

Thermodynamics of Adsorption in Porous Materials

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Thermodynamic equations are developed for adsorption of multicomponent gas mixtures in microporous adsorbents based on the principles of solution thermodynamics. The conventional spreading pressure and surface area variables, which describe 2-D films, must be abandoned for adsorption in micropores, in which spreading pressure cannot be measured experimentally or calculated from intermolecular forces. Adsorption is divided into two steps: (1) isothermal compression of the gas, (2) isothermal immersion of clean adsorbent in the compressed gas. Thermodynamic functions (Gibbs free energy, enthalpy, and entropy) from solution thermodynamics provide a complete thermodynamic description of the system. Applications are described for characterization of adsorbents, gas storage at high pressure, mixture adsorption, enthalpy balances, molecular simulation, adsorption calorimetry, and shape selectivity in catalysis.

Introduction

Brief history of adsorption thermodynamics

The concept of surface excess in adsorption was introduced by J. Willard Gibbs, but the interpretation and application of the Gibbsian version of thermodynamics of surfaces was impeded by the abstruse nature of his writing (Gibbs, 1928). The thermodynamics textbook by Lewis and Randall (1923) exerted an enormous influence upon the development of thermodynamics in the first half of the 20th century. However, their short section on thermodynamics of surfaces was devoted entirely to the surface tension of liquid-vapor interfaces. The revision of Lewis and Randall by Pitzer and Brewer (Lewis et al., 1961) devoted an entire chapter to surface effects, which concluded with a five-page section on adsorption of gases. In particular they defined the *isosteric heat* (q_{st})

$$q_{st} = RT^2 \left(\frac{\partial \ln P}{\partial T} \right)_n \quad (1)$$

This definition of isosteric heat obtained by differentiating a series of adsorption isotherms at constant loading (n) is still used today. Unfortunately, Eq. 1 applies only to a pure, perfect gas and its connection with the enthalpy of the adsorbed phase and its extension to the case of real gas mixtures has led to considerable confusion. The terminology “isosteric heat” intended to mean lines of constant loading is misleading,

because the evolution of a heat of adsorption requires a change in loading. The existence of other heats of adsorption such as the “differential heat of adsorption” equal to ($q_{st} - RT$), the “equilibrium heat of adsorption” obtained by performing the differentiation in Eq. 1 at constant spreading pressure, and others (Valenzuela and Myers, 1989) adds to the confusion. Agreement within the adsorption community on the thermodynamic definition and physical meaning of the energy of adsorption is long overdue.

Important contributions to the thermodynamics of physical adsorption by D. H. Everett, T. L. Hill, and L. E. Drain were summarized by Young and Crowell (1962). The thermodynamics of physical adsorption on solid adsorbents is based on the concept of an inert adsorbent and the introduction of two new variables: surface area (A) and spreading pressure (Π). A typical equation (Eq. 15 of Chapter 3) from Young and Crowell's book is

$$dF_s = -S_s dT + V_s dP + A d\Pi + \mu_s dn_s \quad (2)$$

where $F_s = G_s + \Pi A$ is a free energy and the subscripts refer to the surface phase. This 2-D, surface thermodynamics approach is standard in adsorption (Ruthven, 1984; Yang, 1987;

Valenzuela and Myers, 1989; Suzuki, 1990). The problem with the 2-D approach is that it requires a series of assumptions of unknown validity: inert adsorbent, pure perfect gas, negligible volume of adsorbed phase, and so on. More disturbing is the impossibility of calculating or measuring the spreading pressure inside a micropore. The external surface area of nonporous solids can be measured by microscopy, but the definition and measurement of the surface area of nanometer-sized micropores is fuzzy.

The topic of adsorption has been omitted from chemical engineering textbooks on thermodynamics since the first one by Dodge (1944). Phase equilibrium is properly concentrated upon vapor-liquid systems because of their importance in distillation. Less attention is devoted to equilibria in liquid-liquid and liquid-solid systems and adsorption thermodynamics was ignored entirely until 1996. The reason for this neglect of physical adsorption is that the fundamental equations of solution thermodynamics developed for vapor-liquid equilibria do not apply to adsorbed phases, which require special treatment and the introduction of surface variables (Π and A) as described in recent editions of Smith et al. (1996, 2001).

Advantages of solution thermodynamics

Innovations in adsorption technology such as pressure-swing adsorption require chemical engineers to perform mass and energy balances and calculate phase equilibria for adsorption systems. The objective here is to show how the familiar principles of phase equilibria and solution thermodynamics established for vapor-liquid equilibria can be applied directly and rigorously to physical adsorption from gaseous mixtures, while avoiding the undefined variables of 2-D surface thermodynamics.

Since engineers and chemists have been measuring gas adsorption in porous adsorbents for many years using the methodology developed for thin films, the case needs to be made that the solution thermodynamics approach is superior not just in the nuances of interest to thermodynamic purists, but also in everyday practical usage. Some of the advantages of solution thermodynamics over the conventional 2-D approach are:

(1) Confusion over different heats of adsorption (see above) is eliminated by the solution thermodynamics approach. In solution thermodynamics, the enthalpy of the adsorbed phase is measured relative to a well-defined reference state and there is no confusion about different types of enthalpy.

(2) The 2-D approach is based upon surface area, which for microporous materials cannot be measured experimentally or calculated theoretically. The suitability of approximate procedures such as the BET Point B method (Young and Crowell, 1962) for estimating surface area has been argued for generations. A better characterization of an adsorbent would be the maximum adsorption of a supercritical gas such as argon at room temperature, or the enthalpy of immersion of the adsorbent in a particular fluid.

(3) The isosteric heat defined in conventional 2-D treatments of adsorption has a singularity (goes to infinity) at the point where the amount adsorbed reaches a maximum (Salem et al., 1998; Siperstein et al., 2001), whereas the integral en-

Table 1. Integral and Differential Thermodynamic Functions for Single-Component Adsorption.*

Function	Symbol	Eq.
Surface potential	Φ	$-RT \int_0^P \frac{n^a}{f} df$
Free energy of immersion	ΔG^{imm}	$\Phi + PV^s$
Enthalpy of immersion	ΔH^{imm}	$-T^2 \frac{\partial}{\partial T} \left[\frac{\Phi}{T} \right]_P + PV^s$
Entropy of immersion	ΔS^{imm}	$-\left[\frac{\partial \Phi}{\partial T} \right]_P$
Integral free energy	ΔG^a	$n^a RT \ln \frac{f}{f^\circ} + \Phi$
Integral enthalpy	ΔH^a	$\int_0^{n^a} \Delta \bar{h}^a dn^a$
Integral entropy	ΔS^a	$\frac{\Delta H^a - \Delta G^a}{T}$
Diff. free energy (chem. potential)	$\Delta \bar{g}^a$	$RT \ln \frac{f}{f^\circ}$
Diff. enthalpy	$\Delta \bar{h}^a$	$-RT^2 \left[\frac{\partial \ln f}{\partial T} \right]_{n^a}$
Diff. entropy	$\Delta \bar{s}^a$	$\frac{\Delta \bar{h}^a}{T} - R \ln \frac{f}{f^\circ}$

*The integral enthalpy and heat of immersion are related by $\Delta H^a = \Delta H^{\text{imm}} + n^a \bar{h}^R - PV^s$ and therefore $\Delta H^a = \Delta H^{\text{imm}}$ for a perfect gas at low pressure. For a perfect gas, $f = P$ and except for very high pressure the Poynting term PV^s is negligible. All functions are normally negative in sign.

thalpy of solution thermodynamics is smooth and well-defined under all conditions.

(4) The conventional treatment of thin films is for adsorption of perfect gases on inert, planar solids at low pressures of a few bars. The solution thermodynamics approach applies to adsorption of fluid mixtures in porous materials at high pressure up to 1,000 bars.

(5) The solution thermodynamics approach leads naturally to the *immersional* functions: free energy, enthalpy, and entropy of immersion of the clean adsorbent in the bulk fluid. The obvious physical significance of these functions simplifies their application to the solution of practical problems. The concepts of spreading pressure, differential entropy, and isosteric heat developed in the conventional 2-D approach are difficult to understand, even for experts.

(6) Experimental measurements of adsorption in porous materials using volumetric or gravimetric methods require careful attention to the placement of the Gibbs dividing surface between the gas phase and the solid adsorbent. Conventional 2-D treatments of adsorption do not apply to porous materials.

(7) Since the spreading pressure inside a micropore containing a few dozen molecules cannot be calculated from intermolecular forces, theory cannot be compared with experiment using the conventional 2-D approach. Solution thermodynamics provide a simple connection between theoretical absolute variables (total energy, total number of adsorbate molecules) and experimental excess variables.

The thermodynamic functions for adsorption developed in the next section are summarized in Table 1, and a sample calculation for the Langmuir model is given in the Appendix.

The theoretical development section is followed by numerous applications in adsorption technology.

Theory

Defining adsorption in porous materials

An adsorption system contains two macroscopic phases: a gas phase and a solid phase. For typical adsorbents such as zeolites or activated carbon, adsorption occurs inside the adsorbent in micropores, mesopores, and macropores. Commercial adsorbents are manufactured not as single crystals, but as small particles which are usually shaped into larger particles using binders. Adsorption occurs mainly within the pores of the adsorbent, but may also occur on its external surface and occasionally in the binder.

