Adsorption in Porous Materials at High Pressure: Theory and Experiment

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October 9, 2002

Abstract

We consider the thermodynamics of adsorption of gases in porous solids from both the perspective of absolute properties which appear naturally in theoretical studies and that of excess properties which are measured in experiments. Our thermodynamic description starts by treating the gas (or gas mixture) plus porous solid system as a mixture to which we can apply solution thermodynamics. We show that equations for the absolute thermodynamic properties for adsorption in rigid porous materials do not require an explicit reference to the pressure of the fluid confined in the porous material. We discuss how to relate absolute properties to excess properties by using an estimate of the helium void volume. We illustrate the thermodynamic formalism with calculations for a simple thermodynamic model in which the Langmuir equation is used to describe the absolute adsorption isotherm and the ideal gas equation of state is used for the bulk properties. The simplified model explains the apparently anomalous behavior of the thermodynamic functions for adsorption at high pressure up to 1,000 bar.

1 Introduction

Statistical thermodynamic theories and molecular simulations of adsorption of gases on porous solids are formulated in the language of absolute thermodynamic variables [1]. On the other hand, experimental measurements are reported as excess thermodynamic variables [2]. At low pressure (sub-atmospheric), the difference between absolute and excess adsorption is negligible. However, for higher pressures the difference will be more substantial. In particular, for supercritical fluids adsorbed at high pressure in the range from 10–1000 bars, the absolute amount adsorbed approaches a saturation value but the excess amount adsorbed reaches a maximum and begins to decrease with pressure, eventually becoming negative [3]. This has created some uncertainty as to the utility of the excess function formalism of adsorption thermodynamics for high pressure adsorption [3, 4]. Moreover, experimental data for adsorption excess functions require an estimate of the system volume and this is usually based on helium adsorption. This creates further difficulty in comparing theory and experiment [5, 6].

The primary objective of this paper is to describe methods for converting theoretical absolute variables (amount adsorbed, energy, entropy) into the corresponding experimental excess variables using a simple but rigorous thermodynamic formalism. Instead of using conventional surface thermodynamics, adsorption is described as a special case of solution thermodynamics so that the treatment of multicomponent adsorption at high pressure is similar to standard methods for vapor-liquid equilibrium [7].

Treatments of equilibrium physical adsorption in textbooks [1, 2, 8, 9, 10] and many research articles are based upon surface thermodynamics of thin films. The two-dimensional equation of state of the adsorbed film is described in terms of its spreading pressure, Π, and surface area, A, as for an oil film spreading on a water surface or a monolayer on a flat solid surface. The application of surface thermodynamics to porous materials is of very limited utility because of the complex geometry of the interfaces in the systems. This geometric complexity makes it essentially impossible to analyze the pressure tensor of the confined fluid, the basis for definition of the surface tension. Simple pore geometries such as slits and cylinders are an exception to this, but there are no precise realizations of such situations in nature. A rigorous application of classical thermodynamics to adsorption in porous materials should be free of quantities requiring assumptions about the geometry of the porous material for their definition.

In this paper we treat the thermodynamics of adsorption as a special case of solution thermodynamics for which the adsorbates are the solutes and the adsorbent is the solvent. One of us [11] has presented such an analysis recently within the context of the Gibbs adsorption excess formalism and as part of this work we extend that treatment to the case of absolute quantities. The solution thermodynamics approach to adsorption is not new; for example, Hill [12], Bering et al. [13], and Ruthven [10] have shown how the (ΠA) product may be interpreted in solution thermodynamics as the chemical potential of the solid adsorbent, a feature that also emerges in our treatment. However, the present paper goes beyond previous applications of solution thermodynamics in several respects. Our treatment is free of assumptions about the geometry of the porous material, the volume of the adsorbed phase, gas-phase imperfections, and the inertness of the adsorbent. Moreover, we show how to formulate a thermodynamic description of the adsorbed phase in a rigid porous material without an explicit reference to the pressure of the confined fluid. Our overall goal is to provide a clear exposition of the relationship between absolute and excess variables for adsorption in porous materials, especially as this impinges on the comparison of theoretical predictions with experimental measurements at high pressure. Moreover, the presentation should be accessible to both researchers in applications of adsorption and those in the fundamental molecular physics of adsorption.

Readers will notice that we avoid the use of the expression “heat of adsorption”. The heat exchanged during an adsorption calorimetry experiment depends upon the path of the process, i.e. the nature of the calorimetric measurement [14], and it is inappropriate to use the term heat to denote the change in a thermodynamic property. In our treatment the often poorly defined “isosteric heat” of adsorption is replaced by a differential enthalpy which is useful for energy balances in adsorption columns and adsorption calorimeters. We realize that, given the widespread use of the traditional terminology both in adsorption and bulk thermodynamics, achieving wider acceptance of our position may be difficult. But it is important to recognize that the casual usage of terms like “heat of adsorption” has made it difficult for a systematic and rigorous approach to the classical thermodynamics of adsorption in porous materials to gain acceptance.

The remainder of this paper is organized as follows. In section 2 we consider the calculation of the absolute thermodynamic properties for a system consisting of a fluid confined in a sample of porous material. Next in section 3 we discuss the thermodynamics in terms of the Gibbs adsorption excess properties. In section 4 we show how one set of properties may be converted to the other for comparing experiment with theory or computer simulation. We present illustrative calculations based on a simple thermodynamic model in section 5 and we summarize and conclude the paper in section 6.

2 Absolute thermodynamic variables

Key thermodynamic variables for a bulk fluid mixture are [7]:

$$\begin{aligned} \text{internal energy:} \quad U &= TS - PV + \sum \mu_i n_i && (1) \\ \text{Helmholtz free energy:} \quad F &= U - TS = -PV + \sum \mu_i n_i && (2) \\ \text{grand potential:} \quad \Omega &= F - \sum \mu_i n_i = -PV && (3) \end{aligned}$$

The corresponding set of differential equations for a bulk fluid mixture are:

$$\begin{aligned} \text{internal energy:} \quad dU &= TdS - PdV + \sum \mu_i dn_i && (4) \\ \text{Helmholtz free energy:} \quad dF &= -SdT - PdV + \sum \mu_i dn_i && (5) \\ \text{grand potential:} \quad d\Omega &= -SdT - PdV - \sum n_i d\mu_i && (6) \end{aligned}$$

The grand potential, which is omitted from textbooks on classical thermodynamics, has a special significance for adsorption, since it is the thermodynamic potential for a system with fixed volume, V, chemical potentials, μ_i, and temperature, T, and is related to the grand canonical partition function of statistical mechanics by $\Omega = -kT \ln \Xi$, where Ω is the grand potential and Ξ is the grand canonical partition function. The grand canonical Monte Carlo (GCMC) method [1, 15, 16] is the most widely used approach to the computer simulation of fluids confined in porous materials.

The equations written above for bulk solutions are extended to adsorption by adding an additional term for the solid adsorbent, which in a sense can be viewed as a solvent. For the differential of the internal energy, Eq. (4) becomes:

$$dU = TdS - PdV + \sum_{i=1}^{C} \mu_i dn_i + \mu \, dm \tag{7}$$

where μ is the chemical potential of the solid adsorbent defined on a mass, m, basis. V is the volume of the solid phase and P is the external pressure in the gas phase. Eq. (7) applies to the solid phase containing C species of solutes (adsorbates) inside the pores of the adsorbent. Adsorption phenomena deal with systems such as a packed column or sample cell containing a fixed mass of adsorbent so that the $\mu \, dm$ term in Eq. (7) vanishes. Adsorption systems are open to the C adsorbates but closed with respect to the solid adsorbent. Writing Eq. (7) for the solid phase and then deleting the $\mu \, dm$ term for the adsorbent emphasizes the obvious point that the solid adsorbent is unable to enter the gas phase. However, the chemical potential of the adsorbent (μ) changes with loading, i.e. with the amount of material adsorbed.

Eqs. (1)-(3) for bulk fluids become for adsorption:

$$\begin{aligned}
\text{internal energy:} \quad U &= TS - PV + \sum \mu_i n_i + \mu m && (8)\\
\text{Helmholtz free energy:} \quad F &= U - TS = -PV + \sum \mu_i n_i + \mu m && (9)\\
\text{grand potential:} \quad \Omega &= F - \sum \mu_i n_i = -PV + \mu m && (10)
\end{aligned}$$

The equations we have just presented are applicable to flexible adsorbents such as polymers, resins, or aerogels for which the density of the adsorbent varies with loading [17]. In applying the solution thermodynamics approach to adsorption in the case of a rigid adsorbent it is important to recognize that for this case the adsorbent volume is not an independent variable. Using Eq. (10), we can rewrite Eq. (7) as

$$dU = TdS + \frac{\Omega}{m} dm + \sum_{i=1}^{C} \mu_i dn_i + \frac{Pm}{\rho_s^2} d\rho_s \tag{11}$$

where $\rho_s = m/V$ is the mass density of the porous solid. For a rigid solid (constant ρ_s) this expression becomes

$$dU = TdS + \frac{\Omega}{m} dm + \sum_{i=1}^{C} \mu_i dn_i \tag{12}$$

We can integrate Eq. 12 to obtain

$$U = TS + \Omega + \sum_{i=1}^{C} \mu_i n_i \tag{13}$$

The Helmholtz free energy in Eq. (9) may now be written:

$$F = \Omega + \sum_{i=1}^{C} \mu_i n_i \tag{14}$$

For a fixed mass of rigid adsorbent it is straightforward to show that Eq. (12) for the energy and similar equations for the Helmholtz free energy and grand potential simplify to:

$$\begin{aligned} dU &= \quad TdS + \sum \mu_i dn_i & (15) \\ dF &= -SdT + \sum \mu_i dn_i & (16) \\ d\Omega &= -SdT - \sum n_i d\mu_i & (17) \end{aligned}$$

for adsorption. The summation is over the C adsorbates and the chemical potential of the solid adsorbent does not appear in the differential equations.

