Fundamentals of the Adsorption Theory

1 author:

Cary T Chiou
National Cheng Kung University
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4 Fundamentals of the Adsorption Theory

4.1 INTRODUCTION

Adsorption is a surface phenomenon that is characterized by the concentration of a chemical species (adsorbate) from its vapor phase or from a solution onto or near the surfaces or pores of a solid (adsorbent). This surface excess occurs in general when the attractive energy of a substance with the solid surface (i.e., the adhesive work) is greater than the cohesive energy of the substance itself (Manes, 1998). The adsorptive uptake is amplified if the solid material has a high surface area. If the adsorption occurs by London–van der Waals forces of the solid and adsorbate, it is called *physical adsorption*. If the forces leading to adsorption are related to chemical bonding forces, the adsorption is referred to as *chemisorption*. However, the distinction between physical adsorption and chemisorption is not always sharp. For example, the adsorption of polar vapors onto polar solids may fall under either classification, depending on the adsorption energy. From a thermodynamic point of view, the concentration of a substance from a dilute vapor phase or solution onto a solid surface corresponds to a reduction in freedom of motion of molecules and thereby to a loss in system entropy. As such, the adsorption process must be exothermic to the extent that the negative ΔH is greater in magnitude than the associated negative $T \Delta S$ to maintain a favorable free-energy driving force (i.e., for ΔG to be negative). For more detailed discussions on the thermodynamic aspect of the adsorption process, see Adamson (1967), Gregg and Sing (1982), and Manes (1998).

When a vapor is adsorbed onto a previously unoccupied solid surface or its pore space, the amount of the vapor adsorbed is proportional to the solid mass. The vapor uptake also depends on temperature (T), the equilibrium partial pressure of the vapor (P), and the nature of the solid and vapor. For a vapor adsorbed on a solid at a fixed temperature, the adsorbed quantity per unit mass of the solid (Q) is then only a function of P. The relation between Q and P at a given temperature is called the *adsorption isotherm*. Q is frequently presented as a function of the relative pressure, $P/P°$, where P is normalized to the saturation vapor pressure ($P°$) of the adsorbate at temperature T. The normalized isotherm is often more useful, as it enables one to assess readily the net adsorption heats and other characteristics of vapors over a range of temperatures. For adsorption of solutes from solution, one

constructs similar isotherm forms by relating Q with C_e (the equilibrium concentration) or with the relative concentration, C_e/C_s, where C_s is the solubility of the solute.

Except for rare cases where the microscopic structure of a solid surface is nearly uniform, the surfaces of most solids are heterogeneous, with the result that adsorption energies are variable. The adsorption sites are taken up sequentially, starting from the highest-energy sites to the lowest-energy sites, with increasing partial pressure or solute concentration. Thus the net (differential) molar heat of adsorption decreases with increasing adsorption and vanishes when the vapor pressure or solute concentration reaches saturation. Adsorption isotherms are typically nonlinear because of the energetic heterogeneity and the limited active sites or surfaces of the solid. Since a given site or a surface of the solid cannot be shared by two or more different kinds of adsorbates, the adsorption process is necessarily competitive, which is in contrast to a partition process. The surface area or porosity of the solid is usually the principal factor affecting the amount of vapor adsorption; therefore, a powerful adsorbent must have a large surface area. Adsorption of a solute from solution is subject to competition by the solvent and other components in the solution. Therefore, a powerful adsorbent for single vapors is not necessarily a strong adsorbent for solutes from solution.

A number of adsorption isotherms have been recorded for vapors on a wide variety of solids. Brunauer (1945) grouped the isotherms into five principal classes, types I to V, as illustrated in Figure. 4.1. Type I is characterized by Langmuir-type adsorption (see below), which shows a monotonic approach to a limiting value that corresponds theoretically to the completion of a surface monolayer. Type II is perhaps most common for physical adsorption on relatively open surfaces, in which adsorption proceeds progressively from submonolayer to multilayer; the isotherm exhibits a distinct concave-downward curvature at some low relative pressure ($P/P°$) and a sharply rising curve at high $P/P°$. The point B at the knee of the curve signifies completion of an adsorbed monolayer. It forms the basis of the Brunauer–Emmett–Teller (BET) model for surface-area determination of a solid from the assumed monolayer capacity, described below.