In order to divide the adsorbate molecules and their properties into two phases, it is necessary to distinguish adsorbed molecules from gas-phase molecules. A methane molecule located inside a micropore 4 Å from its internal surface can reasonably be classified as adsorbed. A methane molecule located at a distance of 100 Å from the surface of the adsorbent can reasonably be classified as belonging to the gas phase. Ambiguity arises for intermediate cases. Is a methane molecule located at a distance of 10 Å from the surface of the solid adsorbed? Fortunately, the problem of defining a boundary between the adsorbed and gas phases was solved by Gibbs (1928), whose solution was to propose the construction of a mathematical dividing surface between the two phases. Gibbs was intentionally vague about the exact location of this dividing surface, which is advantageous because it would be difficult to define a dividing surface within the micropores of an adsorbent.

Figure 1a shows the density profile close to the surface for the case of single-component adsorption. The density of the adsorbate (ρ^g) is constant in the gas phase and constant (zero) within the solid. The amount adsorbed within the interface (n^a) obviously depends upon the location of its boundaries. Figure 1b illustrates the Gibbs model in which the actual interface is replaced by a single dividing surface located somewhere within the interfacial region. The gas phase with volume V^g has a homogeneous density (ρ^g) up to the dividing surface. The mass balance for adsorption is

$$n^a = n^t - V^g \rho^g \quad (3)$$

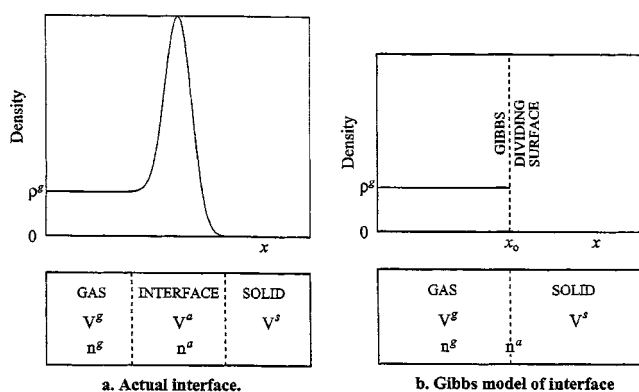


Figure 1. Profile of gas density at gas-solid interface.

The total amount of gas in the system (n^t) and its bulk density (ρ^g) are measured experimentally. The volume of the gas phase (V^g) increases as the dividing surface in Figure 1b moves from left to right, while the amount adsorbed (n^a) decreases from a positive value to zero and finally becomes negative as the dividing surface enters the solid phase. Thus, the amount adsorbed (n^a) depends upon the location (x_0) of the dividing surface.

The location of the dividing surface is fixed by selecting a reference gas for which the amount adsorbed is *defined* to be zero

$$n^a = n^t - V^g \rho^g = 0 \quad (\text{for He}) \quad (4)$$

It follows that

$$V^g = \frac{n^t}{\rho^g} \quad (\text{for He}) \quad (5)$$

Equation 4 provides a method of measuring adsorption *relative to helium* by measuring the volume of the gas phase (V^g) using helium as a reference component. V^g , called the dead space or void volume, is normally measured at the standard conditions of room temperature and low (sub-atmospheric) pressure. The Gibbs procedure of defining adsorption relative to a reference component is independent of whether helium actually adsorbs. Helium was selected as the reference gas, because it is a small, inert molecule, but a smaller inert molecule (if one existed) would measure a slightly larger dead space than helium. The point is that all experiments and theoretical calculations should be based upon the same reference state.

Referring again to Figure 1b, the gas volume (V^g) is required for volumetric experiments and the solid volume (V^s) is required for gravimetric experiments. V^g includes the pores of the adsorbent, and V^s is the skeletal volume of the adsorbent. The skeletal volume, which is the total volume of the solid minus its pore volume, is measured by the buoyancy force exerted in helium gas. The volume displaced by the solid (V^s) is the slope on a plot of apparent weight vs. density of helium. Thus, gravimetric and volumetric experiments are based upon the same assumption: that helium gas does not adsorb at the standard conditions of room temperature and low pressure.

Instead of defining adsorption by Eq. 3, why not measure the total amount of gas contained in the micropores? Unfortunately, an experimental method for measuring the total amount of gas adsorbed in the pores does not exist. The standard volumetric technique measures the total amount of gas in the system but cannot distinguish between molecules in the pores and molecules in the gas phase. The gravimetric method also fails to measure total adsorption in the pores because of the necessity for a buoyancy correction to the apparent weight.

Adsorption measured relative to helium by Eq. 3 is called Gibbs *excess* adsorption. The excess adsorption is the total amount of gas in the pores minus the amount that would be present if the pores were filled with gas at the equilibrium bulk density.

Thermodynamic properties of porous materials

According to the Gibbs model of adsorption depicted in Figure 1b, any extensive thermodynamic function may be written

$$Z' = Z^a + Z^g + Z^s \quad (6)$$

The gas-phase portion is

$$Z^g = V^g \rho^g z^g \quad (7)$$

where ρ^g is the molar density of the bulk gas and z^g is the molar value of Z in the bulk phase at the same values of the intensive variables (T , P , y_i). The molar function $z^g(T, P, y_i)$ is determined from independent PVT measurements on the bulk gas. As explained in the previous section, V^g is determined from Eq. 5 using helium gas. Specifically, from Eq. 7

$$\begin{aligned} n_i^g &= V^g \rho^g y_i \\ U^g &= V^g \rho^g u^g \\ S^g &= V^g \rho^g s^g \\ V^g &= V^g \rho^g v^g = V^g \end{aligned} \quad (8)$$

The solid-phase term (Z^s) in Eq. 6 is determined from independent measurements of the solid adsorbent in its pure standard state.

From Eq. 6

$$\begin{aligned} n_i^a &= n_i^t - n_i^g \\ U^a &= U^t - U^g - U^s \\ S^a &= S^t - S^g - S^s \\ V^a &= V^t - V^g - V^s = 0 \end{aligned} \quad (9)$$

a form which emphasizes the excess nature of the Gibbs model for which the adsorbed phase is a mathematical plane of zero volume ($V^a = 0$). According to Eq. 9, the energy of the adsorbed phase (U^a) includes the energy change of the solid adsorbent relative to its standard state in addition to the energy of the adsorbate molecules. A similar statement applies to the entropy. Solution thermodynamics is unable to distinguish energy changes in the solid from energy changes of the adsorbate molecules.

Referring again to Figure 1b, the total volume is divided into two parts: the gas phase (V^g) and the condensed phase (V^s). The condensed phase includes the adsorbed phase with volume $V^a = 0$ by definition. The Gibbs model ignores possible changes in the volume of the condensed phase in response to increased pressure or because of swelling in the case of polymeric adsorbents. Since the volumetric method is based upon a constant value of V^g and the gravimetric method is based upon a constant value of V^s , deformation or swelling of V^s would be revealed by lack of agreement of volumetric and gravimetric isotherms. Experimental evidence of such a discrepancy has not yet been found.

Another consideration is the variation of V^g and V^s with temperature. Although both volumes are functions of temperature, their temperature dependence is weak. V^s increases with temperature according to the temperature coef-

ficient of expansion of the solid, which is of order $(1/V)(\partial V/\partial T)_P = 10^{-5}$ to 10^{-3} K^{-1} . Changes in V^s may be significant when making gravimetric measurements over a wide range of temperature. Molecular simulations of the helium pore volume of silicalite (Siperstein et al., 2001) indicate that the pore volumes at 300 and 400 K are 0.175 and 0.146 cm^3/g , respectively. The decrease in helium pore volume is due to helium-solid intermolecular forces, not expansion or contraction of the solid. Determinations of void volume should always be accompanied by the temperature of the measurement. At high pressure in the range 100–1,000 bar, the adsorption isotherm is highly sensitive to the void volume.

Fundamental equation for energy

Adsorption in microporous adsorbents falls naturally into the framework of solution thermodynamics, with the distinction that the solvent is a solid. The starting point is the fundamental differential equation for the energy of a microporous adsorbent containing C gaseous adsorbates (Callen, 1985)

$$dU = TdS - PdV + \sum_{i=1}^C \mu_i dn_i + \mu dm \quad (10)$$

The intensive variables of the condensed phase are the temperature (T), the pressure (P), the chemical potentials of the adsorbates (μ_i), and the chemical potential of the solid adsorbent (μ). The chemical potentials of the adsorbates are in J/mol and the chemical potential of the adsorbent is in J/kg. The extensive variables of the condensed phase are the internal energy (U), entropy (S), the amount (number of mols) of each adsorbate (n_i), and the mass of solid adsorbent (m). Equation 10 is written for the solid phase plus the adsorbed phase, that is, the entire condensed phase.

The particle-size distribution, composition, and structure of the individual adsorbent particles are assumed to be uniform throughout the system. Thus, the external surface area of the adsorbent and the extensive thermodynamic properties are directly proportional to the mass of adsorbent present. Stated mathematically

$$U(\eta S, \eta V, \eta n_i, \eta m) = \eta U(S, V, n_i, m) \quad (11)$$

The total energy U of the solid phase is a first-order, homogeneous function of the variables S , V , n_i , and m ; that is to say, doubling the values of S , V , n_i , and m at constant values of the intensive variables (T , P , μ_i , μ) doubles the value of U . It follows from Eq. 11 and Euler's theorem for homogeneous functions (Callen, 1985) that

$$U = TS - PV - \sum_{i=1}^C \mu_i n_i + \mu m \quad (12)$$

Adsorption thermodynamics deals with systems such as a packed column or sample cell containing a fixed mass of adsorbent. The solid phase is open with respect to the adsor-

bates, but closed with respect to the adsorbent. The reversible addition of solid adsorbent to the system corresponding to the μdm term in Eq. 10 is not physically realizable, so $dm = 0$ and the mass of adsorbent is a constant. The extensive variables (U, S, V, n_i) are converted to extensive variables per unit mass so that Eq. 12 may be written in the asymmetric, but more useful, form

$$U = TS - PV + \sum_{i=1}^C \mu_i n_i + \mu \quad (13)$$

In Eq. 13 and, henceforth, all extensive variables (U, S, V, n_i , and so on) are written *per unit mass of adsorbent* and called *mass extensive variables*. For the adsorbent in its pure standard state at the equilibrium pressure and temperature

$$U^s = TS^s - PV^s + \mu^s \quad (14)$$

The pure solid is assumed to be incompressible so that $V^s = V^{s*}$, $U^s = U^{s*}$, and $S^s = S^{s*}$, where the asterisk refers to the clean adsorbent *in vacuo*. However, the pressure affects the enthalpy and free energy so $H^s = H^{s*} + PV^s$, $G^s = G^{s*} + PV^s$, and $\mu^s = \mu^{s*} + PV^s$. The free energy (G^s) of the pure adsorbent is equal to its chemical potential (μ^s); the units of both are J/kg. The PV^s term is a Poynting correction which accounts for hydrostatic pressure (de Azevedo et al., 1999).

