# PHYSICAL ADSORPTION OF GASES: THE CASE FOR ABSOLUTE ADSORPTION AS THE BASIS FOR THERMODYNAMIC ANALYSIS

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ABSTRACT. We discuss the thermodynamics of physical adsorption of gases in porous solids. The measurement of the amount of gas adsorbed in a solid requires specialized volumetric and gravimetric techniques based upon the concept of the surface excess. Excess adsorption isotherms provide thermodynamic information about the gas-solid system but are difficult to interpret at high pressure because of peculiarities such as intersecting isotherms. Quantities such as pore density and heats of adsorption are undefined for excess isotherms at high pressure. For microporous adsorbents, these difficulties vanish when excess isotherms are converted to absolute adsorption. Using the proper definitions, the special features of adsorption can be incorporated into a rigorous framework of solution thermodynamics. Practical applications including mixed-gas equilibria, equations for adsorption isotherms, and methods for calculating thermodynamic properties are covered. Equilibrium properties such as entropy of gases in macroporous adsorbents are undetermined at high pressure for both absolute and excess adsorption.

## 1. INTRODUCTION

The objective of this paper will be obvious to scientists and engineers working in the field of adsorption: to apply the full power of thermodynamics to the field of adsorption. Basically, thermodynamics provides quantitative relationships between seemingly unrelated phenomena such as the amount adsorbed and the heat of adsorption. Thermodynamic analysis is able to quantify the complex behavior of adsorbed mixtures in terms of the adsorption of single gases, one at a time. Thermodynamic equations enable physical chemists to explain adsorption in terms of gas-solid and gas-gas molecular interactions, while providing engineers with reliable estimates of selectivity, heats of adsorption for energy balances, and the difference between the actual and equilibrium chemical potentials which provides the driving force for mass transfer.

A major issue of adsorption addressed in this paper is the perennial argument of how to measure the amount of gas adsorbed by a solid: absolute or Gibbs excess? It would be fair to say that the adsorption community is evenly divided on this issue and we do not expect to convince everyone that our view should prevail. Our intention is to provide a detailed explanation of the problems associated with both definitions and to present our own conclusions. Regardless of the side taken in this argument, some points are indisputable. The amount adsorbed defined by Gibbs excess is the gold standard for experimental measurements. At low pressure (as defined later) absolute and excess adsorption are equal within the accuracy of most experiments. Thus absolute adsorption is always measurable at low pressure, which is the most important region for most applications. At high pressure, the *thermodynamics* of excess adsorption is meaningless. The excess amount adsorbed can be measured but its translation to properties such as energy and entropy generates unphysical singularities. Microporous adsorbents constitute a special case because it is possible to measure their pore volumes experimentally. One must assume that gas (argon or methane) adsorbed near its condensation pressure has a pore density comparable in value to its bulk liquid phase, but this reasonable approximation provides reliable estimates of properties of

adsorbed supercritical gases at pressures up to hundreds of bars, in the same region where Gibbs excess caculations yield absurd results. For macroporous adsorbents, neither absolute nor excess adsorption can be used to calculate adsorptive properties at high pressure. In this region, thermodynamic analysis is limited to the properties of the total amount of gas in the control volume because the gas cannot be subdivided into bulk and adsorbed portions. For these reasons, we recommend that thermodynamic analysis be performed under the framework of absolute adsorption. The absolute approach reduces adsorption thermodynamics to a special case of solution thermodynamics for which the standard tools of vapor-liquid equilibria are well established. Surface tension and surface area variables, which are undefined for adsorption in porous materials, are eliminated by the application of solution thermodynamics.

## 2. General Discussion of Absolute and Gibbs Excess Adsorption

Gibbs excess *amount adsorbed* is a precise physical measurement that can be reproduced by anyone equipped with a supply of helium. For microporous solids, excess adsorption may be converted to absolute adsorption using the micropore volume of the solid.

Gibbs excess adsorption and absolute adsorption may be considered equal at low pressure[1] where the difference between the two quantities is of the order of one percent or less. Calculation of variables such as enthalpy and entropy is simpler in terms of absolute adsorption. Gibbs excess variables are practically indistinguishable from their absolute counterparts but excess thermodynamics is complicated and difficult to interpret.

At high pressure, the calculation of thermodynamic properties from Gibbs excess variables using the excess framework leads to nonsense such as a maximum in adsorption, a singularity in the differential enthalpy, and negative adsorption. In general at high pressure, the excess amount adsorbed is an experimental variable but its interpretation is problematic.

For microporous adsorbents at high pressure, the peculiarities observed for Gibbs excess adsorption vanish after conversion to absolute adsorption. Absolute thermodynamic properties may be calculated from sub-atmosphere pressure up to hundreds of bars and compared to molecular simulations, which yield absolute adsorption variables naturally from the grand canonical ensemble.

At high pressure for macroporous adsorbents such as active carbon or nonporous solids such as graphitized carbon black, identification of the portion of the gas which is adsorbed is impossible. Gibbs excess adsorption can be measured but it is incompatible with thermodynamic calculations. Absolute adsorption in nonporous or macroporous solids is undefined because one cannot decide which molecules are adsorbed and which molecules belong to the bulk gas. Thermodynamic properties for adsorption in macroporous solids at high pressure must be calculated for the entire system consisting of the solid adsorbent and all of the gas inside the control volume. This makes it difficult to interpret molecular interactions inside the macropores at high pressure. For macroporous adsorbents, the physical interpretation of adsorption from equilibrium properties is restricted to low pressure.