A type III isotherm signifies a relatively weak gas–solid interaction, as exemplified by the adsorption of water and alkanes on nonporous low-polarity solids such as polytetrafluroethylene (Teflon) (Graham, 1965; Whalen, 1968; Gregg and Sing, 1982). In this case, the adsorbate does not effectively spread on the solid surface. Type IV and V isotherms are characteristic of vapor adsorption by capillary condensation into small adsorbent pores, in which the adsorption reaches an asymptotic value as the saturation pressure is approached. Adsorption of organic vapors on activated carbon is typically type IV, whereas adsorption of water vapor on activated carbon is type V (Manes, 1998), as shown later. The shape of the adsorption isotherm of a solute from solution depends sensitively on the competitive adsorption of the solvent and other components and may deviate greatly from that of its vapor on the solid.
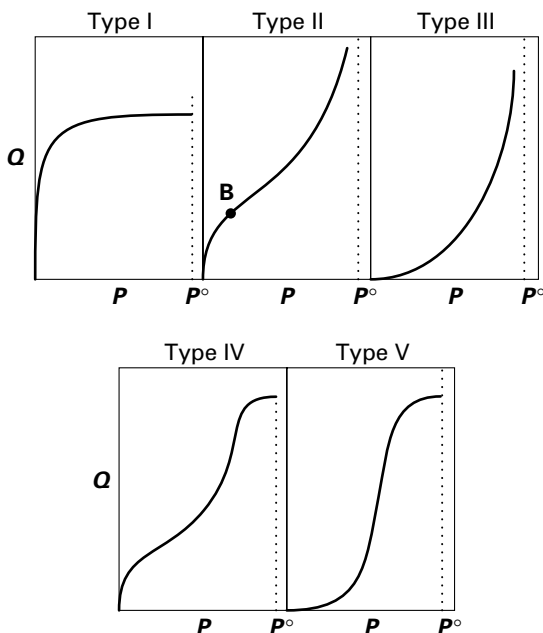
Figure 4.1 The five types of adsorption isotherms according to the classification of Brunauer (1945).

One notes with interest the similarity in shape of type III adsorption isotherm and a special partition isotherm, as depicted in Figure 3.2, when a solute partitions very favorably from water (or other media) into an organic phase (or solvent). Whereas the isotherm in Figure 3.2 is for the solute partition from water into an organic phase, a similar partition isotherm arises when the vapor of a liquid partitions strongly into an organic substance. Illustrative examples of such a vapor partition phenomenon are benzene, toluene, xylene, and carbon tetrachloride on rubber, polystyrene, and polyiosbutylene (Eichinger and Flory, 1968a,b). A practical means to distinguish a type III vapor adsorption isotherm from a similarly shaped vapor partition isotherm is that the vapor partition should display a very high uptake capacity, usually more than 10% by weight at $P/P° = 0.5$, while a type III vapor adsorption exhibits a very low capacity, usually far less than 1% by weight, at $P/P° = 0.5$.

4.2   LANGMUIR ADSORPTION ISOTHERM

Langmuir (1918) considered the adsorption of gases or vapors on a plane surface that contains a fixed number of identical active sites. From a kinetic consideration, the rate of vapor desorption from the occupied sites is set equal to the rate of adsorption on the unoccupied sites at equilibrium:

$$k_d\theta = k_aP(1-\theta) \tag{4.1}$$

where θ is the fraction of the total sites occupied by the vapor at an equilibrium partial pressure P, k_d the desorption rate constant, and k_a the adsorption rate constant. Therefore,

$$\theta = \frac{k_aP}{k_d + k_aP} = \frac{(k_a/k_d)P}{1+(k_a/k_d)P} \tag{4.2}$$

Since the amount Q of vapor adsorbed by a unit mass of the solid is proportional to θ, one gets an adsorption isotherm as

$$Q = \frac{Q_mbP}{1+bP} \tag{4.3}$$

where Q_m is the limiting (monolayer) adsorption capacity (i.e., when the surface is covered with a complete monolayer of the adsorbed vapor) and $b = k_a/k_d$ is related to the heat of adsorption per unit mass (or per mole) of the vapor, which is considered to be independent of the adsorbed amount.