The natural independent variables for the absolute thermodynamic functions are T and n_i:

$$S = -\left[\frac{\partial F}{\partial T}\right]_{n_i} \tag{18}$$

$$U = -T^2 \frac{\partial}{\partial T}\left[\frac{F}{T}\right]_{n_i} \tag{19}$$

An important feature of Eqs. (12)–(19) is the absence of any reference to the pressure. The pressure of a fluid or fluid mixture confined inside a strictly rigid porous material is undefined [4, 18, 19] and mechanical equilibrium with the bulk plays no role in establishing the equilibrium state of the system. For the same reason, the grand potential (Ω) for adsorption in a rigid solid in Eq. (10) cannot be divided into separate terms for PV and μm.

Up to this point in our analysis the absolute enthalpy and absolute Gibbs free energy functions have been avoided. This is because the fundamental property relationships involving these variables have the pressure as an independent variable. Nevertheless the absolute enthalpy and absolute Gibbs free energy can be defined in the usual way as

$$\begin{aligned} H &= U + PV & (20) \\ G &= F + PV & (21) \end{aligned}$$

where P is the pressure external to the system and V is the volume of the solid adsorbent. These definitions also apply for the rigid case and are useful in a formulation of the thermodynamics in terms of excess properties as we shall see in the next section.

It is convenient to convert the extensive variables (U,S,Ω,n_i) to extensive variables per unit mass of adsorbent by dividing each term in Eq. (13) by m. Henceforth, all extensive variables refer to unit mass of adsorbent. The energy variables (U,F,Ω) have units of J kg^{-1} of solid adsorbent; the entropy (S) has units of J kg^{-1} K^{-1}; the loading (n_i) has units of mol kg^{-1}.

The absolute configurational energy calculated from theory or computer simulation in the grand canonical ensemble is

$$\Delta U(T, V, \mu_i) = U(T, V, \mu_i) - \sum n_i u_i^{\circ}(T) - U^s(T) \tag{22}$$

where ΔU is the sum of gas-gas and gas-solid potential energies relative to the molar energy of the perfect gas state (u_i°) and the energy of the solid adsorbent *in vacuo* (U^s). GCMC simulations generate the absolute adsorption of each adsorbate (n_i) and the energy (ΔU), both as functions of the independent variables (T,V,μ_i).

The absolute grand potential is obtained by isothermal integration of Eq. (17) with respect to loading:

$$\Delta\Omega = \Omega - \Omega^s = -\sum_i \int n_i d\mu_i = -RT \sum_i \int_0^{f_i} \frac{n_i}{f_i} df_i \qquad \text{(constant } T\text{)} \tag{23}$$

The reference state for the grand potential ($\Omega = \Omega^s = F^s$) is the clean adsorbent *in vacuo.* ($\Delta\Omega$) is the change associated with isothermal immersion of the adsorbent from its clean state *in vacuo* to the equilibrium pressure of the bulk fluid. For adsorption of a single gas at pressures low enough for the perfect-gas approximation:

$$\Delta\Omega = -RT \int_0^P \frac{n}{P} dP \qquad \text{(constant } T\text{)} \tag{24}$$

Values of the grand potential are needed for mixture calculations. At constant grand potential and constant temperature, Eq. (17) reduces to the isothermal, isobaric Gibbs-Duhem equation of solution thermodynamics [20]:

$$\sum_i n_i \, d\mu_i = 0 \qquad \text{(constant } T,\ \Omega\text{)} \tag{25}$$

Therefore, under the restriction of constant grand potential, adsorbed solutions can be handled as ideal or non-ideal solutions using the same methods and equations developed for vapor-liquid equilibria [21].

2.1 Absolute differential functions

Various differential functions can be defined and the most important one is the differential energy of adsorption. From Eq. (22):

$$\Delta\overline{u}_i = \left[\frac{\partial \Delta U}{\partial n_i}\right]_{T,n_j} = \left[\frac{\partial U}{\partial n_i}\right]_{T,n_j} - u_i^\circ \tag{26}$$

The reference state for the differential energy of adsorption is the perfect gas (infinite separation of the molecules). The differential energy ($\Delta\overline{u}_i$) is a negative quantity and its absolute value has been called the differential heat of adsorption [8]. However, as we discussed in our introduction, the heat of adsorption depends upon the path of the process and it is preferable not to use the term heat to denote the change in a thermodynamic property. Notice that the constancy of V or m for rigid adsorbents is omitted in Eq. (26) and elsewhere for simplicity of notation.

Alternatively, the differential energy of adsorption can be obtained indirectly from the equation (see Appendix):

$$\Delta\overline{u}_i = -RT^2 \left[\frac{\partial \ln f_i}{\partial T}\right]_{n_i,n_j} + RT \tag{27}$$

Comparison of values of differential energy from Eqs. (26) and (27) provides a rigorous and sensitive thermodynamic consistency test of adsorption data [4].

In summary, it has been shown how the absolute thermodynamic functions (U,F,Ω,S) are calculated from statistical thermodynamics, especially GCMC simulations. Next, a parallel set of equations will be obtained for the Gibbs excess functions derived from experimental data.

3 Excess thermodynamic variables

The absolute variables described in the previous section are unavailable from experimental adsorption data. Theoretical calculations are performed with a specific model such as several unit cells of a zeolite in which the absolute adsorption is the number of gas molecules present in the pores. Experiments are performed in the presence of a gas phase so that the amount of gas adsorbed is the *excess* adsorption, which is the total amount of gas present in the two-phase system minus the amount in the gas phase [22]. The mass balance for the determination of excess adsorption by the volumetric method is:

$$n_i^e = n_i - V^g \rho^g y_i \tag{28}$$

where n_i is the total amount of ith component introduced to the sample cell, V^g is the volume of the gas phase, ρ^g is the molar density of the bulk gas phase, and y_i is the mole fraction of ith component in the gas phase. More precisely, V^g is the so-called void volume or dead space of the system, which includes the void volume of the porous material and the space in the adsorption apparatus external to the porous material. We will discuss how this is determined later in the paper. The determination of excess adsorption by the mass balance of Eq. (28) is called the volumetric method. The gravimetric method measures excess adsorption as the apparent increase in weight of the sample corrected for the buoyancy force exerted by the bulk fluid. The choice between the volumetric and gravimetric techniques is a matter of convenience but the gravimetric method is more suitable for automation.

The excess thermodynamic functions are given by:

$$\begin{aligned}
\text{energy:} \quad U^e &= U - U^g - U^s && (29)\\
\text{entropy:} \quad S^e &= S - S^g - S^s && (30)\\
\text{enthalpy:} \quad H^e &= H - H^g - H^s && (31)\\
\text{Gibbs free energy:} \quad G^e &= G - G^g - G^s && (32)\\
& \textit{etc.}
\end{aligned}$$

The excess energy (U^e) is the total energy of the system (gas phase + solid phase) minus the energy of the gas phase (U^g) minus the energy of the clean solid adsorbent (U^s) at the equilibrium temperature and pressure (note that we are still defining all extensive properties per unit mass of adsorbent). Setting the standard state as clean adsorbent is an essential step in the development because the properties of the solid can then be measured independently of adsorption experiments. All of the excess functions (n_i^e, U^e, S^e, etc.) vanish in the case of a non-porous solid with negligible external surface area. As discussed previously for absolute adsorption, the pure solid is assumed to be rigid (constant density) so that its volume, energy, and entropy are unaffected by the external pressure. The free energy (G^s) of the pure adsorbent is equal to its chemical potential (μ^s); the units of both are J kg^{-1}.

The gas-phase properties are expressed in terms of the volume (m^3/kg of solid) of the gas phase (V^g) and its molar density (ρ^g):

$$\begin{aligned} S^g &= V^g \rho^g s^g && (33) \\ H^g &= V^g \rho^g h^g && (34) \\ G^g &= V^g \rho^g g^g && (35) \\ & \textit{etc.} \end{aligned}$$

where s^g is the molar entropy, h^g is the molar enthalpy, and g^g is the molar Gibbs free energy of the gas phase, all determined by independent PVT measurements on the bulk gas. Note that Eq. (28) is defined the same way as the other thermodynamic functions in Eqs. (29)–(32) but the term for the amount of ith component in the clean solid is zero. The excess volume

$$V^e = V - V^g \rho^g v^g - V^s = V - V^g - V^s = 0 \tag{36}$$

is also a special case. Since the total volume (V) is the sum of the volume of the solid phase (V^s) and the gas phase (V^g), the excess volume (V^e) vanishes. Since the excess volume is zero, it follows that:

$$\begin{aligned} \text{enthalpy:} \quad H^e &= U^e = TS^e + \sum \mu_i n_i^e + \mu^e && (37) \\ \text{Gibbs free energy:} \quad G^e &= F^e = U^e - TS^e = \sum \mu_i n_i^e + \mu^e && (38) \\ \text{Grand potential:} \quad \Omega^e &= F^e - \sum \mu_i n_i^e = G^e - \sum \mu_i n_i^e = \mu^e && (39) \end{aligned}$$

The energy and enthalpy functions are identical and the Gibbs and Helmholtz free energy functions are identical. $\mu^e = (\mu - \mu^s)$ is the chemical potential of the solid adsorbent relative to its reference state at the equilibrium temperature *in vacuo*. Physically, $\mu^e = \Omega^e$ is the free energy of immersion of the adsorbent in the bulk fluid. Eqs. (37)-(39) for the excess functions are the companion set to Eqs. (8)-(10) for the absolute functions.