Adsorption is measured experimentally as Gibbs excess. For low pressure, it is convenient to treat Gibbs excess adsorption as absolute adsorption when the two quantities are equal within the accuracy of the measurements. The equations for absolute thermodynamic properties resemble those for bulk fluids so they are familiar. At high pressure, thermodynamic properties can be calculated for absolute adsorption in microporous adsorbents but

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[1]Low pressure is defined as less than 10 bar and high pressure is defined as greater than 10 bar. The value of 10 bar is approximate and depends upon the gas and the temperature. Refer to Section 4.3.1 where the difference between excess and absolute adsorption is related to the bulk density.

not for nonporous or macroporous adsorbents. For macroporous adsorbents at high pressure, thermodynamic calculations of energy and entropy apply to the entire control volume containing a gas in contact with a solid; the properties of the gas cannot be divided into separate terms for bulk gas and adsorbed gas.

It is emphasized that the Gibbs excess *amount adsorbed* is the proper experimental variable for any definition of adsorption. It is the next step, the calculation of thermodynamic excess variables such as energy and entropy that seems unnecessary. At low pressure, the excess variables are equal to their absolute counterparts and at high pressure, the excess variables are meaningless.

## 3. Detailed Discussion of Absolute and Excess Adsorption with Example

Experimental measurements of adsorption in porous solids lead in the first instance to the Gibbs adsorption excess, defined as the difference between the number of moles of gas present in the system (sample cell containing porous solid) and the number of moles that would be present if all the accessible volume in the system were occupied by the adsorbate gas in its bulk state at the same temperature and pressure. A formulation of thermodynamics based upon excess properties (excess adsorption, excess enthalpy etc.) has been almost universally adopted in the thermodynamic analysis of experimental data on adsorption in porous materials even though it presents significant difficulties. Perhaps the most significant difficulty is that properties such as energy and bulk pressure are multivalued functions of the adsorption excess at sufficiently high pressure and temperature. In this paper we challenge the use of the excess property formulation and argue that for adsorption in porous materials thermodynamics should focus on absolute adsorption, defined as the number of moles of gas contained in the porous material. A fully consistent thermodynamic formalism emerges by combining the focus on absolute adsorption with a treatment based on solution thermodynamics where the porous solid and adsorbed gas are treated as components in a mixture. The solution thermodynamics approach to adsorption is not new. We have argued for it previously [17] and it goes back at least to the work of Hill [8]. For adsorption of gases at low pressures the difference between adsorption excess and absolute adsorption lies within the margin of error of typical experimental measurements. However, there is increasing interest in adsorption problems where the bulk gas is dense and nonideal, such as pressure-swing-adsorption (PSA) processes and the storage of supercritical gases. Thus we think it important to set forth the case for abandoning the Gibbs excess formulation of adsorption thermodynamics in favor of an approach that does not lead to inconsistencies in this situation and offers a more rigorous treatment overall. As a bonus, the solution thermodynamics version of adsorption is relatively simple and easy to understand because it is based on standard methods developed for vapor-liquid equilibria.

To illustrate the issues addressed in this paper consider a solid adsorbent of mass $m_s$ that has been freshly degassed under vacuum and at high temperature to remove all traces of gas and impurities. Pack this solid into a sample cell enclosed in a temperature bath and introduce a dose of pure gas from a dosing chamber into the sample cell. Almost all of this first dose will adsorb but a small portion of gas molecules will remain in the gas phase at equilibrium. The amount adsorbed is the total dose less the amount remaining in the gas phase. If the solid is microporous and contains a network of nanometer-sized pores, the space in the cell accessible to gas molecules is the pore volume ($V_p$) plus the gas volume external to the solid ($V_g$). If, after degassing the solid but before the experiment, $n_{He}$ moles of helium gas is introduced at ambient temperature ($T_\circ$) and pressure ($P_\circ$), the so-called "dead space" ($V_d$) inside the sample cell can be measured using the equation of state for helium. Assuming negligible adsorption of helium and a pressure sufficiently low to justify

the perfect gas law:

$$V_d = \frac{n_{He} R T_\circ}{P_\circ} = V_g + V_p \tag{3.1}$$

The standard procedure is to calculate *excess* adsorption using the helium dead-space correction:

$$n_e = \frac{n_t - \rho_g V_d}{m_s} \tag{3.2}$$

The molar density of the gas phase ($\rho_g$) is a function of temperature and pressure as given by its PVT equation of state. Unfortunately this subtraction is an over-correction by the amount of gas that *would* be in the pores ($\rho_g V_p$) if the gas were present at the density of the bulk gas. The actual or absolute amount of gas in the pores ($n_a$) is obtained by correcting for the previous over-correction:

$$\boxed{n_a = n_e + \rho_g v_p} \tag{3.3}$$

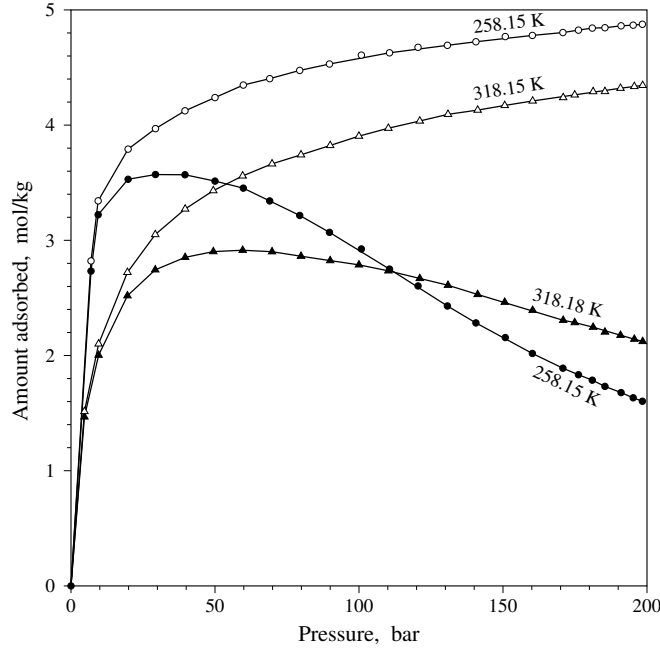where $v_p = V_p/m_s$ is the specific pore volume of the solid.



FIGURE 1. Absolute and excess isotherms for adsorption of $CH_4$ on 13X molecular sieve at 258.15 K and 318.15 K. Closed symbols: experimental data for excess adsorption [22]. Open symbols: absolute adsorption from Eq. (3.3).

A comparison of absolute and excess isotherms related by Eq. (3.3) is shown on Figure 1, based on a pore volume $v_p = 269$ cm$^3$/kg [35]. The excess isotherms exhibit maxima in the range of 30–60 bar. Thermodynamic properties calculated from these excess isotherms have bizarre behavior [22]: the isosteric heat has a singularity which occurs at the maximum in excess adsorption, having a limit of $+\infty$ approaching from the left and a limit of $-\infty$ approaching from the right. The two excess isotherms intersect at about 110 bar; at higher pressure, the excess amount adsorbed *increases* with temperature at constant pressure. The excess amount adsorbed becomes *negative* at very high pressure (not shown on Figure 1). The conclusion is that excess adsorption at high pressure can be measured but its thermodynamic variables are abstract and difficult to interpret.

The excess isotherms shown on Fig. 1 are typical for adsorption of supercritical gases at high pressure. For example, Specovius and Findenegg [31] measured similar excess isotherms for adsorption of methane on graphitized carbon black. There is nothing strange or unusual about the absolute isotherms in Figure 1. The absolute amount adsorbed increases smoothly and monotonically with pressure. Since the micropore density is the amount adsorbed divided by the pore volume, the density should increase indefinitely with pressure, as observed for a different system with a vibrating tube densimeter [5]. Differential properties calculated from the absolute isotherms on Figure 1 are shown on Figure 4 of Section 3; the absolute differential functions are smooth functions of pressure, without the discontinuities observed for differential excess functions. Excess adsorption is abstract; absolute adsorption describes the physical phenomenon of molecules confined in porous materials.
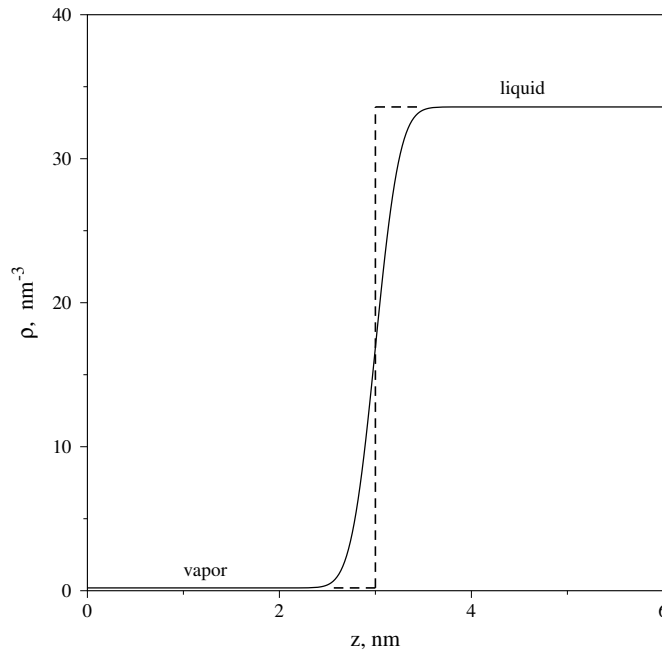


FIGURE 2. Density profile of vapor-liquid interface. $z$ is distance measured perpendicular to the planar interface. The dashed line is the Gibbs dividing surface fixed by Eq. (3.4).