As seen, at low P, where $bP \ll 1$, Q is proportional to P (i.e., $Q = kP$), where k is a constant, and the relation between Q and P is therefore linear. At high P, $bP \gg 1$, Q approaches Q_m asymptotically and the isotherm is concave toward the P axis. The linear relation between Q and P at low P may be referred to as the *Henry region*. The general shape of the Langmuir-type isotherm falls under Brunauer's classification of type I. Examples of systems that closely meet Eq. (4.3) are the adsorption of relatively inert vapors of nitrogen, argon, methane, and carbon dioxide on plane (open) surfaces of mica and glass at liquid air or liquid nitrogen temperature (Langmuir, 1918).

Although Eq. (4.3) is intended originally only for vapor adsorption, a similar form is frequently adapted to fit the adsorption data of a substance (solute) from a solution, in which case the P term in Eq. (4.3) is replaced by the equilibrium solute concentration. The constant Q_m and b in the Langmuir equation may be determined by rewriting the equation as

$$\frac{1}{Q} = \frac{1}{Q_mbP} + \frac{1}{Q_m} \tag{4.4}$$

By Eq. (4.4), a plot of $1/Q$ versus $1/P$ gives a slope of $1/Q_mb$ and an intercept of $1/Q_m$. From the slope and intercept values, Q_m and b can be calculated.

Although the adsorption data of many vapors or solutes on solids conform to the general shape of the Langmuir equation, this is not necessarily a proof that the system complies with the Langmuir model. For most solids, the adsorption sites are energetically heterogeneous, and this energetic heterogeneity along with site limitations may give rise to a *Langmuir-shape isotherm*.

In other words, the *b* constant in Eq. (4.3), which is related to the molar heat of adsorption, varies with the range of *P* in many of these systems. By contrast, the nonlinearity in the original Langmuir derivation is attributed to the degree of site saturation (i.e., to an entropic effect) rather than to an energetic factor. Thus, unless the observed nonlinearity is proven to be truly entropic in nature, the isotherm is more appropriately referred to as a *Langmuir-type isotherm*, or simply a type I isotherm.

4.3 FREUNDLICH EQUATION

The Freundlich equation was developed mainly to allow for an empirical account of the variation in adsorption heat with concentration of an adsorbate (vapor or solute) on an energetically heterogeneous surface. It has the general form

$$Q = K_f C^n \tag{4.5}$$

where Q is the amount adsorbed per unit mass of the solid (adsorbent); C is the vapor or solute concentration at equilibrium; K_f is the Freundlich constant, equal to the adsorption capacity at $C = 1$; and n is an exponent related to the intrinsic heat of vapor or solute adsorption. The n value is in principle less than 1, because the adsorption isotherm is commonly concave to the C axis, and varies with the extent of adsorption (i.e., with Q). Depending on the adsorbent, the constancy of n may apply to a narrow or wide range of C. It can be determined from the slope of the plot of log Q versus log C over a specific range.

Unlike the Langmuir model, the Freundlich equation does not approach (arithmetic) linearity at low C, nor does it approach a limiting (fixed) adsorption capacity as C reaches saturation. These features are opposed to the general adsorption characteristics. Basically, the Freundlich equation with its adjustable parameters offers a simple mathematical tool rather than a physical model to account for the energetic heterogeneity of adsorption at different regions of the isotherm. Interpretation of the temperature effect on adsorption by Freundlich equation is generally difficult. This is because the vapor or solute concentration (C) can be increased by increasing the temperature while the adsorbed mass (Q) usually decreases with increasing temperature. For many applications, however, the Freundlich equation is quite mathematically convenient.

4.4 BET MULTILAYER ADSORPTION THEORY

The Brunauer–Emmett–Teller (BET) theory (Brunauer et al., 1938) was formulated to deal with submonolayer-to-multilayer vapor adsorption on a solid.

The model sets a theoretical basis for calculating the surface area of the solid. The theory was derived on the assumptions that (1) the Langmuir equation applies to each adsorbed layer (i.e., the surface has uniform and localized sites so that there is no interference in adsorption between neighboring sites); (2) the adsorption and desorption occur only onto and from the exposed layer surfaces; (3) at solid–vapor equilibrium, the rate of adsorption onto the ith layer is balanced by the rate of desorption from the $(i + 1)$th layer; and (4) the molar heat of adsorption for the first layer is considered to be higher than for the succeeding layers, the latter assumed to be equal to the heat of liquefaction of the vapor. These considerations lead to an isotherm of the form