The fundamental differential equations for excess variables are [22]:

$$\begin{aligned} dH^e &= TdS^e + \sum \mu_i dn_i^e && (40) \\ dG^e &= -S^e dT + \sum \mu_i dn_i^e && (41) \\ d\Omega^e &= -S^e dT - \sum n_i^e d\mu_i && (42) \end{aligned}$$

Eqs. (40)–(42) for the excess energy functions may be compared with Eqs. (15)–(17) for the absolute energy functions. The chemical potential of the solid adsorbent is absent from both sets of equations even though its value varies with loading.

The most convenient route for calculating the excess functions is through the grand potential by integrating Eq. (42) isothermally:

$$\Omega^e = -\sum_i \int n_i^e d\mu_i = -RT \sum_i \int_0^{f_i} \frac{n_i^e}{f_i} df_i \qquad (\text{constant } T) \tag{43}$$

The reference state for the excess grant potential ($\Omega^e = 0$) is the clean adsorbent *in vacuo.* Ω^e is the excess free energy change associated with isothermal immersion of the clean adsorbent in the bulk fluid. For adsorption of a single gas at pressures low enough for the perfect-gas approximation:

$$\Omega^e = -RT \int_0^P \frac{n^e}{P} dP \qquad \text{(constant } T\text{)} \tag{44}$$

The Gibbs free energy is related to the grand potential by Eq. (39):

Using Eq. (41), one can write formally:

$$S^e = -\left[\frac{\partial G^e}{\partial T}\right]_{n_i^e} \tag{45}$$

However the use of n_i^e as an independent variable at high pressure fails because pressure is a multi-valued function of n_i^e. The appropriate independent variable for excess functions is the pressure. From Eq. (39):

$$G^e = \sum n_i^e \mu_i + \Omega^e \tag{46}$$

$$H^e = \sum n_i^e \overline{h}_i^g - T^2 \frac{\partial}{\partial T}\left[\frac{\Omega^e}{T}\right]_{P,y_i} \tag{47}$$

$$S^e = \sum n_i^e \overline{s}_i^g - \left[\frac{\partial \Omega^e}{\partial T}\right]_{P,y_i} \tag{48}$$

The overline notation for partial molar variables in the bulk gas phase ($\overline{h}_i^g$,$\overline{s}_i^g$) is omitted for the chemical potential (μ_i) because its partial molar character is understood. The derivation of Eqs. (47) and (48) from Eq. (46) is given in the Appendix.

It is convenient to use the perfect-gas reference state for the thermodynamic functions:

$$\Delta G^e = G^e - \sum n_i^e \mu_i^\circ \tag{49}$$

$$\Delta H^e = H^e - \sum n_i^e h_i^\circ \tag{50}$$

$$\Delta S^e = S^e - \sum n_i^e s_i^\circ \tag{51}$$

$$\Delta \Omega^e = \Omega^e \tag{52}$$

Combination of Eqs. (46)–(51) gives:

$$\Delta G^e = \sum n_i^e (\mu_i - \mu_i^\circ) + \Omega^e = \Delta G^{\text{comp}} + \Delta G^{\text{imm}} \tag{53}$$

$$\Delta H^e = \sum n_i^e (\overline{h}_i^g - h_i^\circ) + \left[\frac{\partial(\Omega^e/T)}{\partial(1/T)}\right]_{P,y_i} = \Delta H^{\text{comp}} + \Delta H^{\text{imm}} \tag{54}$$

$$\Delta S^e = \sum n_i^e (\overline{s}_i^e - s_i^\circ) - \left[\frac{\partial \Omega^e}{\partial T}\right]_{P,y_i} = \Delta S^{\text{comp}} + \Delta S^{\text{imm}} \tag{55}$$

Eqs. (53)–(55) show that adsorption may be decomposed into a two-step process:

1. Isothermal compression of n_i^e moles of each gas from its perfect-gas reference state (1 bar) to the equilibrium pressure (P);
2. Isothermal, isobaric immersion of clean adsorbent in the compressed gas.

Step 1 depends only on the properties of the bulk gas. Step 2, immersion of the clean adsorbent, is a physical property of the porous material which deserves to be isolated from the compression step. The absolute value of the free energy of immersion $|\Omega^e|$ is the minimum isothermal work required to regenerate the adsorbent.

As shown by Eqs. (53)-(55), the immersion functions are simply related to the grand potential by:

$$\Delta G^{\text{imm}} = \Omega^e \tag{56}$$

$$\Delta H^{\text{imm}} = \left[\frac{\partial(\Omega^e/T)}{\partial(1/T)}\right]_{P,y_i} \tag{57}$$

$$\Delta S^{\text{imm}} = -\left[\frac{\partial\Omega^e}{\partial T}\right]_{P,y_i} \tag{58}$$

Normally the immersion functions are all negative because adsorption is a spontaneous and exothermic process.

The isothermal compression step in Eqs. (53)-(55) is determined by the properties of the bulk gas:

$$\Delta G^{\text{comp}} = \sum n_i^e(\mu_i - \mu_i^\circ) = \sum n_i^e\Big[\mu_i^R + RT\ln\frac{Py_i}{P^\circ}\Big] \tag{59}$$

$$\Delta H^{\text{comp}} = \sum n_i^e(\overline{h}_i^g - h_i^\circ) = \sum n_i^e h_i^R \tag{60}$$

$$\Delta S^{\text{comp}} = \sum n_i^e(\overline{s}_i^e - s_i^\circ) = \sum n_i^e\Big[s_i^R - R\ln\frac{Py_i}{P^\circ}\Big] \tag{61}$$

The bulk properties necessary to evaluate the compression step are the partial pressures (Py_i) and the residual functions (g_i^R,h_i^R,s_i^R) [20] which vanish for the case of a perfect gas.

In summary, the thermodynamic excess functions for porous solids containing adsorbed gases in equilibrium with the bulk gas phase are characterized by the immersion functions, Eqs. (56)-(58), which have the set of independent variables (T, P, and y_i) associated with experimental data.

3.1 Differential excess functions

The differential enthalpy of adsorption follows from Eq. (50):

$$\Delta\overline{h}_i^e = \left[\frac{\partial\Delta H^e}{\partial n_i^e}\right]_{T,n_j^e} = \left[\frac{\partial H^e}{\partial n_i^e}\right]_{T,n_j^e} - h_i^\circ \tag{62}$$

$\Delta\overline{h}_i^e$ is a negative quantity and $|\Delta\overline{h}_i^e|$ is called the isosteric heat of adsorption. Since heat depends upon the path, it is preferable to define changes in terms of state functions. Thus $\Delta\overline{h}_i^e$ is the differential enthalpy of adsorption and $-\Delta\overline{h}_i^e$ is the differential enthalpy of desorption.

Alternatively, the differential enthalpy of adsorption is given indirectly (see Appendix) from:

$$\Delta\overline{h}_i^e = -RT^2\left[\frac{\partial \ln f_i}{\partial T}\right]_{n_i^e,n_j^e} \tag{63}$$

Other differential excess functions such as differential entropy can be defined. Differential excess functions have singularities at high pressure (see Section 5).

4 Conversion of absolute to excess variables

Conversion of absolute (n_i) to excess (n_i^e) adsorption by Eq. (28) requires the volume of the gas phase (V^g). If the theoretical model ignores adsorption on the external surface of the adsorbent particles, then V^g is the pore volume. If the model accounts for adsorption on the external surface, then V^g is the void volume of the system, which includes the pore volume and the space external to the porous material. This conversion of absolute to excess adsorption is, in principle, precise. However, it does require a definition of pore volume, which as we discuss below depends on the size of the molecule probing the porous material.

The reverse process of calculating absolute adsorption by experimental methods is impossible in principle. Absolute adsorption depends upon the model selected to divide the helium void space into two parts: the space within the potential field of the solid and the space outside the potential field of the solid. For example, a reasonable model of a microporous adsorbent might define the space lying within the potential field of the solid as its pore volume, so that absolute adsorption is the total amount of gas contained in the pores. The experimental helium void volume is the sum of the pore volume plus the external volume of the gas phase. There is no way to determine *experimentally* the space lying within the potential field of the solid.