Given the equilibrium values of T and P , any mass extensive function of the adsorbed phase is obtained by subtracting the function for the pure solid from the corresponding function for the condensed phase

$$\begin{aligned} U^a &= U - U^s \\ S^a &= S - S^s \\ V^a &= V - V^s = 0 \\ n_i^a &= n_i \end{aligned} \quad (15)$$

Subtracting Eq. 14 from Eq. 13, and using Eq. 15

$$U^a = TS^a + \sum_{i=1}^C \mu_i n_i^a + \Phi \quad (16)$$

where

$$\Phi = (\mu - \mu^s) \quad (17)$$

is called the surface potential (Sircar and Myers, 1973a) or grand potential. If no adsorption occurs, then $\mu = \mu^s$ and the surface potential is zero. Writing Eq. 10 for the condensed system containing a constant mass m of adsorbent

$$dU = TdS + \sum_{i=1}^C \mu_i dn_i \quad (18)$$

The PdV term vanishes because $V = V^s$ is assumed constant. For the same mass of adsorbent in its standard state

$$dU^s = TdS^s \quad (19)$$

Subtracting Eq. 19 from Eq. 18, and using Eq. 15

$$dU^a = TdS^a + \sum_{i=1}^C \mu_i dn_i^a \quad (20)$$

Equations 16 and 20 are the integral and differential equations governing the adsorbed phase. Changes in the properties of the adsorbent from its standard-state values (U^s, S^s) are included implicitly in U^a and S^a . In surface thermodynamics, the adsorbent is assumed to be inert so that its chemical potential is unperturbed by isothermal adsorption ($\mu = \mu^s$). Assuming the adsorbent to be inert is acceptable for adsorption on the external surface of solid particles, but, for microporous adsorbents, the concept of an inert adsorbent must be abandoned. The surface potential (Φ) in Eq. 16 vanishes only in the trivial case of no adsorption.

Enthalpy and free energy

The Legendre transformations for the auxiliary functions are (Callen, 1985)

$$\begin{aligned} H &= U + PV \\ F &= U - TS \\ G &= F + PV = H - TS \end{aligned} \quad (21)$$

where H is enthalpy, F is Helmholtz free energy, and G is Gibbs free energy. From Eq 16.

$$\begin{aligned} U^a &= TS^a + \sum \mu_i n_i^a + \Phi \\ H^a &= TS^a + \sum \mu_i n_i^a + \Phi \\ F^a &= \sum \mu_i n_i^a + \Phi \\ G^a &= \sum \mu_i n_i^a + \Phi \end{aligned} \quad (22)$$

In Eq. 22 and, henceforth, summation over the C adsorbates is implicit. The enthalpy is equal to the internal energy, because the volume of the adsorbed phase is zero. The Helmholtz and Gibbs free energies are equal for the same reason. The free energy of the adsorbed phase consists of two parts: the free energy of n_i^a mols of each species in the equilibrium gaseous state plus an additional term, the surface potential (Φ), which is zero if no adsorption takes place.

This is the point at which surface thermodynamics diverges from solution thermodynamics. Surface thermodynamics, which is the standard approach adopted in monographs on adsorption (Ruthven, 1984; Suzuki, 1990; Yang, 1987), assumes an inert adsorbent with chemical potential which is independent of loading. It is difficult at first to accept the fact that the chemical potential of a porous adsorbent varies with the isothermal loading of the adsorbate molecules. In molecular simulation, it is generally assumed that the adsorbent generates an invariant potential field. However, the existence of a potential field is not inconsistent with changes in free energy, which contain both energetic and entropic contributions. From the perspective of solution thermodynamics,

the intimate contact of the adsorbate molecules with the atoms of the porous material alters the chemical potential of the solid. Consider the immersion of clean adsorbent in a compressed gas held at constant pressure and temperature. Since the variables pressure, temperature, and chemical potential of the compressed gas are fixed during the immersion process, the only intensive variable capable of change is the chemical potential of the adsorbent.

Surface thermodynamics is valid when the surface area can be measured experimentally. For example, the external surface area of nonporous carbon black can be measured by microscopy. In this case, the model of an inert adsorbent with adsorption occurring in a 2-D film on its external surface is realistic. However, the concepts of surface area and spreading pressure lose their physical meaning in porous adsorbents such as zeolites.

From Eq. 22

$$H^a = U^a \quad (23)$$

and

$$G^a = F^a = U^a - TS^a \quad (24)$$

From Eqs. 20, 23, and 24, it follows that

$$\begin{aligned} dU^a &= TdS^a + \sum \mu_i dn_i^a \\ dH^a &= TdS^a + \sum \mu_i dn_i^a \\ dF^a &= -S^a dT + \sum \mu_i dn_i^a \\ dG^a &= -S^a dT + \sum \mu_i dn_i^a \end{aligned} \quad (25)$$

The surface potential (Φ) term in Eq. 22 for the integral functions does not appear explicitly in the differential equations for the adsorbed phase.

Equations 22 and 25 are the basic integral and differential equations for the adsorbed phase. Any extensive property of the condensed phase is the sum of the property in the adsorbed phase (H^a , S^a , and so on) plus the corresponding property of the solid adsorbent in the absence of adsorption (H^s , S^s , and so on) as described by Eqs. 14 and 19.

Surface potential

The surface potential, which is the chemical potential of the solid adsorbent relative to its pure standard state, is obtained from Eq. 22

$$\Phi = G^a - \sum \mu_i n_i^a \quad (26)$$

Differentiating and substituting Eq. 25 for dG^a gives

$$d\Phi = -S^a dT - \sum n_i^a d\mu_i \quad (27)$$

This equation is analogous to the Gibbs-Duhem equation for a liquid mixture with the $-VdP$ term replaced by $d\Phi$. At constant temperature, Eq. 27 reduces to the Gibbs adsorp-

tion isotherm

$$d\Phi = -\sum n_i^a d\mu_i \quad (\text{constant } T) \quad (28)$$

Replacing chemical potential by fugacity

$$d\Phi = -RT \sum n_i^a d \ln f_i \quad (\text{constant } T) \quad (29)$$

Since surface potential is a state function, the integration for Φ is independent of the path. The thermodynamic consistency of experimental data may be tested by comparing values of Φ obtained for different paths (Myers and Sircar, 1972). Integrating for pure-component adsorption from the unadsorbed state at zero pressure where $\mu = \mu^s = \mu^{s*}$ and $\Phi = 0$

$$\Phi = -RT \int_{P=0}^P \frac{n^a}{f} df \quad (\text{constant } T) \quad (30)$$

For a perfect gas

$$\Phi = -RT \int_0^P \frac{n^a}{P} dP = -RT \int_0^{n^a} \frac{d \ln P}{d \ln n^a} dn^a \quad (\text{constant } T) \quad (31)$$

In the solution thermodynamics approach, the chemical potential of the nonvolatile adsorbent is determined indirectly by integrating the chemical potential of the gas. An analogous integration is used to calculate the chemical potential of a strong electrolyte in aqueous solution from the change in chemical potential of the water vapor (de Azevedo et al., 1999).

The concept of the adsorbent as a solvent suggests that its chemical potential at the limit of zero loading should be given by Raoult's law. At the limit of zero pressure, the slope of the adsorption isotherm is given by Henry's law: $n^a = KP$. Since the adsorbed gas obeys Henry's law, the solvent (the solid adsorbent) follows Raoult's law over the same dilute range

$$\begin{aligned} \Phi = \mu - \mu^s &= \frac{RT}{M} \ln x^s = \frac{RT}{M} \ln(1 - x^a) \\ &\approx -\frac{RT}{M} x^a \approx -n^a RT \end{aligned} \quad (32)$$

where x^s is the mol fraction of solid adsorbent, x^a is the mol fraction of adsorbate, and n^a is mols of gas per unit mass of adsorbent. The (unknown) molecular weight of the adsorbent (M) cancels in the result. At the limit of zero pressure, the surface potential decreases in direct proportion to the amount adsorbed. The limiting relation $\Phi = -n^a RT$ may be compared to the corresponding equation for a 2-D perfect gas from surface thermodynamics: $\Pi A = n^a RT$. Thermodynamics is indifferent to the name of the property (the ΠA product or the chemical potential of the adsorbent), but the physics of adsorption in micropores is best described within the framework of solution thermodynamics because spreading pressure in a micropore is undefined.