$$\frac{Q}{Q_m} = \frac{Cx}{(1-x)[1+(C-1)x]} \tag{4.6}$$

where Q is the amount of vapor adsorbed at relative vapor pressure $x = P/P°$, P the equilibrium pressure of the vapor, $P°$ the saturation pressure of the vapor at the system temperature, Q_m the (statistical) monolayer capacity of the adsorbed vapor on the solid, and C is a constant related to the difference between the heat of adsorption in the first layer and the heat of liquefaction of the vapor. Equation (4.6) may be transformed into

$$\frac{x}{Q(1-x)} = \frac{(C-1)x}{CQ_m} + \frac{1}{CQ_m} \tag{4.7}$$

A plot of $x/[Q(1 - x)]$ versus x should yield a straight line (usually, at $0.05 < x < 0.30$), with a slope of $(C - 1)/CQ_m$ and an intercept of $1/CQ_m$, from which C and Q_m can be determined. The linear relation of $x/[Q(1 - x)]$ versus x usually does not go beyond $x > 0.30$, much because the multilayer adsorption does not proceed indefinitely as the theory contends. Once Q_m is determined, and if the molecular area of the vapor is known, the surface area of the solid (adsorbent) can then be calculated. The magnitude of C accounts for the curvature of an adsorption isotherm; a large C ($\gg 1$) produces a highly concave-downward shape at low x, and a small C ($\ll 1$) leads to a concave-upward shape at low x.

Generally speaking, the BET model accounts satisfactorily for multilayer adsorption of vapors on surfaces that are not highly heterogeneous (i.e., if the surface area of the solid is small to moderate in magnitude). This is because the model assumes that the solid surface has uniform energetic sites with a constant adsorption energy and that the molar heat of adsorption beyond the first layer is all the same, both of which are not well satisfied in vapor adsorption on microporous solids. The BET model, with an inert gas as the adsorbate, has proven to be the best available analytical method for surface-area determination of solids. Nitrogen (N_2) gas at its boiling point (77 K) is the most commonly used adsorbate, with which the Q_m of N_2 on a solid is obtained;

the surface area is then calculated along with the assumed N_2 molecular area of $16.2 \times 10^{-20}\,m^2$.

4.5 POLANYI ADSORPTION POTENTIAL THEORY

If adsorption is highly energetically heterogeneous, as with high-surface-area microporous solids such as activated carbon and silica gel, the adsorption data exhibit serious deviations from the Langmuir model or the BET model. This is because the force field within a pore space (adsorption space) of a microporous material that attracts a molecule varies considerably with the location. The Polanyi adsorption potential theory (Polanyi, 1916) has long been recognized as the most powerful model for dealing with vapor adsorption on energetically heterogeneous solids (Brunauer, 1945). The basic Polanyi model has been extended to a wide range of vapor- and liquid-phase systems by Manes and co-workers (Manes, 1998), and will therefore be referred to as *Polanyi–Manes model*. The model relates a wide variety of both vapor- and liquid-phase data to each other, and in particular, it correlates liquid-phase with vapor-phase adsorption. For a detailed account of the extended model, see Manes (1998).

The Polanyi theory considers that for a molecule located within the attractive force field of a microporous solid, there exists an (attractive) adsorption potential (ε) between the molecule and the solid surface. This attraction derives from the induced dipole–induced dipole force (i.e., the London force) of the molecule and surface atoms, which is short range in nature. The potential ε at a particular location within the adsorption space may be viewed as the energy required to remove the molecule from that location to a point outside the attractive force field of the solid. Thus, the magnitude of ε for an adsorbate depends on its proximity to the solid surface. It is highest in the narrowest pore (or in the narrowest portion of a pore) because the adsorbate is close to more solid material. A series of equipotential surfaces are formed by connecting the points in adsorption space with the same ε, as shown schematically in Figure 4.2.

When a vapor is placed within an attractive force field of a solid, two opposing thermodynamic effects occur. The system energy is minimized by vapor concentration into the region of the lowest potential energy, but the system entropy is reduced by this concentration. The impact of these two effects at a constant temperature on the molar free energy is given by