4.1 Gas volume and void volume

The concept of surface excess in adsorption is most straightforwardly applicable to a planar geometry such as that at a vapor-liquid interface or for adsorption of a gas on a planar solid surface [1]. For a single component vapor-liquid interface the location of the Gibbs dividing surface is given by the solution of

$$\int_{-\infty}^{z_0}\left[\rho(z)-\rho^l\right]dz+\int_{z_0}^{\infty}\left[\rho(z)-\rho^g\right]dz=0 \tag{64}$$

where z denotes distance in a direction normal to the plane of the interface and $\rho(z)$ is the local density. Thus the dividing surface is chosen so that the excess is zero. For a mixture the dividing surface is chosen to yield zero surface excess for one of the species.

The same idea can be used to define the dividing surface for adsorption at a planar solid-fluid interface where it is natural to place the dividing surface at the surface of the solid [1]. The surface excess for the solid is then zero and the surface excess for the gas is given by

$$n^e=\int_{z_0}^{\infty}\left[\rho(z)-\rho^g\right]dz \tag{65}$$

The correct application of the adsorption excess concept to a fluid confined in a porous material requires some additional care. In this case the Gibbs dividing surface is a complex three dimensional structure defined by the internal surfaces of the porous material. The surface excess is given by

$$n^e = \int_{V^g} [\rho(\mathbf{r}) - \rho^g] \, d\mathbf{r} \tag{66}$$

where the integral is evaluated over the void volume of the system. This equation is a rewriting of Eq. (28) for adsorption of a pure gas. The difficulty we have in both cases is to determine what actually constitutes the void volume of the system. If we had a gas for which $n^e = 0$, we could determine V^g from Eq. (28) by $V^g = n/\rho^g$. For this purpose, it is often assumed that helium is a non-adsorbing gas, although it is now well known that, depending on the conditions, quite significant amounts of helium are adsorbed in many porous materials [6]. Whether or not helium adsorbs is actually unimportant in the determination of adsorption excess. The choice of gas for this calibration is in essence a choice of the dividing surface for the Gibbs excess. Moreover, the adoption of a standard procedure (i.e. choice of gas and reference state conditions) for measuring the void volume is the only sensible way to compare different experimental measurements of adsorption excess. It is important to realize that even if the adsorption excess for a gas is zero, the estimate of V^g obtained in this way depends on the size of the gas molecule. We have illustrated this in Figure 1, which shows the dependence of the void volume inside a porous material upon the diameter of the probe molecule. Also, as we will show below, the void volume obtained will be temperature and pressure dependent. However, as long as the same probe molecule is used at the same temperature and pressure, the procedure is a correct realization of the Gibbs excess concept.

For consistency with experiment, the theoretical calculation of surface excess requires the simulation of helium molecules in the pores of the adsorbent [5, 6]. Most theories of adsorption in porous materials are based upon the reasonable assumption that adsorption on the external surface of the solid can be neglected. In Monte Carlo simulations, the system is a small (but hopefully representative) sample of the porous solid, typically of the order of 20-100 Å on a side. Periodic boundary conditions are consistent with the assumption that adsorption on the external surface of the solid can be neglected. Thus the theoretical value of V^g is an estimate of the internal pore volume in the simulation box. Again this need be done at only a single reference state. We discuss next how this can be done in the limit of low pressure.

In the limit of low pressure the excess adsorption is given by

$$n^e = \frac{BP}{RT} \tag{67}$$

where B is the adsorption second virial coefficient or Henry's law coefficient [8], which for porous adsorbents is written:

$$B = \frac{1}{m} \int e^{-E(\mathbf{r})/kT} d\mathbf{r} \; - \; V^g \tag{68}$$

E is the gas-solid potential energy of a single molecule and m is the mass of a representative sample of solid adsorbent used for the integration. The integration performed over the sample vanishes inside the solid where $E \to \infty$. In order for theory to mimic experiment, n^e and the second virial coefficient for helium must be zero so:

$$V^g = \frac{1}{m} \int e^{-E(\mathbf{r})/kT} d\mathbf{r} \qquad \text{(for He)} \tag{69}$$

E is the gas-solid potential energy for a single helium atom. Notice that the exponential is greater than unity at the center of a micropore where $E < 0$; the exponential goes to zero inside the solid. Also, it is apparent from Eq. (69) that the helium pore volume is temperature dependent. Usually a reference temperature of 25°C is chosen for the experimental determination of helium void volume. The theoretical determination of the pore volume by Eq. (69) is the key step in the transformation of absolute to excess adsorption. The fact that the energy E in Eq. (69) for helium is non-zero inside a micropore emphasizes the point made previously that helium is a reference gas for measuring excess adsorption of all other gases. Whether or not helium actually "adsorbs" at 25°C is irrelevant. The requirement is that the recipe for measuring pore volume be identical for theory and experiment.

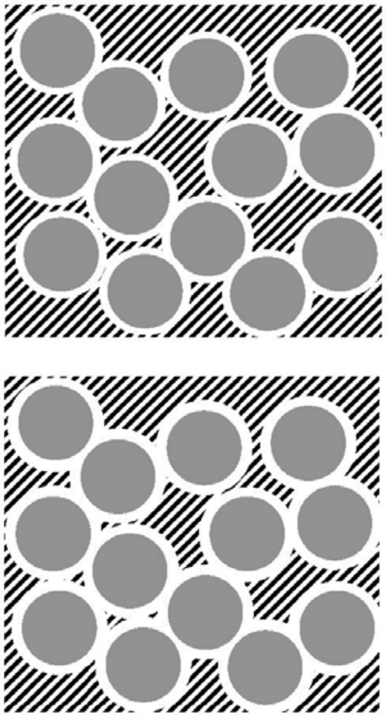

Fig. 1. An illustration of the Gibbs dividing surface concept for a fluid in a porous material treated as a collection of spherical solid particles. The cross-hatched area is the space accessible to the center of a probe molecule. The illustration shows how the accessible space changes with the diameter of the probe molecule. In the lower picture a larger probe molecule is used and the accessible space is significantly lower.

It is evident from this treatment that close agreement between theory and experiment will depend on the theory giving an accurate treatment of both the helium adsorption as well as that of the gas or gas mixture of interest.

4.2 Conversion of amount adsorbed

Given the theoretical pore volume from Eq. (69), the conversion of absolute amount adsorbed to excess amount adsorbed by Eq. (28) is straightforward. For the case of single-component adsorption:

$$n^e = n - \frac{V^g P}{zRT} \tag{70}$$

where $z = P/(\rho RT)$ in the compressibility factor in the bulk gas phase at the equilibrium temperature and pressure. The other excess thermodynamic functions can be calculated from $n^e(T,P,y_i)$ using the equations in section 3. However, it is easier to convert the absolute energy functions directly to excess functions as shown next.

4.3 Conversion of thermodynamic functions

4.3.1 Grand potential

The excess grand potential is:

$$\Omega^e = \Omega - \Omega^s - \Omega^g = \Delta\Omega + PV^g \tag{71}$$

where $\Omega^g = -PV^g$ from Eq. (3). P in Eq. (71) is the pressure of the bulk gas phase, not the pressure inside the pore. The pressure inside the pore has no physical meaning as explained previously.

4.3.2 Enthalpy

The relationship between the excess enthalpy (ΔH^e) of experiment and the theoretical absolute energy (ΔU) follows from Eqs. (22), (28), (29), (34), (37), (50) and the following equalities for the bulk gas: $H^g = U^g + PV^g$; $h_i^\circ = u_i^\circ + RT$; $h^R = h^g - h^\circ$:

$$\Delta H^e = \Delta U + PV^g - nRT - V^g \rho^g h^R \tag{72}$$

All of the quantities on the right-hand-side of Eq. (72) are either absolute variables (ΔU, n) or properties of the bulk gas phase. For a perfect gas, the residual enthalpy $h^R = 0$. However, $PV^g \neq nRT$, even at low pressure, because P is the pressure in the gas phase and n is the absolute amount of gas in the pores.

No simple relationship between the absolute differential energy of Eq. (26) and the excess differential enthalpy (isosteric heat) of Eq. (62) exists. The theoretical differential enthalpy is obtained by converting the absolute energy to excess enthalpy with Eq. (72) followed by differentiation according to Eq. (62).

The excess Gibbs free energy (ΔG^e) and excess entropy (ΔS^e) functions contain terms for the compression of the bulk gas which are independent of the adsorption process. Therefore, for adsorption, the primary focus is on the immersion functions.

4.3.3 Immersion Functions

The immersion functions are calculated from Eqs. (56)-(58) by converting the absolute grand potential to the excess grand potential using Eq. (71):

$$\Delta G^{\mathrm{imm}} = \Delta\Omega + PV^{g} \tag{73}$$

Combination of Eqs. (54), (57) and (72) gives for the enthalpy of immersion:

$$\Delta H^{\mathrm{imm}} = \Delta U + PV^{g} - nRT - nh^{R} \tag{74}$$

where h^R is the residual enthalpy of the gas phase at the equilibrium temperature, pressure, and composition. All of the quantities on the right-hand-side of Eq. (74) are either theoretical absolute variables (ΔU,n) or properties of the bulk gas phase.

The entropy of immersion follows from $\Delta G^{\mathrm{imm}} = \Delta H^{\mathrm{imm}} - T\Delta S^{\mathrm{imm}}$.