The central thesis of this paper is that the use of the Gibbs excess formulation for calculating thermodynamic properties from adsorption isotherms is inappropriate for porous solids. To understand this argument it is useful to begin by discussing the Gibbs excess formulation as applied to planar interfaces. The concept was originally applied to the vapor-liquid interface [20] where the density varies between the vapor and liquid phase in the manner shown in Figure 2. We see that there is a region where the density smoothly varies from that of the vapor to that of the liquid. In order to focus on the properties of this interfacial region without precisely determining its extent, the Gibbs excess is introduced together with the concept of the Gibbs dividing surface, determined in this case by the condition that the Gibbs excess ($\Gamma$) vanishes.

$$\Gamma = \int_{-\infty}^{z_{div}} [\rho(z) - \rho_v]\, dz + \int_{z_{div}}^{\infty} [\rho(z) - \rho_l]\, dz = 0 \qquad (3.4)$$

For a planar solid-fluid interface where the solid is considered inert the fluid density profile might look something like that in Figure 3, with the detailed form of the profile depending on whether the bulk is gas or liquid and the nature of the solid-fluid and fluid-fluid interactions. Again we are dealing with a spatially varying density and an interfacial region of unknown extent. The Gibbs excess formulation is again perfectly appropriate for this situation. The Gibbs dividing surface in this case is chosen as the surface of the solid.
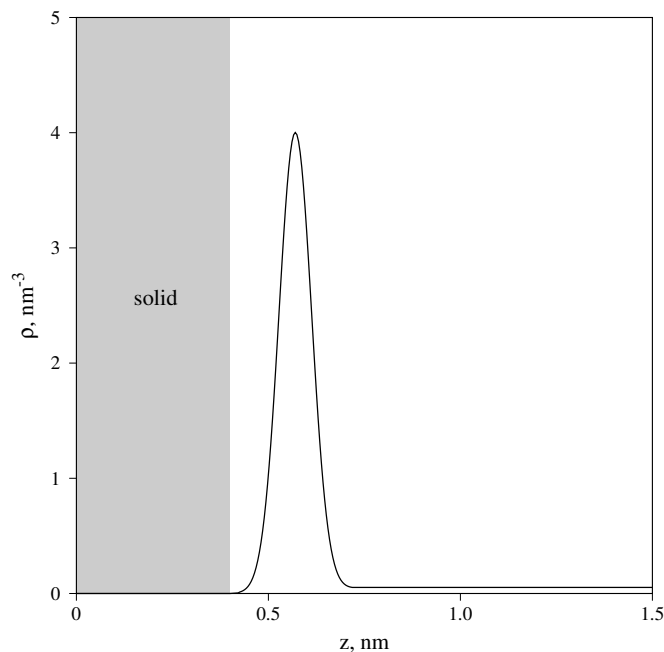


FIGURE 3. Profile of gas density adjacent to gas-solid interface. Distance $z$ is measured perpendicular to the planar surface of the solid.

Consider now adsorption in a porous material in contact with a bulk fluid phase. The sample morphologies encountered encompass a wide spectrum. This spectrum includes single crystals of a zeolite with adsorption mainly within the micropores of the zeolite crystal, ordered mesoporous materials like MCM-41 with fairly uniform cylindrical mesopores, and disordered materials like activated carbons or silica gels, which are collections of porous particles of various sizes with micropores and mesopores within the particles and macropores in the spaces between them (we adopt the IUPAC definition of micropores, mesopores and macropores for the purposes of this discussion). In general we have a bulk fluid (gas or liquid) in contact with another phase consisting of porous solid and adsorbed fluid. The fluid density inside the porous material is certainly locally inhomogeneous. However this does not preclude the treatment of the porous solid and adsorbed fluid as a single phase system. The situation is comparable to that encountered in the thermodynamics of bulk phases in equilibrium (vapor-liquid, solid-liquid etc.) where we can measure or compute the state of the system without inquiring as to the nature of the interface between these bulk phases. This is also appropriate for adsorption equilibrium between a bulk fluid phase and a porous solid phase containing an adsorbed fluid. For convenience we will refer to the latter as the solid phase.

Since adsorption experiments yield the Gibbs excess it is necessary to convert this quantity to absolute adsorption and we review methods for doing this, which involve estimating the pore volume of the porous material. We then proceed to lay out the formulation of

adsorption thermodynamics in terms of absolute quantities, treating each phase, bulk fluid or porous solid plus adsorbed fluid, by the equations of solution thermodynamics. The first benefit of the absolute property approach is that the fluid density is always a monotonically increasing function of the bulk pressure or chemical potential and can therefore itself be treated as an independent state variable. Consequently the concept of "isosteric" temperature derivatives of adsorption isotherms is valid under all conditions in the absolute property formulation. The equations for mixture adsorption in this formalism are quite similar to those based on the excess formalism with excess properties replaced by absolute properties. The definition of the ideal adsorbed solution is modified so that the reference state for each component is the pure adsorbed fluid at the same grand potential as the adsorbed mixture. Throughout the presentation we provide illustrative calculations using simple models and experimental data. We emphasize that the solution thermodynamics approach based on absolute quantities for adsorption in porous materials is not just an alternative to Gibbs excess thermodynamics; it is a rigorous replacement for a somewhat flawed structure. It is also evident from our presentation that quantities like surface tension or spreading pressure, concepts associated with adsorption at planar solid-fluid interfaces, need not appear in the thermodynamics of adsorption in porous materials.