Degrees of freedom and independent variables

The number of degrees of freedom from the Gibbs phase rule is

$$F = C + 2 - P \quad (33)$$

where C is the number of chemical components present and P is the number of phases. Since one component is the adsorbent

$$F = C + 3 - P = C + 3 - 2 = C + 1 \quad (34)$$

if C is the number of adsorbates present. For example, for binary adsorption, there are three degrees of freedom. The natural independent variables for the integral functions are T, P, y_1 ; the dependent variables are then $n_i^a, \Delta H^a, \Delta S^a, \Phi$, and so on. The natural independent variables for the differential functions are T, n_1^a, n_2^a ; the dependent variables are then P, y_1 , and so on.

Equality of chemical potentials at equilibrium

Up to this point it has been assumed without proof that the chemical potential in the adsorbed phase (μ^a) is equal to the chemical potential in the gas phase (μ^g). Here, the assumed equality of chemical potentials is verified by minimizing the Gibbs free energy of the total system at constant temperature and pressure. From Eq. 6

$$G^t = G^a + G^g + G^s \quad (35)$$

Since these are extensive functions per unit mass of adsorbent, G^s is the chemical potential of the adsorbent in its standard state

$$dG^s = d\mu^s = -S^s dT + V^s dP \quad (36)$$

Differentiating Eq. 35

$$dG^t = dG^a + dG^g + dG^s \quad (37)$$

From Eq. 25

$$dG^a = -S^a dT + \sum \mu_i^a dn_i^a \quad (38)$$

For the bulk gas phase (Sandler, 1998)

$$dG^g = -S^g dT + V^g dP + \sum \mu_i^g dn_i^g \quad (39)$$

Minimizing G^t at constant T and P under the constraint

$$n_i^t = n_i^a + n_i^g = \text{constant} \quad (40)$$

gives

$$dG^t = \sum \mu_i^a dn_i^a + \sum \mu_i^g dn_i^g = \sum (\mu_i^g - \mu_i^a) dn_i^g = 0 \quad (41)$$

Since equality of chemical potentials $\mu_i^g = \mu_i^a$ corresponds to equilibrium ($dG^t = 0$), the use of the notation μ_i for the chemical potential in either phase is justified.

Determination of void volume

The measurement of Gibbs excess variables according to Eq. 9 requires prior determination of the void volume (dead space) of the apparatus using Eq. 5

$$V^g = \frac{n^t}{\rho^g} \quad (\text{for He}) \quad (42)$$

The standard procedure is to measure the void volume using pure helium gas at low pressure and room temperature (T°) by assuming that helium does not adsorb. n^t is the total number of mols of helium admitted to the sample cell per unit mass of adsorbent; V^g is the specific void volume of the apparatus measured in cm^3 per unit mass of adsorbent; ρ^g is the helium density. At low pressure, use of the perfect-gas law in Eq. 42 gives

$$V^g = \frac{n^t RT^\circ}{P} \quad (\text{for He}) \quad (43)$$

The experimental determination of dead space is based on Eq. 43. The theoretical value is calculated from statistical thermodynamics, which at the limit of low pressure gives for the excess adsorption

$$n^a = \frac{BP}{RT^\circ} \quad (44)$$

where B is called the adsorption second virial coefficient (Steele, 1974)

$$B = \frac{1}{m} \int [e^{-E(r)/kT^\circ} - 1] dr \quad (45)$$

E is the gas-solid potential energy of a single molecule, and m is the mass of a representative sample of solid adsorbent. The integration is performed over the gas phase including the pore volume. In order for theory to mimic experiment, the second virial coefficient for helium must be zero so that

$$V^g = \frac{1}{m} \int e^{-E(r)/kT^\circ} dr \quad (\text{for He}) \quad (46)$$

E is the gas-solid potential energy of a helium atom. The integration in Eq. 46 is performed over the entire condensed phase as well as the gas phase, since the exponential vanishes within the solid where $\phi \rightarrow \infty$.

Integral and differential properties of the adsorbed phase

The integral functions free energy, enthalpy, and entropy, which arise naturally from solution thermodynamics, are missing from the traditional surface thermodynamics approach based upon spreading pressure, 2-D films, isosteric

heat, and other differential quantities. A special feature of the integral functions is that their natural independent variables (temperature, pressure, and gas-phase composition) are controllable experimentally. The integral functions are needed for engineering calculations and are useful for characterization of adsorbents, as shown below. The integral functions for the adsorbed phase are defined relative to the perfect-gas reference state at the same temperature

$$\begin{aligned}\Delta G^a &= G^a - \sum n_i^a \mu_i^\circ = \Delta H^a - T\Delta S^a \\ \Delta H^a &= H^a - \sum n_i^a h_i^\circ \\ \Delta S^a &= S^a - \sum n_i^a s_i^\circ\end{aligned}\quad (47)$$

The quantities μ_i° , h_i° , and s_i° refer to the molar values in the perfect-gas reference state. The integral free energy and enthalpy (ΔG^a , ΔH^a) are measured in joules per kilogram of adsorbent. Substituting for G^a in Eq. 47 from Eq. 22

$$\begin{aligned}\Delta G^a &= \sum n_i^a (\mu_i^g + \mu_i^\circ) + \Phi \\ \Delta H^a &= \sum n_i^a (\bar{h}_i^g - h_i^\circ) - T^2 \frac{\partial}{\partial T} \left[\frac{\Phi}{T} \right]_{P,y_i} \\ \Delta S^a &= \sum n_i^a (\bar{s}_i^g - s_i^\circ) - \left[\frac{\partial \Phi}{\partial T} \right]_{P,y_i}\end{aligned}\quad (48)$$

The overline notation for partial molar variables in the bulk gas phase (\bar{h}_i^g, \bar{s}_i^g) is omitted for the chemical potential (μ_i^g) since its partial molar character is understood. The expression for ΔS^a is obtained by combining Eq. 47 with the partial differential of Eq. 27 with respect to temperature; then $\Delta H^a = \Delta G^a + T\Delta S^a$.

The equations for ΔG^a , ΔH^a , and ΔS^a contain two parts: (1) changes for isothermal compression of the gaseous adsorbates from their perfect-gas reference states to the equilibrium pressure; (2) changes for isothermal, isobaric adsorption (Φ and its derivatives). Consider isothermal immersion of clean, evacuated adsorbent into the compressed gas; the free energy of immersion is

$$\Delta G^{\text{imm}} = (G^a - \sum n_i^a \mu_i^g) + (G^s - G^{s*}) \quad (49)$$

ΔG^{imm} is the change in the free energy of the condensed phase caused by adsorption, measured relative to compressed gas and evacuated adsorbent. The first term on the righthand side of Eq. 49 is the free energy of adsorbed gas relative to bulk compressed gas; the second term is the free energy of the adsorbent in its standard state (T, P) relative to the evacuated state ($T, \text{in vacuo}$). Combining Eqs. 47–49 and observing that $(G^s - G^{s*}) = PV^s$

$$\begin{aligned}\Delta G^{\text{imm}} &= \Phi + PV^s \\ \Delta H^{\text{imm}} &= -T^2 \frac{\partial}{\partial T} \left[\frac{\Phi}{T} \right]_{P,y_i} + PV^s \\ \Delta S^{\text{imm}} &= - \left[\frac{\partial \Phi}{\partial T} \right]_{P,y_i}\end{aligned}\quad (50)$$

At low pressure, the Poynting correction (PV^s) for the enthalpy and free energy may be ignored. Thus, disregarding the (PV^s) nuisance term, the surface potential is equal to the free energy of immersion. The free energy of immersion is negative because adsorption is spontaneous. The enthalpy of immersion (ΔH^{imm}) may be measured directly by calorimetry (see below) or indirectly by differentiating the surface potential according to Eq. 50. Since the heat of immersion is exothermic, ΔH^{imm} is negative in sign. Since the adsorption process is associated with a loss of entropy, the entropy of immersion (ΔS^{imm}) is also a negative quantity. The free energy and enthalpy of immersion in a pure liquid can be used to predict adsorption from liquid mixtures (Sircar and Myers, 1973b).

The surface potential (Φ) and associated immersional functions ($\Delta G^{\text{imm}}, \Delta H^{\text{imm}}, \Delta S^{\text{imm}}$) are more closely related to the adsorption process than the integral functions ($\Delta G^a, \Delta H^a, \Delta S^a$) in Eq. 48, which contain an additional term for isothermal compression of the bulk gas

$$\begin{aligned}\Delta G^{\text{comp}} &= \sum n_i^a (\mu_i^g - \mu_i^\circ) = RT \sum n_i^a \ln \frac{Py_i}{P^\circ} + \sum n_i^a g_i^R \\ \Delta H^{\text{comp}} &= \sum n_i^a (\bar{h}_i^g - h_i^\circ) = \sum n_i^a h_i^R \\ \Delta S^{\text{comp}} &= \sum n_i^a (\bar{s}_i^g - s_i^\circ) = -R \sum n_i^a \ln \frac{Py_i}{P^\circ} + \sum n_i^a s_i^R\end{aligned}\quad (51)$$

The compression terms for the bulk gas are obtained from partial pressures (Py_i) and from residual functions (g_i^R, h_i^R, s_i^R) (Smith et al., 2001) which vanish for a perfect gas.

The integral and immersional functions derived from solution thermodynamics are related to the molar and differential functions generated by 2-D surface thermodynamics. The integral functions in Eq. 48 are converted to molar variables by dividing each function by the total amount adsorbed $n_i^a = \sum_i n_i^a$

$$\begin{aligned}\Delta g^a &= \frac{\Delta G^a}{n_i^a} = \Delta h^a - T\Delta s^a \\ \Delta h^a &= \frac{\Delta H^a}{n_i^a} \\ \Delta s^a &= \frac{\Delta S^a}{n_i^a}\end{aligned}\quad (52)$$

The molar integral functions Δg^a and Δh^a have units of J/mol.