5 Illustrative calculations with a simple thermodynamic model

In order to illustrate the formalism we present a series of calculations using a simple thermodynamic model of gas adsorption. We use the Langmuir equation for the adsorbed phase with ideal gas behavior in the bulk. With this model analytic expressions can be developed for all relevant thermodynamic properties. As is well known the Langmuir equation can be derived in many ways. Usually it is regarded as an equation for adsorption on a flat surface. However, the equation also appears for the case of a fluid confined in a porous material as a simple approximation to the adsorption isotherm obtained by applying statistical mechanics in the grand canonical ensemble. We stress that the Langmuir model has been selected not for its numerical accuracy but for its ability to reproduce the qualitative features of adsorption using simple analytical equations.

The absolute functions for adsorption in a microporous material for the Langmuir model are summarized in Table 1. The constant C in the Langmuir equation is a function of temperature:

$$C = \frac{1}{P^{\circ}} \exp\Big(\frac{A}{R}\Big) \exp\Big(\frac{-B}{RT}\Big) \tag{75}$$

B is the enthalpy of adsorption (kJ mol^{-1}) and $P^{\circ} = 1$ bar is the pressure at the perfect-gas reference state. The temperature-independent group $(1/P^{\circ})\exp(A/R)$ is called the entropic factor and Table 1 shows that the constant A is the molar entropy at saturation ($\lim_{P\to\infty} \Delta S/n$). We believe that this physical interpretation of the entropic factor, which is helpful in understanding the Langmuir model, has not been discussed previously. As expected for a model which ignores cooperative forces and energetic heterogeneity, the isothermal differential energy is independent of the amount adsorbed. The reference state for the absolute functions (ΔU, ΔF, ΔS, etc.) is the adsorbent *in vacuo* and the adsorbate at its perfect-gas reference pressure (P°).

The excess functions for adsorption in a microporous material for the Langmuir model are summarized in Table 2. Given the absolute functions, the only additional information needed for conversion to excess functions is the internal pore volume V^g.

Table 1: Absolute functions for single-component adsorption based upon the Langmuir equation for the adsorbed phase and the ideal gas equation of state for the bulk phase. The values of the properties relative to the reference state of clean adsorbent and perfect gas at $P^\circ = 1$ bar are the sum of two steps: (1) isothermal compression (comp) of the bulk gas from P° to the equilibrium pressure P; (2) isothermal, isobaric immersion (imm) of clean adsorbent in the compressed gas. m is saturation capacity (mol/kg). A and B are constants and $C = (1/P^\circ)e^{A/R}e^{-B/RT}$. P is the pressure in the bulk gas phase.

Function	Equation	Limit as $P \to \infty$
Amount adsorbed	$n = \dfrac{mCP}{1+CP}$	m
Energy	$\Delta U = \Delta U^{\text{imm}} + \Delta U^{\text{comp}}$	$m(B+RT)$
	$\Delta U^{\text{imm}} = n(B+RT)$	$m(B+RT)$
	$\Delta U^{\text{comp}} = 0$	0
Entropy	$\Delta S = \Delta S^{\text{imm}} + \Delta S^{\text{comp}}$	mA
	$\Delta S^{\text{imm}} = \dfrac{nB}{T} + mR\ln(1+CP)$	∞
	$\Delta S^{\text{comp}} = -nR\ln\dfrac{P}{P^\circ}$	$-\infty$
Free energy	$\Delta F = \Delta F^{\text{imm}} + \Delta F^{\text{comp}}$	$m(B-AT+RT)$
	$\Delta F^{\text{imm}} = -mRT\ln(1+CP) + nRT$	$-\infty$
	$\Delta F^{\text{comp}} = nRT\ln\dfrac{P}{P^\circ}$	∞
Grand potential	$\Delta\Omega = -mRT\ln(1+CP)$	$-\infty$
Diff. energy	$\Delta\overline{u} = B + RT$	$B+RT$

Table 2: Excess functions for single-component adsorption based upon the Langmuir equation for the adsorbed phase and the ideal gas equation of state for the bulk phase. The values of the properties relative to the reference state of clean adsorbent and perfect gas at $P^\circ = 1$ bar are the sum of two steps: (1) isothermal compression (comp) of the bulk gas from P° to the equilibrium pressure P; (2) isothermal, isobaric immersion (imm) of clean adsorbent in the compressed gas. m is saturation capacity (mol/kg). V^g is the pore volume of the adsorbent. A and B are constants and $C = (1/P^\circ)e^{A/R}e^{-B/RT}$.

Function	Equation	Location of extremum
Amount adsorbed	$n^e = n - \dfrac{PV^g}{RT}$	$P = \dfrac{\sqrt{\frac{mCRT}{V^g}} - 1}{C}$ $n^e_{\text{max}} = m\Big[1 + \frac{RT}{B}\Big]$
Enthalpy	$\Delta H^e = \Delta H^{\text{imm}} + \Delta H^{\text{comp}}$ $\Delta H^{\text{imm}} = nB + PV^g$ $\Delta H^{\text{comp}} = 0$	$P = \dfrac{\sqrt{\frac{-mCB}{V^g}} - 1}{C}$
Entropy	$\Delta S^e = \Delta S^{\text{imm}} + \Delta S^{\text{comp}}$ $\Delta S^{\text{imm}} = \dfrac{nB}{T} + mR\ln(1 + CP)$ $\Delta S^{\text{comp}} = -n^e R \ln \dfrac{P}{P^\circ}$	$P = \frac{1}{C}\Big[\frac{-B}{RT} - 1\Big]$ $\Delta S^{\text{imm}}_{\text{min}} = mR\Big[1 + \frac{B}{RT} + \ln\Big(\frac{-B}{RT}\Big)\Big]$
Free energy	$\Delta G = \Delta G^{\text{imm}} + \Delta G^{\text{comp}}$ $\Delta G^{\text{imm}} = -mRT\ln(1 + CP) + PV^g$ $\Delta G^{\text{comp}} = n^e RT \ln \dfrac{P}{P^\circ}$	$P = \dfrac{\frac{mCRT}{V^g} - 1}{C}$
Grand potential	$\Delta\Omega^e = -mRT\ln(1 + CP) + PV^g$	$P = \dfrac{\frac{mCRT}{V^g} - 1}{C}$
Diff. enthalpy	$\Delta\overline{h}^e = \dfrac{B + \frac{V^g(1+CP)^2}{mC}}{1 - \frac{V^g(1+CP)^2}{mCRT}}$	singularity at $P = \dfrac{\sqrt{\frac{mCRT}{V^g}} - 1}{C}$

Methane adsorbed in silicalite is chosen as an example. The constants are $m = 3.1$ mol kg^{-1}, $B = -19.7$ kJ mol^{-1}, $A = -9.24R$, and $V^g = 175$ cm^3 kg^{-1}. The molar entropy of adsorption at saturation is close to the value of Trouton's constant for the entropy of liquefaction of a liquid at its normal boiling point ($-10R$). The pore volume was determined by molecular simulation [23] and the other constants were extracted from experimental data [24] for the Henry constant and differential enthalpy at 25°C.

Comparison of the model with experimental data is shown on Figure 2. The dashed line is absolute adsorption calculated from the Langmuir equation. The points are experimental data for excess adsorption obtained from volumetric measurements at 298 K [24, 25]. The two solid lines are excess adsorption from Eq. (28). Solid line A is calculated from the Langmuir equation for the adsorbed phase and the perfect-gas equation for the bulk gas phase. Solid line B was obtained by molecular simulation [23]. The molecular simulations, which are based upon intermolecular potentials for gas-gas and gas-solid interactions in silicalite, agree with experiment in the range where data are available (pressures up to 10 bar).

It is apparent from Figure 2 that the simplified model (solid line A) reproduces the qualitative features of high-pressure supercritical adsorption. At sub-atmospheric pressure, the pore density is much higher than the bulk density of methane. Both densities increase with pressure but the bulk density increases more rapidly than the pore density and eventually at the maximum, both densities are increasing at the same rate so that pressure has no effect on the excess amount adsorbed. At very high pressure of the order of 1000 bar, the bulk density continues to increase with pressure while the pore density approaches a saturation condition where no more molecules can fit into the pores. The excess adsorption is zero at the pressure where the bulk and pore densities are equal.

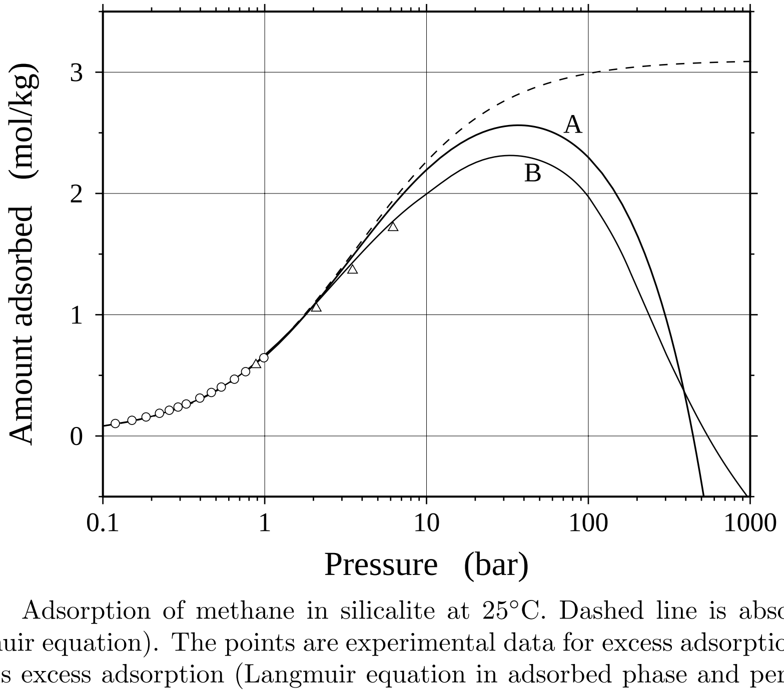

Fig. 2. Adsorption of methane in silicalite at 25°C. Dashed line is absolute adsorption (Langmuir equation). The points are experimental data for excess adsorption [24, 25]. Solid line A is excess adsorption (Langmuir equation in adsorbed phase and perfect gas in bulk gas phase). Solid line B is excess adsorption obtained from molecular simulations [23].