The remainder of the paper is organized as follows. In section 4 we review the methods for quantifying adsorption (Gibbs excess, net adsorption, absolute adsorption) and show how they are determined by volumetric and gravimetric measurements. Next we present the solution thermodynamics approach to adsorption in section 5. Section 6 covers ideal adsorbed solutions in the framework of solution thermodynamics, including a numerical calculation. We discuss excess mixing functions and activity coefficients in section 7 and liquid mixtures adsorption in section 8. We consider calorimetric measurements in section 9 and in section 10 we briefly discuss the impact of this formalism in modeling adsorption column dynamics. We give a summary of the points raised in this paper and our conclusions in section 11.

## 4. Quantifying Adsorption

Porous adsorbents may contain pores ranging from micropores with pore diameters of less than 1 nm to macropores with diameters of 50 nm or more. The degree of order of the solid ranges from crystalline materials like zeolites to highly disordered materials such as activated carbons. Typical adsorbents are silica gel, activated carbon, zeolites, metal organic frameworks, ordered mesoporous materials (e.g. MCM-41 [33]), and carbon nanotubes. Regardless of the chemical composition and structure of the adsorbent, there are three definitions for the amount of gas or vapor adsorbed in the solid:

- Gibbs excess
- Net
- Absolute

The first two definitions, Gibbs excess and net adsorption, are measured experimentally using macroscopic methods. A thorough discussion of net adsorption is given in a recent paper by Gumma and Talu [7]. The third definition, absolute adsorption, is the "actual" amount of gas in the solid phase. Absolute adsorption is required for thermodynamic calculations and arises naturally in theoretical models and molecular simulations. Therefore the conversion of excess or net adsorption to absolute adsorption is a crucial step toward the understanding and analysis of experimental data.

Two techniques are used for the measurement of Gibbs excess and net adsorption:

- Volumetric
- Gravimetric

The volumetric technique is more accurate at low pressure because almost all of the metered dose is adsorbed. The gravimetric technique has the disadvantage at low pressure that the amount adsorbed is the difference of two nearly equal numbers. At high pressure, the volumetric technique gives the amount adsorbed as the sum of a large number of doses with an associated cumulative error. The gravimetric technique is more accurate at high pressure because the measured amount adsorbed is referenced to the weight of the adsorbent in a vacuum. Both techniques can be automated.

### 4.1. **Gibbs Excess Adsorption.**

4.1.1. *Volumetric method.* The volumetric technique is to introduce a known mass $(m_s)$ of adsorbent into a sample cell of calibrated volume $(V_t)$. Following desorption of the solid using high temperature and vacuum, a fixed temperature is imposed by a temperature bath and a measured dose of gas $(\Delta n)$ is introduced to the sample cell. After adsorption is complete, at equilibrium, the temperature $(T)$ and pressure $(P)$ are measured and the specific excess amount adsorbed $(n_e)$ is defined by a mass balance:

$$n_e = \frac{n_t - \rho_g V_d}{m_s} \qquad (4.1)$$

where $V_d$ is the helium dead space of the sample cell, $\rho_g(T, P)$ is the density of the bulk gas (mol/m$^3$) obtained from an equation of state and $n_t = \sum_j (\Delta n_j)$ is the total amount of gas in the sample cell. At sufficiently low pressure, the density of the bulk gas phase is given by the perfect gas law $(\rho_g = P/RT)$.

The helium dead space $(V_d)$ is obtained from a calibration with helium gas at ambient temperature $(T_\circ)$ and pressure $P_\circ$ before starting the experiment. If the pressure is sufficiently low, the perfect gas law gives:

$$V_d = \frac{n_{He}}{\rho_{He}} = \frac{n_{He} R T_\circ}{P_\circ} \qquad (4.2)$$

Eq. (4.2) follows from Eq. (4.1) by setting $n_e$ equal to zero (for helium). The determination of the dead space does not depend on the perfect gas law, which can be replaced if necessary by the experimental molar density of helium $(\rho_{He})$ from an equation of state. The implicit assumption of Eq. (4.2) is that helium does not adsorb at $T_\circ$ and therefore measures the pore volume of the solid as well as the volume of the bulk gas phase. The question of whether corrections should be applied for the small but finite adsorption of helium inside the pores is considered in Section 2.6.

The total volume of the sample cell is:

$$V_t = V_d + V_{sk} \qquad (4.3)$$

$V_{sk}$ is the skeletal volume or "backbone" of the solid material which is inaccessible to gas molecules. The reporting of experimental adsorption isotherms should include the specific skeletal volume:

$$v_{sk} = \frac{V_{sk}}{m_s} = \frac{V_t - V_d}{m_s} \qquad (4.4)$$

because it allows the pore volume of the solid $(v_p)$ to be calculated from its specific volume $(v_s)$, or the reverse.

$$v_s = v_{sk} + v_p \qquad (4.5)$$

4.1.2. *Gravimetric method.* A mass $(m_s)$ of solid adsorbent is loaded into a bucket attached to a microbalance. Following desorption of the solid using high temperature and vacuum, a fixed temperature is imposed by a temperature bath and gas is admitted to the sample cell. After adsorption is complete, at equilibrium, the temperature $(T)$ and pressure $(P)$ are measured and the adsorption is determined from the weight of the bucket containing the solid and adsorbed gas. The weight of gas adsorbed is equal to the weight of the bucket containing the solid minus its degassed tare weight under full vacuum $(\Delta w)$. Using the local "$g$", the corresponding mass of gas adsorbed is $\Delta m = \Delta w / g$. The Gibbs excess amount adsorbed is:

$$n_e = \frac{\Delta m}{M m_s} + \rho_g v_{\text{sk}}$$

(4.6)

where $M$ is the molecular weight of the gas.