The differential functions for component i in a multicomponent mixture are obtained from the integral functions. Differentiation of the functions ΔG^a , ΔH^a , and ΔS^a in Eq. 47 gives

$$\begin{aligned}\Delta \bar{g}_i^a &= \left[\frac{\partial \Delta G^a}{\partial n_i^a} \right]_{T,n_i^q} = \mu_i^a - \mu_i^\circ = RT \ln \left[\frac{f_i}{f_i^\circ} \right] \\ \Delta \bar{h}_i^a &= \left[\frac{\partial \Delta H^a}{\partial n_i^a} \right]_{T,n_i^q} = \bar{h}_i^a - h_i^\circ = -RT^2 \left[\frac{\partial \ln f_i}{\partial T} \right]_{n_i^a, n_i^q} \\ \Delta \bar{s}_i^a &= \left[\frac{\partial \Delta S^a}{\partial n_i^a} \right]_{T,n_i^q} = \bar{s}_i^a - s_i^\circ = -\frac{\partial}{\partial T} \left[RT \ln \frac{f_i}{f_i^\circ} \right]_{n_i^a, n_i^q}\end{aligned}\quad (53)$$

The relations $\mu_i^a = (\partial G^a / \partial n_i^a)_{T, n_j^a} = \mu_i^a$ and $(\partial S^a / \partial n_i^a)_{T, n_j^a} = -(\partial \mu_i^a / \partial T)_{n_i^a, n_j^a}$ necessary for the derivation of Eq. 53 were obtained from the total differential for G^a in Eq. 25. The independent variables for the differential functions are temperature and mol numbers (n_i^a). f_i is fugacity and f_i° is the standard-state fugacity (1 bar). The overline notation in these functions (such as $\Delta \bar{h}_i^a$) is used to distinguish differential functions from molar integral functions (Δh^a); the differential character of the chemical potential is implicit. The differential functions $\Delta \bar{g}_i^a$ and $\Delta \bar{h}_i^a$ have units of J/mol and, like the integral and molar integral functions, are based on the perfect-gas reference state. For a pure bulk fluid, the partial molar and molar functions are equal. The molar and differential functions for the adsorbed phase are unequal, even for a pure adsorbate.

The relationships in Eq. 53 are similar to those for partial molar quantities in a bulk fluid. However, for a bulk fluid, the partial molar derivatives are at constant pressure; for an adsorbed fluid, the partial derivatives are at constant loading.

A sample calculation of the integral, immersional, molar integral, and differential functions summarized in Table 1 is provided in Appendix A. The immersional functions of Eq. 50 are more closely related to the adsorption process than the other functions, which contain additional terms for isothermal compression of the gas.

Differential enthalpy and isosteric heat

Confusion about the meaning of isosteric heat is widespread in the adsorption literature. For example, Eqs. 29–46 in the revised version of Lewis et al.'s (1961) textbook gives the following relation between the differential entropy and the isosteric heat (q_{st})

$$\Delta \bar{s}^a = \frac{q_{st}}{T} - R \ln \frac{f}{f^\circ} \quad (54)$$

Equation 54 has a sign error: the first term should be $(-q_{st}/T)$ (cf. Table 1). Errors like this one could be avoided by replacing the ill-defined isosteric heat with the differential enthalpy of adsorption. Differential enthalpy is *not* a heat of adsorption, the value of which would depend upon the path. Differential enthalpy is a state function which can be measured either by calorimetry (see below) or by differentiating a series of adsorption isotherms at constant loading

$$\Delta \bar{h}_i^a = -RT^2 \left[\frac{\partial \ln f_i}{\partial T} \right]_{n_i^a, n_j^a} \quad (55)$$

For a pure, perfect gas

$$\Delta \bar{h}^a = -RT^2 \left[\frac{\partial \ln P}{\partial T} \right]_{n^a} \quad (56)$$

Except for the minus sign, this equation is identical to Eq. 1. The isosteric heat is a positive quantity by definition, but the differential enthalpy of adsorption is negative (exothermic).

The integral enthalpy can be calculated by differentiating the surface potential $\Phi(T, P, y_i)$ according to Eq. 48, or by

integrating the differential enthalpies; for example, from Eq. 53 for a binary mixture

$$d(\Delta H^a) = \Delta \bar{h}_1^a dn_1^a + \Delta \bar{h}_2^a dn_2^a \quad (\text{const. } T) \quad (57)$$

Since ΔH^a is a state function, the integral is independent of the path and the differential enthalpies are related by Maxwell-type equations

$$\left[\frac{\partial \Delta \bar{h}_1^a}{\partial n_2^a} \right]_{T, n_1^a} = \left[\frac{\partial \Delta \bar{h}_2^a}{\partial n_1^a} \right]_{T, n_2^a} \quad (58)$$

The differential mixture enthalpies (whose absolute values are called isosteric heats in the literature of adsorption) are functions of loading and can be measured experimentally or predicted from single-gas adsorption data (Siperstein and Myers, 2001). For pure-component adsorption, the integral is

$$\Delta H^a = \int_0^{n^a} \Delta \bar{h}^a dn^a \quad (\text{const. } T) \quad (59)$$

The differential enthalpy $\Delta \bar{h}^a$ is a function of loading (n^a), but its variation with temperature is weak and the assumption of its constancy over a moderate range of temperature is a useful approximation. For pure-component adsorption of a perfect gas, Eq. 56 gives for constant $\Delta \bar{h}^a$

$$\ln \left[\frac{P}{P^\circ} \right] = \frac{\Delta \bar{h}^a}{R} \left[\frac{1}{T} - \frac{1}{T^\circ} \right] \quad (\text{constant } n^a) \quad (60)$$

which provides the function $P(T)$ given a reference point $P^\circ(T^\circ)$ at the same loading (n^a).

Heat capacity

A useful and frequently used approximation is that the differential ($\Delta \bar{h}^a$) and integral (ΔH^a) enthalpies of the adsorbed phase are independent of temperature, at least over some modest interval of temperature. With this approximation, the heat capacity at constant loading from Eq. 70 simplifies to

$$C_p^a = \left[\frac{\partial H^a}{\partial T} \right]_{n_i^a} = \sum_i n_i^a (c_p^\circ)_i \quad (61)$$

so that the heat capacity of the adsorbate is equal to its heat capacity in the perfect-gas state. If in addition the gas phase is ideal, the heat capacity of the system follows from Eq. 6

$$C_p^t = C_p^g + C_p^a + C_p^s = \sum_i n_i^g (c_p^\circ)_i + \sum_i n_i^a (c_p^\circ)_i + C_p^{s*} = \sum_i n_i^t (c_p^\circ)_i + C_p^{s*} \quad (62)$$

The heat capacity of the adsorbent in its pure standard state (C_p^s) is equal to its heat capacity *in vacuo* (C_p^{s*}). Thus, the

heat capacity of the entire system (condensed phase and gas phase) may be estimated from the heat capacity of the evacuated solid adsorbent and the ideal-gas heat capacities of the adsorbates (Sircar, 1991).

Equation of state

The intensive variables pressure, temperature, and gas-phase composition determine the gas-phase properties (density, molar enthalpy, chemical potential, and so on), the solid-phase properties *in vacuo*, and the adsorbed-phase properties from Eq. 9. The equation of state for the adsorbed phase is the surface potential $\Phi(T, P, y_i)$. From Eq. 31, the adsorption isotherm for a pure, perfect gas is

$$n^a = -\frac{P}{RT} \left[\frac{\partial \Phi}{\partial P} \right]_T \quad (63)$$

The integral enthalpy from Eq. 48 for a pure, perfect gas is

$$\Delta H^a = -T^2 \frac{\partial}{\partial T} \left[\frac{\Phi}{T} \right]_P \quad (64)$$

The surface potential of an adsorbent in a pure liquid determines the selectivity for adsorption from liquid mixtures (Sircar and Myers, 1973b): the higher the value of $|\Phi|$ in a pure component, the greater its preferential adsorption from liquid mixtures. The surface potential is also required for calculations of mixed-gas adsorption (Siperstein and Myers, 2001).

Example. The equation of state at the limit of zero pressure is given by Eq. 32: $\Phi = -n^a RT$. Using Eq. 63

$$\lim_{P \rightarrow 0} \left[\frac{n^a}{P} \right] = \left[\frac{\partial n^a}{\partial P} \right]_T \quad (65)$$

which is true if and only if $n^a = K(T)P$. Thus, the equation of state predicts Henry's law for the adsorption isotherm. From Eqs. 59 and 64

$$\lim_{P \rightarrow 0} \left[\frac{\partial \ln n^a}{\partial T} \right]_P = \frac{\Delta \bar{h}^a}{RT^2} \quad (66)$$

Equation 66 for calculating the zero-pressure limit of the differential enthalpy from the temperature coefficient of adsorption should be more accurate than the usual procedure of extrapolating Eq. 56 or differentiating Henry constants (Valenzuela and Myers, 1989)

$$\lim_{P \rightarrow 0} \Delta \bar{h}^a = RT^2 \left[\frac{d \ln K}{dT} \right] \quad (67)$$

Applications

Characterization of adsorbents

Table 1 summarizes the integral and differential thermodynamic equations needed for characterization of adsorbents and for engineering calculations.

Adsorption of gas mixtures

Equations 48 and 50 apply to multicomponent adsorption of an imperfect gas, but the integration for the surface potential term according to Eq. 29 requires experimental, isothermal mixture data for the loading as a function of fugacity. Similarly, the integration for the integral enthalpy by Eq. 57 requires differential enthalpies for adsorbed mixtures. Experimental mixture isotherms and enthalpies are seldom available so reliable methods of predicting mixture data from single-gas adsorption isotherms are essential (Siperstein and Myers, 2001).

