frac{A}{\beta E_o}\right)^2$ yields a linear trend, wherein the y-intercept gives the maximal uptake (n_{max}) and the slope gives the characteristic energy (E_o). The parameter n_{max} may be used to determine the total micropore volume of the adsorbent by multiplying by the established molecular volume of the adsorbate. The parameter E_o may be used to estimate an average micropore width.

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