$$d\,\overline{G} = -d\varepsilon + \overline{V}\,dP \tag{4.8}$$

where $-d\varepsilon$ is the differential potential energy change per mole of the vapor, $\overline{V}$ the molar volume of the vapor, and dP the differential change in vapor partial pressure. At adsorption equilibrium, $d\,\overline{G} = 0$, and the reduction in potential energy offsets the loss in entropy:
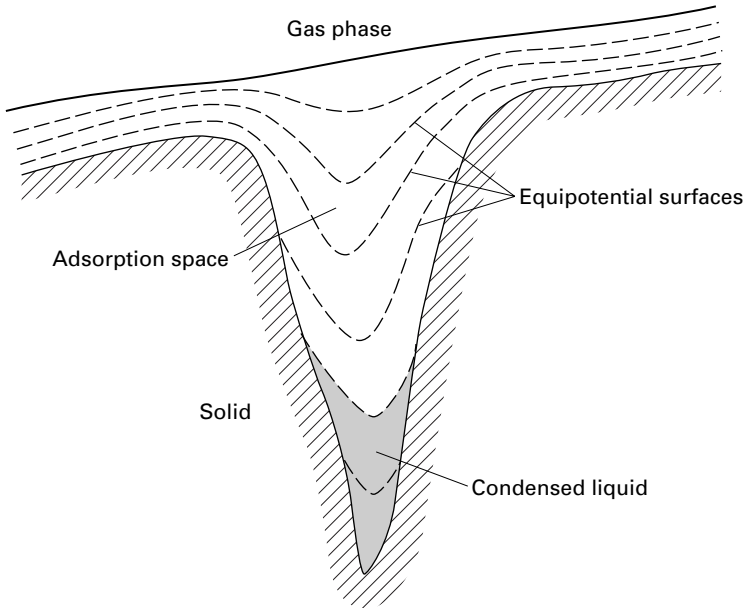
Figure 4.2   Rough schematic model for a region of the porous carbon surface (pore) showing the equipotential surfaces corresponding to successively lower values of the adsorption potential with increasing pore size. The vapor liquefies wherever the adsorption potential required to concentrate it to saturation is equaled or exceeded.

$$d\varepsilon = \overline{V}\,dP \tag{4.9}$$

and

$$\varepsilon = \int \overline{V}\,dP \tag{4.10}$$

According to the Polanyi theory, a vapor will condense to form a liquid or liquidlike adsorbate if ε (taken as positive) at an equipotential surface is greater than or equal to the work required to concentrate the vapor from ambient pressure P (where $\varepsilon = 0$) to its saturation pressure P° at the equipotential surface. If the vapor follows the ideal-gas law, Eq. (4.10) becomes

$$\varepsilon = RT \ln(P^\circ/P) \tag{4.11}$$

Thus, if a porous solid (adsorbent) is exposed to increasing partial pressure of a vapor, condensation takes place beginning with the region of the highest potential (or in the finest pore) and then with the region of progressively lower adsorption potential until all adsorption space is filled as the ambient pressure becomes saturated (i.e., as the adsorption potential becomes zero).

For a vapor at a given equilibrium $P/P°$ or a given ε, which corresponds to a given equipotential surface inside the adsorption space, the volume enclosed by the equipotential surface and the solid surface is the adsorbed volume. The net molar heat of adsorption at the equilibrium potential surface is $-\varepsilon$. If the vapor is condensed as a liquidlike adsorbate, the total molar heat of adsorption is $-(\varepsilon + \Delta\overline{H}_{evap})$, where $\Delta\overline{H}_{evap}$ is the molar heat of evaporation of the liquid. If the vapor is condensed as a solid adsorbate, the total molar heat of adsorption is $-(\varepsilon + \Delta\overline{H}_{sub})$, where $\Delta\overline{H}_{sub}$ is the molar heat of sublimation of the adsorbate.

For vapor adsorption on a relatively inert porous solid (e.g., activated carbon) that involves primarily London forces (i.e., in the absence of chemisorption or specific interaction), the adsorption potential (ε) is independent of temperature. A direct consequence of this temperature independence and of the vapor condensation is that a plot of the total adsorbed liquid (or solid) volume (ϕ) against ε at that volume (called a *characteristic curve*) is temperature invariant and depends only on the vapor and the solid structure. Thus, once the characteristic curve is obtained for a vapor on a porous solid from its adsorption data at one temperature, it can be used in a reverse manner to construct the isotherm at a different temperature. The Polanyi model postulates no specific mathematical form for the characteristic curve, which is fixed instead by the structure of the porous solid.