The second term $(\rho_g v_{\text{sk}})$ in Eq. (4.6) is a buoyancy correction. Since the solid is weighed while immersed in a gas, a buoyancy correction equal to the weight of bulk gas displaced is added to the weight registered by the microbalance. The Gibbs excess model is based on the pore volume being filled with gas at its bulk density, so this portion of the solid needs no buoyancy correction. The correction for buoyancy is restricted to the skeletal volume of the solid. The specific skeletal volume is determined by a helium calibration of the degassed adsorbent:

$$v_{\text{sk}} = \frac{(-\Delta m)}{\rho_g \, M m_s}$$

(4.7)

where $\Delta m$ is the recorded mass increase of the adsorbent in helium gas relative to its tare weight in a perfect vacuum. The molar density $(\rho_g)$ and molecular weight $(M)$ refer to the helium. $\Delta m$ is negative because the displaced helium exerts a lifting force. Eq. (4.7) follows from (4.6) by setting $n_e$ to zero (for helium).

Regardless of the experimental method, volumetric or gravimetric, the skeletal volume of the solid must be determined separately by helium calibration. The value of the skeletal volume provides useful information about absolute adsorption through Eq. (4.5).

## 4.2. **Net Adsorption.**

4.2.1. *Volumetric method.* Net adsorption uses the entire container as the thermodynamic system [8]. The volumetric technique for net adsorption $(n_n)$ is the same as for Gibbs excess but the definition [7] is:

$$n_n = \frac{n_t - \rho_g V_t}{m_s}$$

(4.8)

where $V_t$ is the total volume of the sample cell. No helium calibration is required.

4.2.2. *Gravimetric method.* Net adsorption $(n_n)$ is measured gravimetrically using the procedure described for Gibbs excess but using the definition:

$$n_n = \frac{\Delta m}{M m_s}$$

(4.9)

Consider the specific volume of the solid $(v_s)$. This space experiences a buoyancy force from the displaced bulk gas, but the same space devoid of adsorbent experiences the same buoyancy force. Since net adsorption is relative to the space filled with gas but devoid of adsorbent, the buoyancy correction for the adsorbent cancels exactly with the buoyancy correction for the reference state. As for the volumetric method, no helium calibration is required for the determination of net adsorption.

4.3. **Absolute Adsorption.** Absolute adsorption ($n_a$) is defined in terms of the volumetric method by a mass balance:

$$n_a = \frac{n_t - \rho_g V_g}{m_s} \tag{4.10}$$

where $n_t$ is the total amount of gas introduced to the sample cell, $V_g$ is the volume of the bulk gas phase, and $\rho_g(P,T)$ is the molar density of the bulk gas phase. In other words, the adsorbed gas is the total amount of gas in the sample cell less the amount in the gas phase. Comparing Eqs. (4.1) and (4.10):

$$n_a = n_e + \frac{\rho_g(V_d - V_g)}{m_s} \tag{4.11}$$

The dead space $V_d$ determined by the helium calibration is divided into two parts, a bulk gas phase $V_g$ and a pore volume $V_p$:

$$V_d = V_g + V_p \tag{4.12}$$

Eq. (4.11) becomes:

$$n_a = n_e + \frac{\rho_g V_p}{m_s} \tag{4.13}$$

or

$$\boxed{n_a = n_e + \rho_g v_p} \tag{4.14}$$

where $v_p = V_p/m_s$ is the specific pore volume of the solid.

Determination of $v_p$ in Eq. (4.14) is discussed in Section 4.4.

4.3.1. *Comparison of Absolute and Excess Adsorption.* The difference between absolute and excess adsorption can best be understood by comparing bulk density with pore density. Referring to Eq. (4.14), the difference is negligible if:

$$\rho_g v_p \ll n_a \tag{4.15}$$

or

$$\rho_g \ll \frac{n_a}{v_p} \tag{4.16}$$

but $n_a/v_p$ is pore density ($\rho_p$) so absolute and excess adsorption may be considered equal for:

$$\rho_g \ll \rho_p \tag{4.17}$$

In the low-pressure region of the adsorption isotherm where Henry's law is valid:

$$n_a = HP = HRT\rho_g \tag{4.18}$$

or

$$\frac{\rho_p}{\rho_g} = \frac{HRT}{v_p} \tag{4.19}$$

For supercritical gases, typical values of the ratio $\rho_p/\rho_g$ are in the range of $10^4$ to $10^5$ and Eq. (4.17) is easily satisfied. This large ratio is explained by the Boltzmann factor $(e^{-U_{1S}/k_B T})$ for the probability of finding molecules inside the pores of the solid, as compared to the bulk gas phase, where $U_{1S}$ is gas-solid potential energy.