Adsorption at high pressure

At high pressure, according to Eq. 3, the total amount of gas contained in the micropores (n^t) tends toward a limit called the saturation capacity, while the density in the gas phase (ρ^g) increases without limit. Eventually, when the density in the gas phase increases with pressure at the same rate as the absolute density in the pores (n^t/V^p), the excess adsorption (n^a) passes through a maximum and then begins to decline with pressure. At very high pressure, when the absolute density in the pores is equal to the bulk-gas density, the excess adsorption is zero. Although adsorption loses its potential for storage and separation applications under these conditions, high-pressure adsorption has been studied extensively (Bénard and Chahine, 2001).

Once the adsorption isotherm has passed through a maximum, the amount adsorbed becomes an invalid *independent* variable because it is not single-valued. The differential enthalpy (isosteric heat) and differential entropy have no meaning under these conditions. However, the integral functions (ΔG^a , ΔH^a , ΔS^a), for which the independent variable is the pressure, are well defined even when the excess amount adsorbed passes through a maximum and declines to negative values.

Enthalpy and entropy balances

The solution thermodynamics approach to adsorption gives the thermodynamic properties of the entire system as the sum over the gas, adsorbed, and solid phases. The most important property is the enthalpy for energy balances; calculations of lost work and efficiency are based upon entropy balances. The enthalpy and entropy functions for the entire system are given by Eq. 6

$$\begin{aligned} H^t &= H^g + H^a + H^s \\ S^t &= S^g + S^a + S^s \end{aligned} \quad (68)$$

Gas Phase. The thermodynamic properties for the gas phase are conveniently calculated from perfect-gas heat capacities and residual functions (Smith et al., 2001)

$$\begin{aligned} H^g &= \sum_i n_i^g \left[h_i^\circ + \int_{T^\circ}^T (c_p^\circ)_i dT + h_i^R \right] \\ S^g &= \sum_i n_i^g \left[s_i^\circ + \int_{T^\circ}^T (c_p^\circ)_i \frac{dT}{T} - R \ln \frac{P}{P^\circ} + s_i^R \right] \end{aligned} \quad (69)$$

h° and s° are molar enthalpy and molar entropy, respectively, at the reference temperature (T°) and standard pressure (P°). c_p° is the ideal-gas heat capacity. h^R and s^R are the residual enthalpy and entropy, respectively, at temperature T ; the residual functions are zero for a perfect gas. As usual, the mass extensive variables (H^g , S^g , n^g) refer to a unit mass of solid adsorbent.

Adsorbed Phase. Similarly, the thermodynamic properties for the adsorbed phase are calculated from ideal-gas heat capacities and the integral functions of Eq. 48

$$H^a = \sum_i n_i^a \left[h_i^\circ + \int_{T^\circ}^T (c_p^\circ)_i dT \right] + \Delta H^a$$

$$S^a = \sum_i n_i^a \left[s_i^\circ + \int_{T^\circ}^T (c_p^\circ)_i \frac{dT}{T} \right] + \Delta S^a \quad (70)$$

Solid Adsorbent. The thermodynamic properties of the solid adsorbent in its standard state at the equilibrium temperature and pressure are

$$H^s = H^{s*} + \int_{T^\circ}^T (C_p^s)^* dT + PV^s$$

$$S^s = S^{s*} + \int_{T^\circ}^T (C_p^s)^* \frac{dT}{T} \quad (71)$$

where the asterisk refers to the properties of the adsorbent per unit mass *in vacuo*. Equation 71 is *not* based on the assumption that the solid adsorbent is inert; isothermal changes in the enthalpy or entropy of the solid adsorbent induced by adsorption are included in the ΔH^a and ΔS^a functions for the adsorbed phase.

Calorimetry

The differential enthalpy of adsorption defined in Eq. 53 can be measured by calorimetry. An isothermal batch calorimeter consists of a dosing cell and a sample cell connected through a valve. When the valve is opened, an increment of gas expands from the dosing cell into the sample cell and a portion of the increment adsorbs. The total energy of the calorimeter is

$$U^t = U^g + U^a + U^s + U^{\text{cell}} \quad (72)$$

$U^{\text{cell}}(T)$ includes the walls of the sample and dosing cells and the valve. $U^s(T)$ is the energy of the adsorbent in its standard state. According to the first law for a closed system

$$dU^t = dU^g + dU^a = dQ \quad (73)$$

Equation 73 and the following equations are for constant temperature. The differentials dU^s and dU^{cell} vanish under isothermal conditions and no work is done on the composite system. The mass balance is

$$n^t = n^g + n^a = \text{const.} \quad (74)$$

so

$$dn^g = -dn^a \quad (75)$$

Combining Eqs. 23, 47, 53, 73 and 75 for the case of single-component adsorption

$$\Delta \bar{h}^a = \frac{dQ}{dn^a} + \frac{dU^g}{dn^g} - h^\circ \quad (76)$$

In general, the derivative (dU^g/dn^g) depends upon the equation of state of the bulk gas, but for a perfect gas $U^g = n^g u^\circ$ and

$$\frac{dU^g}{dn^g} = u^\circ = h^\circ - RT \quad (77)$$

For a perfect gas, Eq. 76 simplifies to

$$\Delta \bar{h}^a = \frac{dQ}{dn^a} - RT \quad (78)$$

Since adsorption is exothermic, the differential heat dQ/dn^a is negative.

The measurement of the differential enthalpy of adsorption from mass and energy balances applied to a calorimeter is straightforward compared to derivations for the measurement of the ill-defined isosteric heat (Young and Crowell, 1962; Siperstein et al., 1999).

Molecular simulation of adsorption

The grand canonical partition function (McQuarrie, 1976) used in grand canonical Monte Carlo (GCMC) simulations is

$$\Xi = \sum_{j,N} e^{-E_j(N,V)/kT} e^{N\mu/kT} \quad (79)$$

The independent variables are volume (V) temperature (T), and chemical potential of the adsorbate molecules (μ). The grand potential $\mathcal{G} = U - TS - \mu N$ is related to the partition function by

$$\mathcal{G} = -kT \ln \Xi(V, T, \mu) \quad (80)$$

For bulk fluids, $\mathcal{G} = -PV$. For 2-D surface thermodynamics, $\mathcal{G} = -\Pi A$, where Π is spreading pressure and A is surface area. Within the framework of solution thermodynamics, the grand potential of an adsorbed phase is equal to its surface potential, $\mathcal{G} = \Phi$.

The volume is a simulation box containing a representative sample of the microporous adsorbent. The dependent variables are the specific potential energy (ϕ) in J/kg and the specific total (absolute) amount of adsorbate in the pores (n^t) in mol/kg. These total variables must be converted to excess functions, especially the excess amount adsorbed (n^a) and the integral enthalpy (ΔH^a), for comparison with experiment. For single-gas adsorption, from Eqs. 8 and 9

$$n^a = n^t - V^g \rho^g \quad (81)$$

and

$$U^a = U^t - V^g \rho^g u^g - U^s \quad (82)$$

V^g is calculated from the adsorption second virial coefficient of helium, Eq. 46. The potential energy (ϕ) is the total energy of gas-gas and gas-solid interactions relative to the perfect-gas reference state and the solid adsorbent *in vacuo*

$$\phi = U^t - n^t u^o - U^s \quad (83)$$

A combination of Eqs. 81–83 with Eqs. 23 and 47 gives

$$\Delta H^a = \phi + PV^g - n^t RT - V^g \rho^g h^R \quad (84)$$

where h^R is the residual enthalpy in the bulk gas phase (Smith et al., 2001). For a perfect gas, $h^R = 0$.

Equations 81 and 84 are key equations for converting simulation variables to experimental variables. The correction term containing the pore volume (V^g) is sometimes negligible at low temperature and low pressure, but dominates at very high pressure and causes the excess amount adsorbed (n^a) to pass through a maximum. The density factor (ρ^g) in the correction term of Eq. 81 suggests that the difference between absolute and excess functions is zero at low pressure since $\lim_{P \rightarrow 0} \rho^g = P/RT$. Actually, the Henry's constants and the zero-pressure differential enthalpies differ for absolute and excess adsorption (Talu and Myers, 2001) and the magnitude of the difference increases with temperature.

The absolute differential energy $[\partial\phi/\partial n^t]_T$ may be calculated directly from fluctuations in ϕ and n^t (Nicholson and Parsonage, 1982), but there is no simple relationship between this simulation variable and the differential enthalpy $\Delta \bar{h}^a$ of experiment. The most direct conversion is the definition $\Delta \bar{h}^a = (\partial\Delta H^a/\partial n^a)_T$ using excess variables from Eqs. 81 and 84.