The numerical accuracy of the model is improved by using a more accurate equation of state for the bulk properties of methane. Solid line A in Figure 2 was calculated from the perfect gas law, which gives large errors in the range 100–1000 bar. Solid line A in Figure 3 shows the improvement when the bulk properties of methane are calculated from the Redlich-Kwong [20] equation instead of the perfect gas law. For pressures below 100 bar, disagreement in Figures 3 between the experimental data and the model (solid line A) is mainly due to the failure of the Langmuir equation. The Langmuir equation is incapable of fitting experimental data over two decades of pressure from 0.1 to 10 bars.

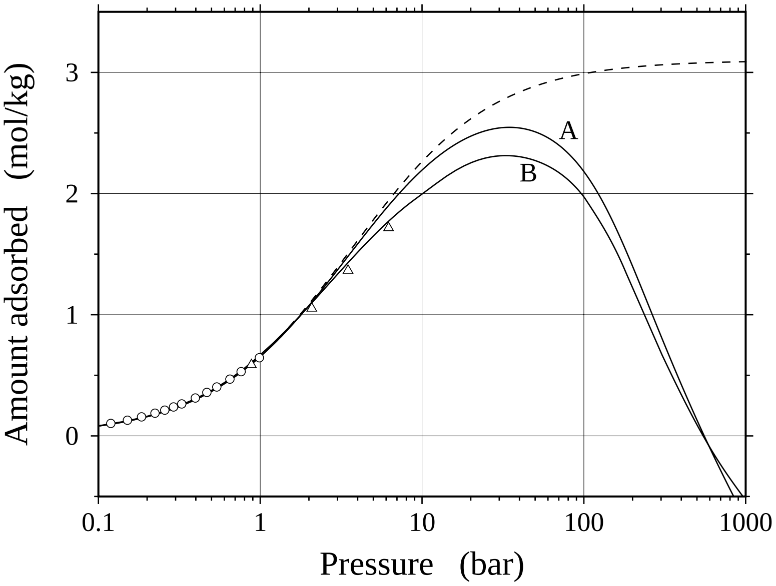

Fig. 3. Adsorption of methane in silicalite at 25°C. Dashed line is absolute adsorption (Langmuir equation). The points are experimental data for excess adsorption [24, 25]. Solid line A is excess adsorption (Langmuir equation in adsorbed phase and Redlich-Kwong equation of state in bulk gas phase). Solid line B is excess adsorption obtained from molecular simulations [23].

The normal boiling point of methane is 111.4 K and its critical temperature is 190.6 K. Adsorption isotherms calculated from the Langmuir model are plotted on Fig. 4 for the subcritical region. Notice that the pressures of interest in this temperature range are all very low, below 0.005 bar. Adsorption isotherms in the supercritical region are plotted on Fig. 5; in this temperature range the pressure is restricted to sub-atmospheric values. In both cases (subcritical and supercritical), the difference between absolute and excess adsorption is negligible. The subcritical and supercritical regions for methane are illustrated with the expectation that other adsorbates should exhibit similar behavior at equal values of reduced temperature (T/T^c). The inference is that differences in absolute and excess adsorption may be ignored in the very low pressure subcritical region and in the sub-atmospheric supercritical region.

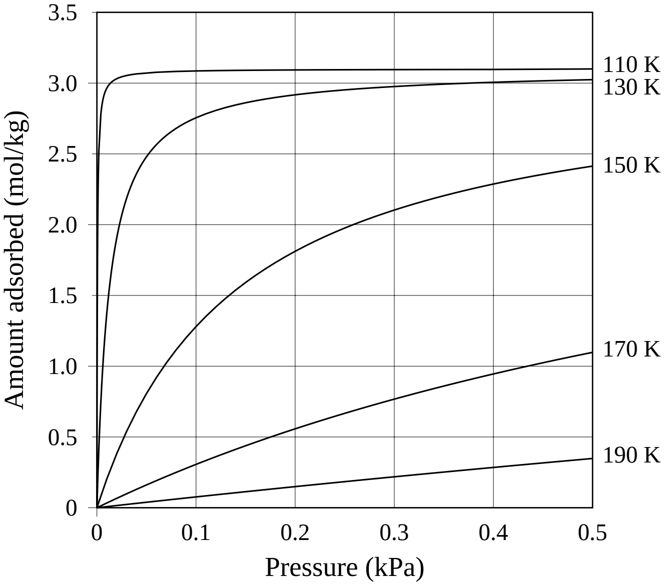

Fig. 4. Adsorption isotherms calculated for adsorption of methane in silicalite under subcritical conditions. Absolute and excess isotherms are indistinguishable in this region.

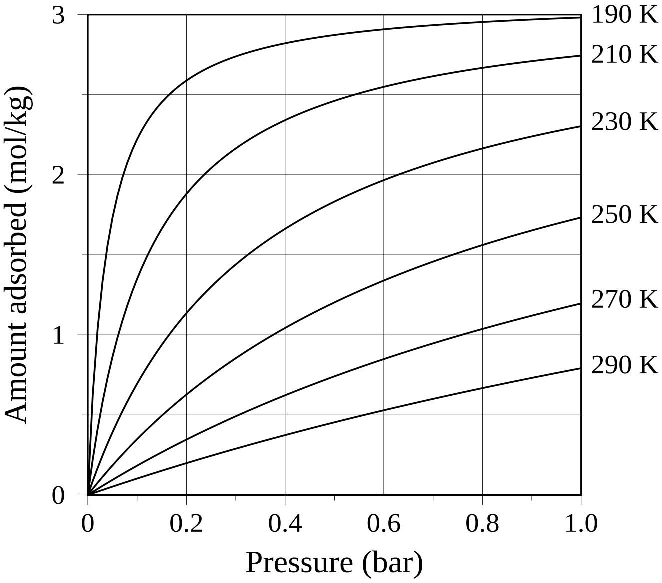

Fig. 5. Adsorption isotherms calculated for adsorption of methane in silicalite under supercritical conditions. Absolute and excess isotherms are indistinguishable below atmospheric pressure.

In the very low-pressure subcritical and sub-atmospheric supercritical regions shown on Figs. 4 and 5, Eq. (63) can be used to interpolate and extrapolate adsorption isotherms. To the extent that the differential enthalpy ($\Delta\overline{h}^e$) is temperature-independent, $ln(f) = ln(P)$ is a linear function of $(1/T)$ at constant loading (n^e). These straight lines called "adsorption isosteres" are shown on Fig. 6 for constant loadings of 0.5 and 2.5 mol/kg. Although these lines are for the Langmuir model, similar excellent results are obtained with experimental data provided that the pressure is limited to sub-atmospheric values [26]. At higher pressure, the plots become nonlinear as shown on Fig. 7. The extrapolation of the linear sub-atmospheric region shown as a dashed line does not agree with the model. Notice that the pressure axis is a logarithmic scale so that error incurred by linear extrapolation above atmospheric pressure is very large. The conclusion is that the usefulness of adsorption isosteres shown on Fig. 6 is limited to sub-atmospheric pressures.

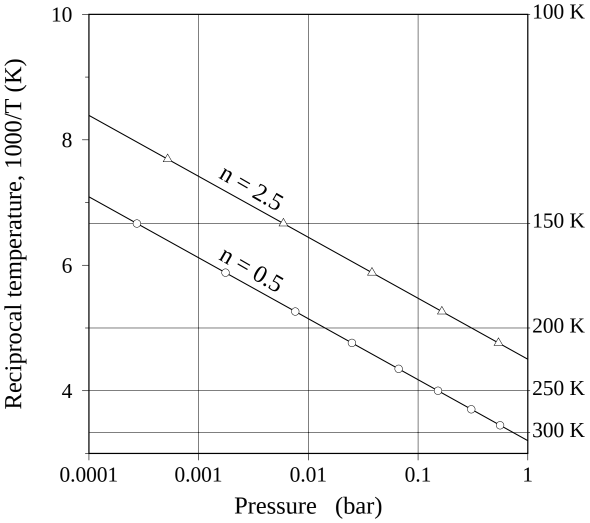

Fig. 6. Plot of $\ln P$ versus $(1/T)$ calculated for adsorption of methane in silicalite in the sub-atmospheric pressure range. The straight lines at constant loading or "adsorption isosteres" are useful for interpolation of data.