If there is no molecular sieving involved in vapor adsorption, the Polanyi model expects the characteristic curves for all vapor adsorbates on a chemically inert porous solid to have a common shape and a common limiting adsorbate volume (at $\varepsilon = 0$). For any adsorbed volume, the adsorption potentials of different vapor adsorbates are related to each other by constant characteristic factors. Therefore, all characteristic curves on a given solid can be made to collapse into a single curve by appropriate divisors of the individual adsorption potentials for any given adsorbed volumes. The most effective and convenient divisors are found to be the liquid molar volumes ($\overline{V}$) of the vapor adsorbates (Dubinin and Timofeyev, 1946). The resulting plot of the adsorbed volume versus $\varepsilon/\overline{V}$ for a vapor adsorbate is called a *correlation curve* (Lewis et al., 1950). As shown by Polanyi and Manes, correlation curves provide a basis to predict the adsorption of a solute from solution on an inert porous solid from the respective vapor isotherms of the pure solute and solvent.

If a solute in solution is partially miscible with the solvent, the basic Polanyi model expects that the solute condense into the adsorption space as a liquid or a solid phase, depending on the state of the pure solute at the system temperature. Therefore, the critical difference between vapor-phase and liquid-phase adsorption is that the vapor condenses in a hitherto unoccupied space, whereas the liquid or solid solute condenses to displace an equal volume of the solvent. According to Polanyi, the adsorption potential of a partially miscible solute can thus be expressed as

$$\varepsilon_{sl} = \varepsilon_s - \varepsilon_l(\overline{V}_s/\overline{V}_l) = RT \ln(C_s/C_e) \tag{4.12}$$

where ε_s is the (molar) adsorption potential of the solute, ε_l the adsorption potential of the solvent, ε_{sl} the adsorption potential of the solute from solution, $\overline{V}_s$ and $\overline{V}_l$ the respective molar volumes of the solute and solvent, C_s the solute solubility in the solvent, and C_e the solute concentration in the solvent at equilibrium. Equation (4.12) may be further converted to give

$$\varepsilon_{sl}/\overline{V}_s = \varepsilon_s/\overline{V}_s - \varepsilon_l/\overline{V}_l = (RT/\overline{V}_s)\ln(C_s/C_e) \tag{4.13}$$

As seen, the net adsorption potential density of the solute ($\varepsilon_{sl}/\overline{V}_s$) is simply the difference between the potential densities of pure solute ($\varepsilon_s/\overline{V}_s$) and solvent ($\varepsilon_l/\overline{V}_l$). Thus one may in principle predict the adsorption of a partially miscible solute from solution from established or estimated correlation curves of the pure solute and solvent. Equation (4.13) has been found most successful for partially miscible liquid solutes in solution, in which the effective molar volume of the liquid adsorbate ($\overline{V}_s$) is practically the same as the molar volume of the pure liquid. For solid solutes, the effective adsorbate molar volume may well exceed that of the pure substance, because packing of the condensed solid crystallite into fine-pore adsorption spaces may be hindered significantly by crystalline structure; therefore, for solid solutes, adjustment of molar volumes for packing efficiency is often required. Manes (1998) extended the Polanyi theory to a wide range of vapor and solution systems, including single and multiple vapors and solutes that are either completely or partially miscible to each other.

   In adsorption from solution, the net heat of adsorption for a partially miscible solute (ε_{sl}) is usually smaller than that of its single vapor-phase adsorption (ε_s) because of the energy required to displace the solvent, as depicted by Eq. (4.12). In such systems (i.e., where the solute separates out as a liquid or a solid phase in adsorption space), the total molar heat of adsorption is $-(\varepsilon_{sl} + \Delta\overline{H}_{sol})$, where $\Delta\overline{H}_{sol}$ is the molar heat of solution of the solute. One may recall from the discussion in Chapter 3 that the $\Delta\overline{H}_{sol}$ for solid solutes includes the associated heats of fusion ($\Delta\overline{H}_{fus}$).

4.6   SURFACE AREAS OF SOLIDS

The surface area of a solid (adsorbent) plays a fundamental role in the physical adsorption of vapors. The BET method with appropriate adsorbate gases has become a universal method for determining the solid surface area. Suitable vapor adsorbates must be chemically inert, not subject to molecular sieving by the solid pore, and confined only to the exterior of the solid (i.e., no vapor penetration into the interior network). The use of an inert vapor as the adsorbate is to eliminate any specific interaction (or reaction) with either solid surface or its interior network. Prevention of molecular sieving is accomplished by the use of small adsorbates. Measurement at low temperature

ensures that the adsorbate solubilization into the solid matrix is minimized. Although N_2 vapor at its normal boiling point (ca. 77 K) is used most frequently as the adsorbate, the choice is by no means restricted to N_2, and use of a wide variety of other inert vapor adsorbates (e.g., krypton) should yield similar results. The surface area, considered as the solid–vapor or solid–vacuum interfacial area, which is external to solid material, is assumed to predate the experiment and to be unchanged by the experiment. The surface area is therefore a property of the solid; that is, within the precision of the measurement method, it should be independent of the choice of any suitable adsorbates used.