Shape selectivity in catalysis

The Henry constant (K) defined by

$$K = \lim_{P \rightarrow 0} \frac{n^a}{P} \quad (85)$$

can be related to free energy by combining Eqs. 48 and 51

$$\Delta G^a = n^a RT \ln \left[\frac{n^a}{KP^o} \right] + \Phi. \quad (86)$$

Using Eq. 32

$$\Delta g^a = \frac{\Delta G^a}{n^a} = RT \left(\ln \left[\frac{n^a}{KP^o} \right] - 1 \right). \quad (87)$$

Since the limit at infinite dilution ($n^a \rightarrow 0$) is $\Delta g^a = -\infty$, a standard state must be chosen. For example, for Ar on silicalite at 32.6°C, the Henry constant $K = 0.00173$ mol/(kg kPa) (Dunne et al., 1996). For $P^o = 100$ kPa and $n^a = 0.001$ mol/kg, $\Delta g^a = -15.64$ kJ/mol. Selecting a small, but other-

wise arbitrary, loading for the standard state in the adsorbed phase

$$\Delta g^a = -RT \ln K + \text{const.} \quad (88)$$

Comparison of two adsorbates in identical standard states gives

$$\Delta g_1^a - \Delta g_2^a = -RT \ln \frac{K_1}{K_2} \quad (89)$$

The comparison in Eq. 89 is independent of the standard state chosen for the adsorbed state. This equation was used recently (Schenk et al., 2001) to compare the Gibbs free energies of formation of various alkane molecules in zeolites using Monte Carlo calculations. For example, the free energy of formation of 3,3,5-trimethylheptane relative to *n*-decane at 415 K is 33 kJ/mol in MFI, but near zero in FAU or in the gas phase. Thus, MFI strongly favors the formation of *n*-decane relative to 3,3,5-trimethylpentane, because the shape of *n*-decane is commensurate with the pore shape (Schenk et al., 2001).

Conclusions

Adsorption in microporous adsorbents can be treated as a particular case of solution thermodynamics in which the solvent is a solid adsorbent. Spreading pressure and surface area variables is unnecessary.

An obvious difference between adsorbed and bulk fluids is the relative importance of the interfacial region. In vapor-liquid equilibrium, two macroscopic phases are separated by a gas-liquid interfacial region which is too small to influence the thermodynamic properties of either phase. In adsorption equilibrium, two macroscopic phases (gas and solid adsorbent) are separated by a gas-solid interfacial region, which may contain more molecules than the bulk gas phase.

A subtle difference between adsorbed and bulk fluids is observed in the differential variables. For a pure bulk fluid, the partial molar variables are identical to the molar quantities, for example, the partial molar enthalpy $(\partial H/\partial n)_{T,P}$ is equal to the molar enthalpy (H/n). For adsorbed fluids, the differentials are *not* partial molar variables because the pressure is not held constant for the differentiation. Consequently, for a pure adsorbed fluid (see Figure 4), the differential entropy ($\Delta \bar{s}$) is not equal to the molar entropy ($\Delta S/n$).

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Notation

- A = specific surface area, m²/kg
- A = constant in Eq. A2, J/(mol·K)
- B = adsorption second virial coefficient, cm³/g
- B = constant in Eq. A2, J/mol
- c_p^o = heat capacity of perfect gas, J/(mol·K)
- C = const. in Eq. A2, Pa⁻¹
- C_p = specific heat capacity, J/(kg·K)
- $(C_p^s)^*$ = heat capacity of solid adsorbent *in vacuo*, J/(kg·K)
- E = energy, J

f = fugacity, Pa
 F = specific Helmholtz free energy, J/kg
 G = specific Gibbs free energy, J/kg
 ΔG^a = integral free energy of adsorbed phase, J/kg
 \mathcal{G} = grand potential ($U - TS - \mu N$), J/kg
 g = molar Gibbs free energy, J/mol
 g_i^R = residual Gibbs free energy of i th gaseous component, J/mol
 Δg^a = molar integral free energy of adsorbed phase, J/mol
 $\Delta \bar{g}^a$ = differential free energy in adsorbed phase, J/mol
 h = molar enthalpy, J/mol
 h° = molar enthalpy of perfect gas, J/mol
 \bar{h}^g = partial molar enthalpy in gas phase, J/mol
 h_i^R = residual enthalpy of i th component in gas phase, J/mol
 $\Delta \bar{h}^a$ = molar integral enthalpy of adsorbed phase, J/mol
 $\Delta \bar{h}^a$ = differential enthalpy in adsorbed phase, J/mol
 H = specific enthalpy, J/kg
 ΔH^a = integral enthalpy of adsorbed phase, J/kg
 k = Boltzmann constant, 1.3806×10^{-23} J/K
 K = Henry constant, mol/(kg·Pa)
 m = mass of adsorbent, kg
 M = molecular weight, kg/mol
 N = number of molecules
 n = specific amount adsorbed, mol/kg
 P = pressure, Pa
 P° = standard pressure, 1 bar
 q_{st} = isosteric heat, J/mol
 Q = specific heat absorbed by system, J/kg
 R = gas constant, 8.3145 J/(mol·K)
 s = molar entropy, J/(mol·K)
 s° = molar entropy of perfect gas, J/(mol·K)
 \bar{s}^g = partial molar entropy in gas phase, J/(mol·K)
 s_i^R = residual entropy of i th component in gas phase, J/(mol·K)
 ΔS^a = molar integral entropy of adsorbed phase, J/(mol·K)
 $\Delta \bar{S}^a$ = differential entropy in adsorbed phase, J/(mol·K)
 S = specific entropy, J/(kg·K)
 ΔS^a = integral entropy of adsorbed phase, J/(kg·K)
 T = temperature, K
 T° = room temperature; reference temperature, K
 u = molar internal energy, J/mol
 U = specific internal energy, J/kg
 v = molar volume, m³/mol
 V = specific volume, m³/kg
 V^g = specific void volume of system, m³/kg
 V^s = specific volume of solid adsorbent, m³/kg
 x = mol fraction in condensed phase
 x = distance perpendicular to Gibbs dividing surface, m
 y_i = mol fraction of i th adsorbate in gas phase
 μ = chemical potential of adsorbent, J/kg
 μ^s = chemical potential of pure adsorbent in std. state, J/kg
 μ_i = chemical potential of i th adsorbate, J/mol
 Ξ = grand canonical partition function
 Π = spreading pressure, N/m
 ρ = molar density, mol/m³
 ϕ = specific gas-gas + gas-solid potential energy, J/kg
 Φ = surface potential, J/kg

Subscript

i = refers to i th adsorbate component

Superscripts

a = refers to adsorbed phase
 comp = refers to isothermal compression of gas
 g = refers to gas phase
 imm = refers to isothermal immersion of pure adsorbent in compressed fluid
 $^\circ$ = refers to value in perfect-gas standard state
 s = refers to pure solid
 s^* = refers to pure solid *in vacuo*
 t = refers to total value for system

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Appendix

The enthalpy, free energy, and entropy functions are calculated for the Langmuir model of adsorption of a pure, perfect gas. Although the Langmuir model seldom fits experimental data quantitatively, it predicts qualitatively the behavior of the thermodynamic functions in microporous adsorbents. The Langmuir adsorption isotherm is

$$n^a = \frac{mCP}{1 + CP} \quad (\text{A1})$$

n^a is specific loading in mol/kg, m is the saturation capacity in mol/kg, P is the pressure, and C is a function of temperature

$$C = \frac{1}{P^\circ} e^{A/R} e^{-B/RT} \quad (\text{A2})$$

where A and B are constants: it is shown below that A is the molar integral entropy at saturation and B is the (constant) differential enthalpy of adsorption. P° is the standard-state pressure. Assuming a perfect gas, the surface potential is obtained by substituting Eq. A1 in Eq. 31

$$\Phi = -mRT \ln(1 + CP) \quad (\text{A3})$$

From Eqs. 48 and 51

$$\Delta G^a = n^a RT \ln \frac{P}{P^\circ} + \Phi \quad (\text{A4})$$

Using Eq. A3

$$\Delta G^a = n^a RT \ln \frac{P}{P^\circ} - mRT \ln(1 + CP) \quad (\text{A5})$$

From Eqs. 48 and 51 for a perfect gas ($h^R = 0$)

$$\Delta H^a = -T^2 \frac{\partial}{\partial T} \left[\frac{\Phi}{T} \right]_P \quad (\text{A6})$$

Using Eqs. A2 and A3

$$\Delta H^a = n^a B \quad (\text{A7})$$

From Eqs. 47, A5, and A7

$$T\Delta S^a = \Delta H^a - \Delta G^a = n^a B + mRT \ln(1 + CP) - n^a RT \ln \frac{P}{P^\circ} \quad (\text{A8})$$

Having calculated the integral functions ΔG^a , ΔH^a , and ΔS^a ,

the molar integral functions are obtained by dividing by n^a

$$\begin{aligned} \Delta g^a &= \frac{\Delta G^a}{n^a} = RT \ln \frac{P}{P^\circ} - \frac{m}{n^a} RT \ln(1 + CP) \\ \Delta h^a &= \frac{\Delta H^a}{n^a} = B \\ T\Delta s^a &= \frac{T\Delta S^a}{n^a} = B + \frac{m}{n^a} RT \ln(1 + CP) - RT \ln \frac{P}{P^\circ} \quad (\text{A9}) \end{aligned}$$

Equation A9 shows that the constant B in Eq. A2 is equal to the molar integral enthalpy, which, in general, varies with loading, but is a constant for the Langmuir model. In preparation for calculating the differential functions, the pressure is eliminated from Eq. A5 using A1

$$\Delta G^a = -mRT \ln \left[\frac{m}{m - n^a} \right] + n^a RT \ln \left[\frac{1}{CP^\circ} \cdot \frac{n^a}{m - n^a} \right] \quad (\text{A10})$$

Using Eq. 53

$$\begin{aligned} \Delta \bar{g}^a &= RT \ln \frac{P}{P^\circ} \\ \Delta \bar{h}^a &= B \\ T\Delta \bar{s}^a &= B - RT \ln \frac{P}{P^\circ} \quad (\text{A11}) \end{aligned}$$

Taking the limit as $P \rightarrow \infty$ and $n^a \rightarrow m$ in Eq. A9 gives for the molar integral entropy

$$\lim_{P \rightarrow \infty} \Delta s^a = \frac{B}{T} + R \ln(CP^\circ) = A \quad (\text{A12})$$

which shows that the constant A in Eq. A2 is the molar integral entropy at saturation. Experimental data for adsorption of gases near their critical temperatures in zeolites (Myers and Siperstein, 2001) gives values in the range $-10R$ to $-12R$ for the molar integral entropy at saturation. This is comparable to a typical value of $-10R$ for the entropy of condensation of liquids at their normal boiling points (Smith et al., 2001).