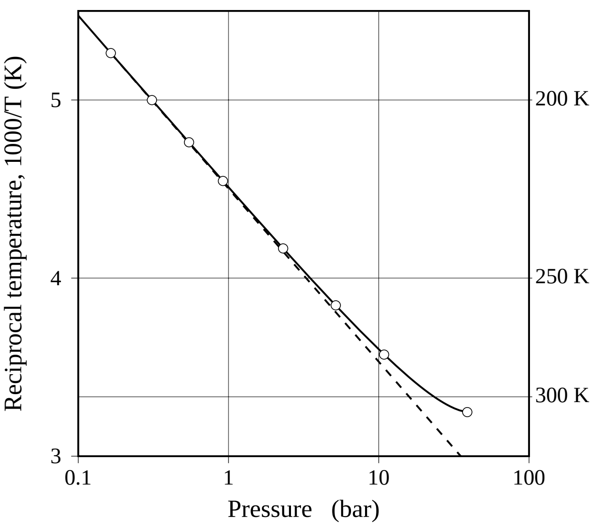

Fig. 7. Plot of $\ln P$ versus $(1/T)$ calculated for adsorption of methane in silicalite at constant loading of 2.5 mol/kg. The linearity observed in Figure 6 fails for pressure higher than 1 bar. The dashed line is the linear extrapolation from low pressure.

Excess adsorption isotherms above atmospheric pressure in the supercritical region are shown on Fig. 8. While the absolute adsorption isotherms increase monotonically with pressure, the excess isotherms exhibit maxima. Several interested features are apparent in Fig. 8. The pressure corresponding to the maximum increases with temperature. The isotherms intersect, so that for each temperature there exists a pressure at which the isobaric temperature coefficient of adsorption is zero.

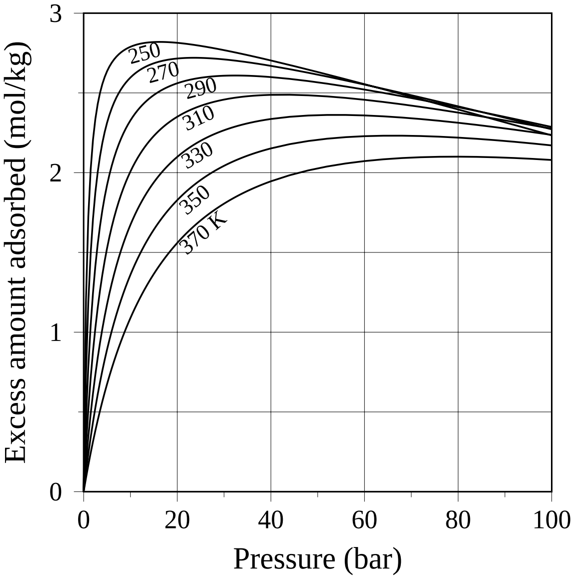

Fig. 8. Excess adsorption isotherms calculated for adsorption of methane in silicalite at high-pressure supercritical conditions. Maximum excess adsorption occurs at a pressure which increases with temperature. The temperature coefficient of adsorption is zero at the point where two isotherms intersect.

The nonlinearity of adsorption isosteres shown on Fig. 7 is related to the singularity in the differential enthalpy, as shown on Fig. 9 for methane adsorbed at its critical temperature. The cause of the singularity is apparent from the relation:

$$\Delta\overline{h}^e = \left[\frac{\partial \Delta H^e}{\partial n^e}\right]_T = \frac{\left[\dfrac{\partial \Delta H^e}{\partial P}\right]_T}{\left[\dfrac{\partial n^e}{\partial P}\right]_T} \tag{76}$$

so that the singularity coincides with the maximum in the adsorption isotherm where its slope is zero. The existence of a maximum in the adsorption isotherm eliminates the surface excess (n^e) as an independent variable at high pressure. n^e is a valid dependent variable, but in the region surrounding its maximum any function of n^e (such as pressure) has multiple values. This behavior does not affect the use of n^e as an independent variable if the pressure is restricted to values below the maximum. As a rule, the usefulness of variables such as differential enthalpy and differential entropy is restricted to sub-atmospheric pressures far removed from the maximum in n^e, as illustrated by Fig. 10 for methane in silicalite at 25°C.

The existence of a singularity in the differential enthalpy shown on Fig. 10 at 25°C and 37 bar has no influence on the immersion functions. Fig. 11 shows the immersion functions at the same temperature (25°C) for methane in silicalite. The singularity in the differential enthalpy at 37 bar is not evident for the enthalpy, entropy, and free energy immersion functions, which are smooth and well-behaved functions of pressure.

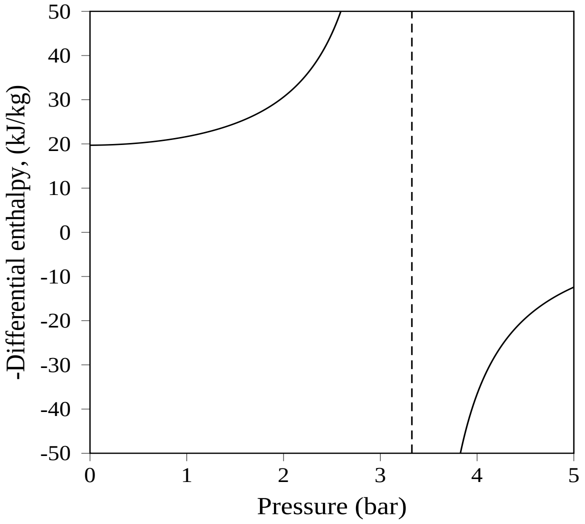

Fig. 9. Differential enthalpy (isosteric heat) calculated for methane adsorbed in silicalite at 190 K. The pressure at which the singularity occurs coincides with the maximum in the adsorption isotherm at 190 K.

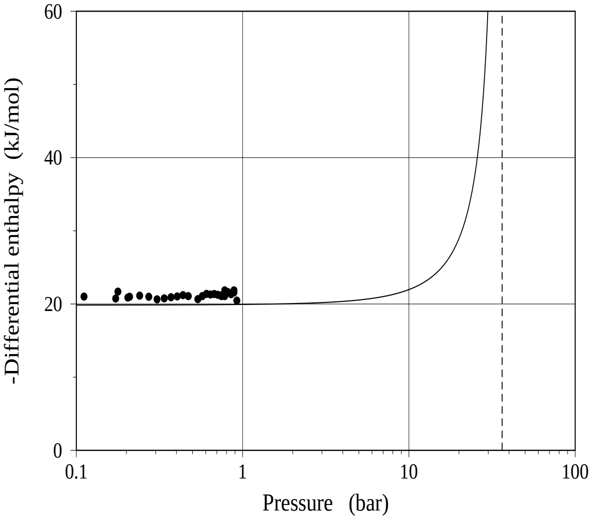

Fig. 10. Differential enthalpy (isosteric heat) of methane adsorbed in silicalite at 25°C. The points are experimental calorimetric data [24]. The pressure at which the singularity occurs coincides with the maximum in the adsorption isotherm at 25°C.

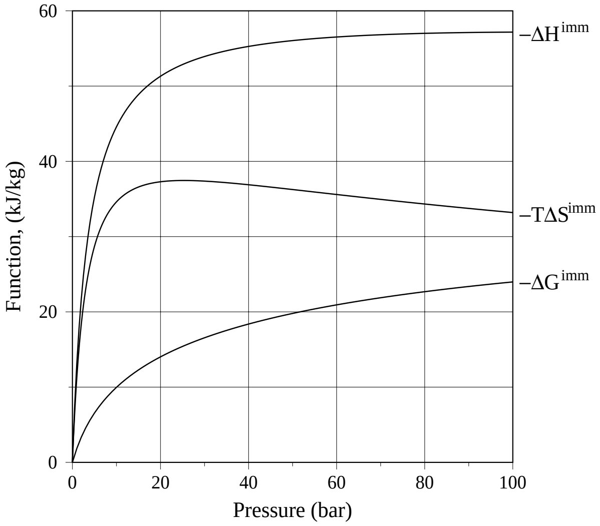

Fig. 11. Immersion (excess) functions calculated for methane adsorbed in silicalite at 25°C and high pressure. The qualitative behavior of the functions is similar to that for the corresponding absolute functions shown in Figure 12. The excess and absolute entropy functions are identical.

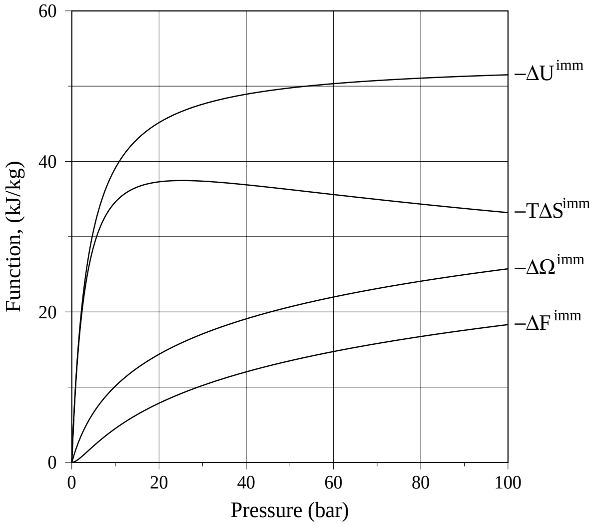

Fig. 12. Immersion (absolute) functions calculated for methane adsorbed in silicalite at 25°C and high pressure.