For highly porous solids, the term *internal surface* is frequently used to refer to the surface associated with the walls of pores that have narrow openings, which extend inward from the granule surface to the interior of the granule. On the other hand, the term *external surface* is used to refer to the surface from all prominences and those cracks that are wider than they are deep (Gregg and Sing, 1982). It is understood that the internal surface is restricted to open-ended pores and does not apply to sealed-off pores (i.e., those having no openings to the exterior of the granule). Although these two kinds of surfaces are somewhat operational in their definitions, it is understood that the internal surface is nonetheless *external* to the material and accessible to gases, as is measured in surface-area determination. Thus, as long as the adsorbate does not penetrate the field of force that exists between the atoms, ions, or molecules inside the solid, it is considered to be on the external surface, despite the fact that it may adsorb on the solid's internal surface (Brunauer, 1945). For a highly microporous solid such as activated carbon, one may then say that the solid has a very high surface area, as determined by the BET method, because it has a large internal surface.

It is unfortunate that the term *internal surface* practiced in soil science literature gives a confusing implication to the surface area. The confusion initiates from the use of the amounts of some polar solvents (e.g., water and ethylene glycol) retained by a unit mass of the soil or mineral sample under certain evacuating conditions for determining the *total surface area* of the sample. By taking the surface area from the BET method using an inert gas (e.g., N_2) as the external surface area, the difference between the thus determined total surface area and the external surface area is considered to be the internal surface area of the sample. Evidently, the analytical method leading to the internal surface area does not comply with the accepted criterion in surface area determination, and consequently, this internal surface area is mainly an artifact of the method. As mentioned earlier, appropriate adsorbates for surface-area determination must be chemically inert so that they neither alter the structure of the solid nor penetrate the molecular network of the solid. Because some polar solvents can potentially alter the solid structure, such as by a solvation process with some clay minerals, or penetrate the soil organic matter by dissolution, the resulting internal surface area is often a measure of phenomena other than physical adsorption. As pointed out by

Brunauer (1945), when an adsorbate penetrates the interior of the solid, it either dissolves in the solid to form a solution or reacts with the solid to form a new compound. We shall see in Chapter 6 that the uptake of polar vapors or liquids by soils and certain minerals is eminently consistent with this expectation.

4.7   ISOSTERIC HEAT OF ADSORPTION

Because the adsorbent surface is commonly energetically heterogeneous, the exothermic heat of adsorption of a vapor (or a solute) usually varies with the amount adsorbed. To account for the variation in adsorption heat, the isosteric heats of adsorption at some fixed adsorbate loadings are determined from the equilibrium vapor pressures (or solute concentrations) of the isotherms at different temperatures with the aid of the Clausius–Clapeyron equation. Although the concept of isosteric heat is originally intended for adsorption systems, it has been extended to nonadsorption systems (e.g., partition) to elucidate whether a concentration-dependent heat effect occurs with the system. For adsorption of a vapor by an solid, consider the adsorption isotherms at T_1, T_2, and T_3 (in K) in Figure 4.3, with $T_1 < T_2 < T_3$, where the amount of vapor uptake (Q) at each temperature is plotted against the equilibrium partial pressure (P). Similarly, for adsorption of a solute from solution, one considers the isotherms at different temperatures in which the solute uptake (Q) is plotted against the equilibrium solute concentration (C_e).
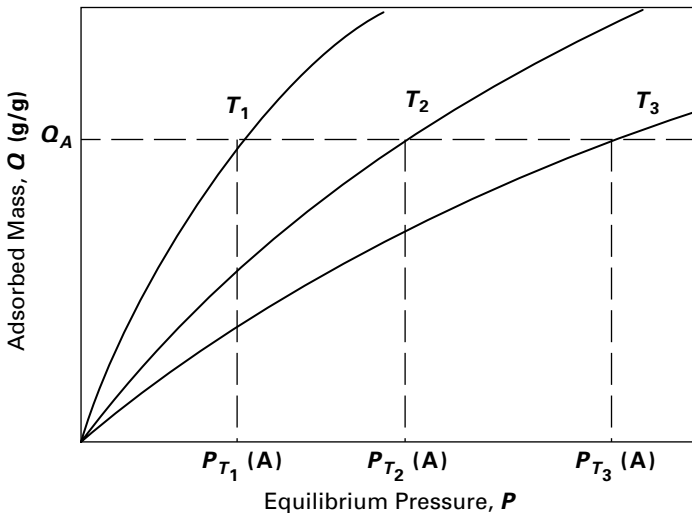