Finally, the immersional functions are calculated from Eq. 50 using A3

$$\begin{aligned} \Delta G^{\text{imm}} &= -mRT \ln(1 + CP) \\ \Delta H^{\text{imm}} &= \frac{mBCP}{1 + CP} \\ T\Delta S^{\text{imm}} &= \frac{mBCP}{1 + CP} + mRT \ln(1 + CP) \quad (\text{A13}) \end{aligned}$$

The nuisance term PV^s in Eq. 50 is negligible at low pressure. All three functions are negative in sign. The equation for the enthalpy of immersion has the same functional form

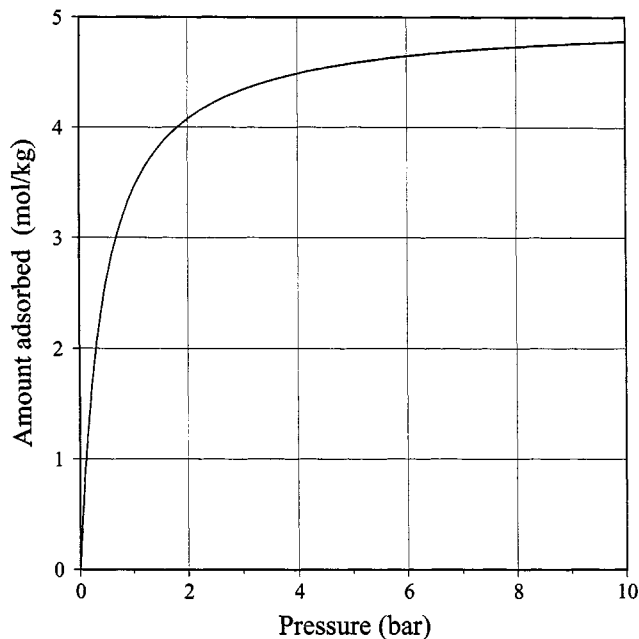


Figure A1. Langmuir adsorption isotherm at 298.15 K.
 Differential enthalpy = -28 kJ/mol; capacity = 5 mol/kg;
 molar integral entropy at saturation = $-10.5R$.

as the adsorption isotherm. The expression for the entropy of immersion contains two terms of opposite sign ($T\Delta S^{imm} = \Delta H^{imm} - \Delta G^{imm}$) so that $T\Delta S^{imm}$ has a minimum. For adsorption of subcritical fluids, condensation of the vapor at its vapor pressure may occur first, before the minimum is reached.

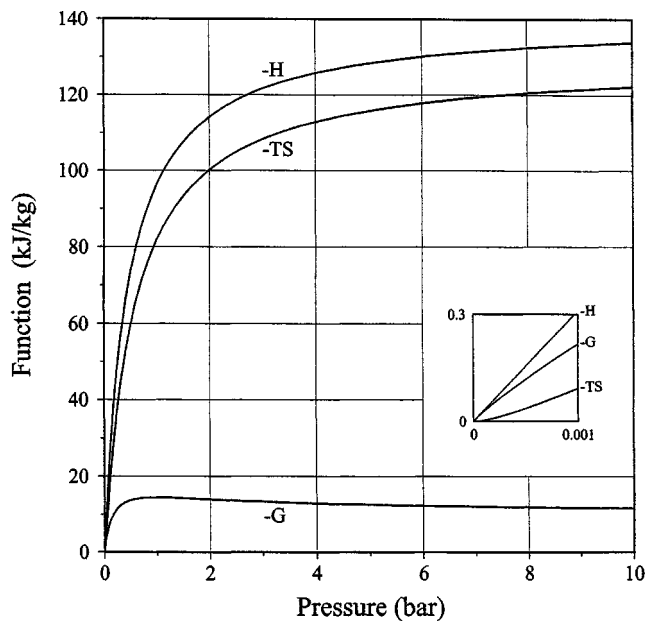


Figure A2. Integral functions (ΔG^a , ΔH^a , ΔS^a) at 298.15 K relative to perfect-gas reference state.

Constants same as Figure A1.

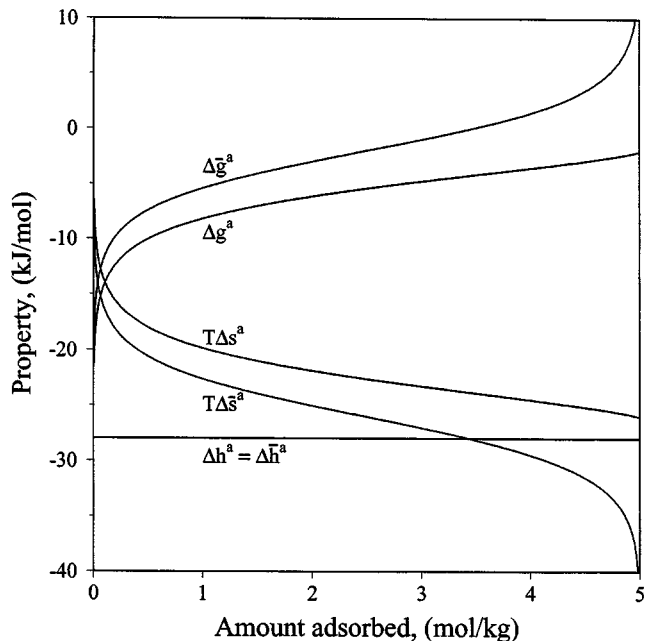


Figure A3. Differential ($\Delta \bar{g}^a$, $\Delta \bar{h}^a$, $\Delta \bar{s}^a$) and molar functions (Δg^a , Δh^a , Δs^a) at 298.15 K relative to perfect-gas reference state.

Constants same as Figure A1.

Numerical example

Let constants $A = -10.5R$, $B = -28$ kJ/mol, and $m = 5$ mol/kg; let variables $P^\circ = 1$ bar and $T = 298.15$ K. From Eq. A2, $C = 2.214$ bar $^{-1}$.

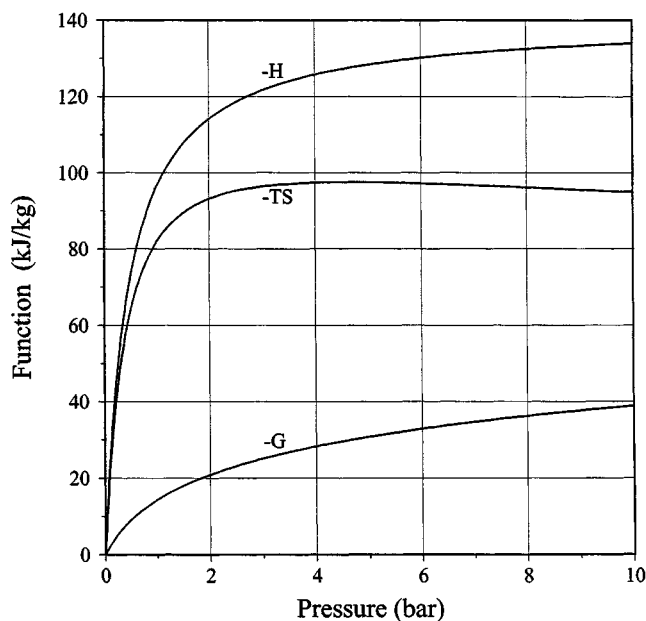


Figure A4. Immersional functions (ΔG^{imm} , ΔH^{imm} , ΔS^{imm}) at 298.15 K relative to compressed gas and clean adsorbent.

Constants same as Figure A1.

The Langmuir adsorption isotherm (Eq. A1) is plotted on Figure A1. The integral thermodynamics functions for the adsorbed gas (ΔG^a , ΔH^a , ΔS^a) from Eqs. A5, A7 and A8 are plotted on Figure A2. Values for all three functions are relative to the perfect-gas reference state at 298 K and 1 bar. The inset in Figure A2 shows that the ΔG^a and $T\Delta S^a$ functions intersect at low pressure (0.01 bar), because ΔS^a has zero slope at the origin.

The differential and molar integral functions from Eqs. A9 and A11 are plotted on Figure A3. The differential Gibbs free energy ($\Delta \bar{g}^a$) is equal to the chemical potential of the gas (μ^a). Notice that the differential and molar functions are unequal. The Langmuir model has the unusual property that the molar and differential enthalpies are equal. For a real system, the differential enthalpy is neither constant nor equal to the molar enthalpy. Furthermore, for a real system, the differential enthalpy ($\Delta \bar{h}^a$) is undefined (goes to infinity) at high loading approaching the saturation capacity.

The immersional functions from Eq. A13 are plotted on Figure A4. For subcritical fluids, these functions terminate at the vapor pressure. For supercritical fluids, there is no limit to the pressure, but the Langmuir model does not account for excess variables according to Eq. 3 and therefore fails at high pressure.

This example shows that the behavior of the integral functions (ΔG^a , ΔH^a , ΔS^a) plotted on Figure A2 and their differentials plotted on Figure A3 is complex, even for the Langmuir model. However, the immersional functions (ΔG^{imm} , ΔH^{imm} , ΔS^{imm}) on Figure A4 have simple shapes, finite non-zero slopes at the origin, and no singularities. The free energy of immersion is the equation of state for the adsorbed phase according to Eq. 63. The immersional functions are clearly defined physically as the change accompanying the isothermal, isobaric contact of clean adsorbent with compressed fluid.

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