The ratio of densities ($\rho_p/\rho_g$) decreases as the pore density approaches a limit comparable to the density of a liquid. Referring to a bulk gas at STP, the molecular density is 0.026 nm$^{-3}$. The molecular density of a liquid is $\approx 10$ nm$^{-3}$. With these numerical references in mind, Table 1 shows how the ratio varies with bulk density. The difference between excess and absolute adsorption becomes significant for $\rho_g > 0.1$ nm$^{-3}$, for which the ratio $\rho_p/\rho_g$ cannot exceed 100. At a bulk density of $\approx 1$ nm$^{-3}$, the ratio of $\rho_p/\rho_g$ cannot exceed 10. Under these conditions, the excess adsorption exhibits a maximum even though the absolute adsorption is increasing with bulk density (see Figure 1). At a bulk density of

| density, nm$^{-3}$ | comments |
|---|---|
| 0.01 | $(n_e - n_a)$ difference negligible |
| 0.1 | $(n_e - n_a)$ difference 1% of $n_a$ |
| 1.0 | $n^e$ has maximum value |
| 10.0 | $n^e = 0$ |

TABLE 1. Effect of bulk molecular density upon difference between absolute adsorption $(n_a)$ and Gibbs excess $(n_e)$.

$\rho_g = 10$ nm$^{-3}$, the pore density is approximately equal to the bulk density and the excess adsorption is zero.

In summary, at a bulk density less than 0.1 nm$^{-3}$, the values for excess and absolute adsorption may be considered equal within experimental error. At values of bulk density exceeding 1 nm$^{-3}$, the surface excess presents a misleading picture of adsorption in pores because the thermodynamic properties have multiple values and non-physical singularities. The density values in Table 1 are imprecise but provide guidance about the difference between absolute and excess adsorption.

4.3.2. *Absolute Adsorption from Net Adsorption.* In the measurement of net adsorption using Eq. (4.8), the pre-calibrated total volume of the sample cell $(V_t)$ is the sum of two macroscopic phases, the gas phase and the solid phase:

$$V_t = V_g + V_s \tag{4.20}$$

Comparing Eqs. (4.8) and (4.10) and using Eq. (4.20):

$$\boxed{n_a = n_n + \rho_g v_s} \tag{4.21}$$

If the specific volume of the solid $(v_s)$ is known, absolute adsorption can be calculated directly from the net adsorption by Eq. (4.21), thus bypassing entirely the measurement of surface excess using a helium calibration of the dead space.

Net adsorption isotherms have the same shape as the excess isotherms on Figure 1 but $n_a > n_e > n_n$. Excess adsorption is preferred over net adsorption because it is closer to absolute adsorption at low pressure.

Net adsorption is useful for studying the gas storage capacity of adsorbents at high pressure because the maximum in the net adsorption isotherm identifies the pressure of maximum adsorptive storage capacity compared to pure compression.

4.3.3. *Absolute Adsorption from Molecular Simulation and Theory.* Molecular theory and simulations of adsorption yield the absolute adsorption. For instance, absolute adsorption emerges naturally from grand canonical Monte Carlo (GCMC) simulations. The absolute amount adsorbed $(n_a)$ is obtained as an ensemble average for fixed values of the independent variables: the chemical potential (fugacity) and temperature. The absolute differential energy is calculated from fluctuations in the energy and amount adsorbed or directly by differentiation of an isotherm of energy versus the amount adsorbed [34]. The pore volume of the solid $(v_p)$ can be calculated for a molecular model from the ensemble average for the amount of helium in the pores at ambient temperature and low pressure, thus mimicking the actual experiment. Much of this carries over to the study of adsorption via classical density functional theory [11]. Classical density functional theory yields a prediction of the density distribution in a porous material, and again naturally yields the absolute adsorption by integration of this distribution.

4.4. **Measurement of Pore Volume.** The characterization of porous solids is a highly developed field focused on measuring the pore size distribution and other properties of adsorbent materials. Monographs are available [10, 19] and an IUPAC commission has [25] provided recommendations for the measurement and analysis of adsorption data for the purposes of pore structure characterization. The most widely accepted method for pore volume estimation is the adsorption of nitrogen or argon at their respective boiling points. Plateaus in the resulting isotherms, associated with the filling of micropores can be used to estimate pores volumes assuming that the average density in the filled pores is equal to the bulk liquid density [25].

Extensive databases of pore volumes calculated from structural data are available online for zeolites [3] (http://helios.princeton.edu/zeomics) and metal-organic-frameworks (MOF) [4] (http://helios.princeton.edu/mofomics).

As stated previously, conversion of excess to absolute adsorption is restricted to microporous materials.

4.5. **Reporting Experimental Data.** Experimental measurements should be reported as Gibbs excess adsorption so that the raw data can be converted by Eq. (4.14) to absolute adsorption based upon the currently accepted value for the pore volume. If published as absolute adsorption, the pore volume should be stated. For either choice, excess or absolute, the data should include the skeletal volume of the solid obtained by the helium calibration (Eq. (4.4) or Eq. (4.7)).