Figure 4.3   Schematic drawing showing the equilibrium pressures (P) of a vapor at three temperatures ($T_1 < T_2 < T_3$) with a fixed adsorbate mass (Q_A) on an adsorbent.

The isosteric-heat data describe how sensitively the molar heat of adsorption of a vapor or a solute varies with the amount adsorbed by a solid. To determine the isosteric heat of adsorption at a given Q (say, Q_A in Figure 4.3), one accounts for the variation of P (or C_e) with T at a fixed Q using the general form of the Clausius–Clapeyron equation:

$$\frac{d \log P}{dT} = \frac{\Delta \overline{H}_d}{2.303RT^2} = \frac{-\Delta \overline{H}_a}{2.303RT^2} \tag{4.14}$$

or

$$\frac{d \log P}{d(1/T)} = \frac{-\Delta \overline{H}_d}{2.303R} \tag{4.15}$$

Similarly,

$$\frac{d \log C_e}{dT} = \frac{\Delta \overline{H}_d}{2.303RT^2} = \frac{-\Delta \overline{H}_a}{2.303RT^2} \tag{4.16}$$

or

$$\frac{d \log C_e}{d(1/T)} = \frac{-\Delta \overline{H}_d}{2.303R} \tag{4.17}$$

where $\Delta \overline{H}_d$ is the molar heat of desorption and $\Delta \overline{H}_a$ is the molar heat of adsorption ($\Delta \overline{H}_d = -\Delta \overline{H}_a$). By repeating the calculations for $\Delta \overline{H}_a$ at other fixed Q, the dependence of $\Delta \overline{H}_a$ on Q can then be determined. For vapor or solute adsorption, the $\Delta \overline{H}_a$ should have the largest negative value (i.e., the molar exothermic heat) at the lowest Q and hence the smallest negative value at the highest Q. As stated before, if the adsorbed vapor forms a condensed phase on the adsorbent, the $\Delta \overline{H}_a$ should be more exothermic than the molar heat of vapor condensation (i.e., $-\Delta \overline{H}_{\text{evap}}$ or $-\Delta \overline{H}_{\text{sub}}$). Similarly, if the adsorbed solute displaces the solvent to form a separate phase on the adsorbent surface, $\Delta \overline{H}_a$ should be more exothermic than the reverse molar heat of solute solution (i.e., $-\Delta \overline{H}_{\text{sol}}$). When the adsorption reaches the maximum on an adsorbent, the net adsorption heat is zero and thus $\Delta \overline{H}_a$ is equal to the heat of adsorbate condensation. In systems where the adsorption energy is not high enough to condense the vapor into a separate phase or to condense the solute by displacing the solvent, the adsorption will be weak. In this case, the thermicity of adsorption would be small and notably less exothermic than the heat of adsorbate condensation. However, as long as a net adsorption occurs, the system will nevertheless exhibit an exothermic effect, despite the fact that it may be very

small. When adsorption is weak, the isotherm usually assumes a relatively linear shape over the entire range. For strong adsorption, which normally involves adsorbate condensation, the isotherm develops a marked concave-downward shape at low P or C_e.

Because the sorption of organic compounds to many natural solids may be dictated by processes other than adsorption (e.g., by a partition interaction), the isosteric plot of the isotherms provides useful heat data for the undergoing process. For example, in a typical partition process of an organic solute from water to a partially miscible organic phase, the isotherm is usually highly linear over a wide concentration range, and therefore the molar isosteric heat of sorption is largely constant, independent of solute concentrations. This unique characteristic enables one to distinguish an uptake by partition from that by adsorption for a contaminant of interest. As we will find out later, ordinary soils act as a dual sorbent in uptake of organic compounds, where either adsorption on soil minerals or partition into soil organic matter may predominate the soil uptake, depending on the system condition. The detected isosteric heat for the system helps to pinpoint the dominant mechanism.