The excess immersion functions on Fig. 11 can be compared with the absolute immersion functions on Fig. 12. The values of the excess enthalpy (ΔH^{imm}) and absolute energy (ΔU^{imm}) differ by less than 10%. The excess Gibbs free energy (ΔG^{imm}) differs from the absolute grand potential ($\Delta\Omega^{\text{imm}}$) by less by 10%. It is interesting that the excess entropies (ΔS^{imm}) for absolute and excess variables are identical for this model!

6 Summary and Conclusions

In this paper we have presented a self contained discussion of the thermodynamics of adsorption in porous materials focusing on both the formulations in terms of absolute quantities, which arise naturally in theory and computer simulation, and excess properties, which arise naturally in experiments. Our goal has been to help bridge the gap between the important work in adsorption thermodynamics that has been carried out in the theoretical and experimental research communities in recent years.

Our treatment clarifies the status of the bulk pressure as a thermodynamic variable in adsorption and shows that it is unnecessary to attempt to identify what is meant by the pressure of a fluid adsorbed in a porous material. We discuss the role of the helium dead space volume in experiments and argue that the choice of helium as a reference gas is equivalent to a choice of Gibbs dividing surface for the definition of excess properties. We also describe the conversion of absolute properties from theory and simulation into excess properties using estimates of the helium pore volume. We argue that it is only necessary to estimate the helium dead space volume or pore volume at a single reference state in order to have a rigorous implementation of the Gibbs adsorption excess concept. The acceptance of a uniform standard for this reference state would facilitate comparisons between experimental adsorption data from different laboratories and between theory or simulations and experiment.

We have found that the immersion functions are suitable for the characterization of supercritical adsorption at high pressure (see example on Figure 11). In contrast the usefulness of differential enthalpy (isosteric heat) and adsorption isosteres (plots of $\ln P$ versus $1/T$ at constant loading) is limited to sub-atmospheric pressure.

We have used a simple thermodynamic model, consisting of the Langmuir equation for the adsorption isotherm and the ideal gas equation of state for bulk properties, to make illustrative calculations. This simple model gives a complete qualitative description of the issues discussed here.

7 Acknowledgments

Support from the National Science Foundation is gratefully acknowledged by P.A.M. (Grant No. CTS-9906794) and A.L.M. (Grant No. CTS-0080915).

8 Notation

B	adsorption second virial coefficient, $\mathrm{m}^3\ \mathrm{kg}^{-1}$
F	Helmholtz free energy, $\mathrm{J\ kg}^{-1}$
f	fugacity, Pa
G	Gibbs free energy, $\mathrm{J\ kg}^{-1}$
g	molar Gibbs free energy of gas, $\mathrm{J\ mol}^{-1}$
H	enthalpy, $\mathrm{J\ kg}^{-1}$
h	molar enthalpy of gas, $\mathrm{J\ mol}^{-1}$
$\overline{h}_i$	partial molar enthalpy of ith gaseous component, $\mathrm{J\ mol}^{-1}$
$\Delta\overline{h}$	differential enthalpy of adsorption, $\mathrm{J\ mol}^{-1}$
m	mass of adsorbent, kg
n	amount adsorbed, $\mathrm{mol\ kg}^{-1}$
P	pressure, Pa
R	gas constant, 8.3145 $\mathrm{J\ mol}^{-1}\ \mathrm{K}^{-1}$
S	entropy, $\mathrm{J\ kg}^{-1}\ \mathrm{K}^{-1}$
s	molar entropy of gas, $\mathrm{J\ mol}^{-1}\ \mathrm{K}^{-1}$
$\overline{s}_i$	partial molar entropy of ith gaseous component, $\mathrm{J\ mol}^{-1}\ \mathrm{K}^{-1}$
T	temperature, K
U	internal energy, $\mathrm{J\ kg}^{-1}$
u	molar internal energy of gas, $\mathrm{J\ mol}^{-1}$
$\Delta\overline{u}$	differential energy of adsorption, $\mathrm{J\ mol}^{-1}$
V	volume, $\mathrm{m}^3\ \mathrm{kg}^{-1}$
z	compressibility factor of bulk gas
Greek letters	
μ_i	chemical potential of ith adsorbate component, $\mathrm{J\ mol}^{-1}$
μ	chemical potential of solid adsorbent, $\mathrm{J\ kg}^{-1}$
ρ	molar density, $\mathrm{mol\ m}^{-3}$
ρ_s	mass density of solid phase, $\mathrm{kg\ m}^{-3}$
Ω	grand potential, $\mathrm{J\ kg}^{-1}$
Superscripts	
comp	refers to compression step
imm	refers to immersion of clean adsorbent
e	denotes excess function
g	refers to gas phase
$\circ$	refers to perfect-gas reference state
R	denotes residual function relative to perfect-gas reference state
s	refers to adsorbent in degassed standard state
Subscripts	
i	refers to ith adsorbate component
j	refers to jth adsorbate component

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Appendix

Pressure variable for excess functions.

Eqs. (46)–(48) are derived starting with Eq. (39):

$$G^e = \Omega^e + \sum n_i^e \mu_i \tag{A1}$$

Using Eq. (42) for the differential of the excess grand potential:

$$\left[\frac{\partial \Omega^e}{\partial T}\right]_{P,y_i} = -S^e - \sum n_i^e \left[\frac{\partial \mu_i}{\partial T}\right]_{P,y_i} \tag{A2}$$

From the calculus:

$$-T^2 \frac{\partial}{\partial T}\left[\frac{\Omega^e}{T}\right]_{P,y_i} = \Omega^e - T\left[\frac{\partial \Omega^e}{\partial T}\right]_{P,y_i} \tag{A3}$$

Substituting Eqs. (A1) and (A2) into (A3):

$$-T^2 \frac{\partial}{\partial T}\left[\frac{\Omega^e}{T}\right]_{P,y_i} = G^e + TS^e - \sum_i n_i^e \left(\mu_i - T\left[\frac{\partial \mu_i}{\partial T}\right]_{P,y_i}\right) \tag{A4}$$

Noting that $G^e = H^e - TS^e$ and

$$\mu_i - T\left[\frac{\partial \mu_i}{\partial T}\right]_{P,y_i} = -T^2 \frac{\partial}{\partial T}\left[\frac{\mu_i}{T}\right]_{P,y_i} = \overline{h}_i \tag{A5}$$

Eq. (A4) becomes:

$$H^e = \sum n_i^e \overline{h}_i - T^2 \frac{\partial}{\partial T}\left[\frac{\Omega^e}{T}\right]_{P,y_i} \tag{A6}$$

Then, using Eqs. (A1) and (A6) with $G^e = H^e - TS^e$ and $\mu_i = \overline{h}_i - T\overline{s_i}$ for the bulk gas:

$$S^e = \sum n_i^e \overline{s}_i - \left[\frac{\partial \Omega^e}{\partial T}\right]_{P,y_i} \tag{A7}$$

Q.E.D.

Thermodynamic equation for absolute differential energy.

The derivation of Eq. (27) begins with the differential equation for energy, Eq. (15):

$$\left[\frac{\partial U}{\partial n_i}\right]_{T,n_j} = T\left[\frac{\partial S}{\partial n_i}\right]_{T,n_j} + \mu_i \tag{A8}$$

The Maxwell relation from Eq. (16) for the Helmholtz free energy is:

$$\left[\frac{\partial S}{\partial n_i}\right]_{T,n_j} = -\left[\frac{\partial \mu_i}{\partial T}\right]_{n_i,n_j} \tag{A9}$$

Substituting Eq. (A9) in (A8):

$$\left[\frac{\partial U}{\partial n_i}\right]_{T,n_j} = \mu_i - T\left[\frac{\partial \mu_i}{\partial T}\right]_{n_i,n_j} = -T^2\frac{\partial}{\partial T}\left[\frac{\mu_i}{T}\right]_{n_i,n_j} \tag{$A10$}$$

The chemical potential is related to fugacity by:

$$\mu_i = \mu_i^\circ + RT\ln\frac{f}{f^\circ} \tag{$A11$}$$

The standard-state enthalpy of the bulk gas is:

$$h_i^\circ = -T^2\frac{d}{dT}\left[\frac{\mu_i^\circ}{T}\right] \tag{$A12$}$$

Substituting Eqs. (A11) and (A12) in (A10):

$$\left[\frac{\partial U}{\partial n_i}\right]_{T,n_j} = h_i^\circ - RT^2\left[\frac{\partial \ln f_i}{\partial T}\right]_{n_i,n_j} \tag{$A13$}$$

The thermodynamic equation for the differential energy of adsorption is obtained by substituting Eq. (A13) into (26) and using $h_i^\circ = u_i^\circ + RT$ for the perfect-gas reference state:

$$\Delta\overline{u}_i = -RT^2\left[\frac{\partial \ln f_i}{\partial T}\right]_{n_i,n_j} + RT \tag{$A14$}$$

Q.E.D.

Thermodynamic equation for excess differential enthalpy (isosteric heat).

The derivation of Eq. (63) for the differential enthalpy is similar to that for the absolute differential energy but uses Eqs. (40), (41), and (62) for the excess functions.