4.6. **Helium Calibration.** Experimental measurement of Gibbs excess adsorption by volumetric or gravimetric methods requires a pre-calibration with helium gas to measure the dead space and skeletal volume of the solid adsorbent. This dependence of the Gibbs excess measurement upon helium calibration has led some people to advocate net adsorption, which does not require a helium calibration for its measurement. Hill [8] said in regard to net adsorption: "This is the program that must be adopted to be absolutely rigorous thermodynamically, and it is certainly important that workers in the field realize it. However, in the present writer's opinion, if this program were actually used by experimentalists, the severe price paid, in loss of contact with molecular reality inside the container, would far exceed the value of the last ounce of exactness gained."

The standard procedure for volumetric or gravimetric determination of Gibbs excess is to measure the dead space in the system using helium gas at low pressure and at ambient temperature ($\approx 25°$C). The assumption is that helium does not adsorb under these conditions. Adsorption of helium at ambient temperature and low pressure is very small but non-zero. This had led to the suggestion that the helium calibration be modified to account for helium adsorption [6, 29]. The helium calibration at ambient temperature would be replaced by a more complicated procedure which requires the determination of the Henry constant for adsorption of helium. The value calculated for the dead space would decrease slightly and change slightly the value of excess adsorption. However, the value of the pore volume would decrease by the same amount so that the value obtained for absolute adsorption would be unaffected by the choice of helium calibration procedure. We do not support the recommendation that the dead space measurement be corrected for adsorption of helium because nothing is gained by the extra effort. The traditional definition of Gibbs excess as the amount adsorbed relative to "non-adsorbing" helium at ambient temperature is convenient and should be retained.

For low-temperature experiments, (e.g. 77 K), the helium calibration should be performed at ambient temperature because adsorption of helium in the pores at 77 K is not negligible. Adsorption thermodynamics is based upon the assumption that the specific volume of the solid, including its pore volume, is independent of temperature.

4.7. **Experimental Methods for Mixtures.** Eq. (4.1) for volumetric adsorption of a single gas also applies to excess adsorption of the $i$th component of a mixture; the density ($\rho$) of the bulk gas is replaced by the bulk density of the $i$th component. Calculation of this density requires the composition of the bulk gas inside the sample cell, which is difficult to measure without disturbing the equilibrium conditions.

Gravimetric measurements by Eq. (4.6) cannot be extended to mixtures. However, binary gas measurements of the total mass adsorbed (at constant temperature and pressure) as a function of gas-phase composition can be converted to excess adsorption for the individual components using a rigorous procedure based upon the Gibbs adsorption isotherm [16].

Binary mixture adsorption can be calculated from simultaneous volumetric and gravimetric measurements [9]. The volumetric method measures the total amount adsorbed (moles) and the gravimetric method measures the total mass adsorbed. If the molecular weights of the gases are different, the individual amounts adsorbed are obtained as solutions of a pair of linear algebraic equations.

All of these methods require the temperature, pressure, and composition of the bulk gas phase. Equilibration of mixture adsorption is a slow process due to the need to relax the composition distribution in the system. Reversibility should be checked by approaching data points from different directions.

4.8. **Isotherms with Hysteresis Loops.** In many instances adsorption isotherms exhibit hysteresis between adsorption and desorption. This is especially true for adsorption in mesoporous materials [11], where it is associated with metastability of vapor-like and liquid-like states in the pores. Most studies of hysteresis are done for subcritical bulk gases, e.g. nitrogen at its normal boiling temperature, at low pressures where the difference between excess and absolute adsorption is small. In general it is not expected that presentation of hysteresis loops in terms of absolute adsorption rather than adsorption excess should affect the interpretation of the behavior.

## 5. Solution Thermodynamics Formulation of Adsorption Equilibrium in Terms of Absolute Adsorption

For the reasons given in Section 1, the remainder of this paper is devoted to the application of solution thermodynamics to adsorption in terms of absolute variables. Adsorption is cast as a special case of phase equilibrium between a solid and a gas phase. Equations written in the language of solution thermodynamics are straightforward and are derived without any discussion of a dividing surface, Gibbs excess, or spreading pressure.

5.1. **Conditions for Equilibrium.** The equilibrium conditions are the equality in both phases of temperature and the chemical potential of each gaseous component. If we restrict the treatment to inert solids (nonvolatile and incompressible) then the equality of pressure in both phases is not an equilibrium condition. The chemical species are the solid adsorbent and one or more adsorbed gases. Compositions are normally described in terms of the mole fraction of each component, but mole fractions do not apply to adsorption because the solid adsorbent has no molecular weight. The composition of the solid phase is expressed as a ratio: moles of adsorbate per kilogram of solid adsorbent (mol/kg) for each adsorbate component.

The chemical potential of the solid adsorbent varies with temperature and with the amount of gas adsorbed but it is otherwise inert. Since the adsorbent exists only in the solid phase, its chemical potential is redundant for the determination of equilibrium. The equilibrium condition for equality of chemical potential in the solid and gas phases applies to the adsorbates only.

For $N_c$ gaseous components and two phases (gas and solid), there are $(N_c+1)$ thermodynamic degrees of freedom for the system. For adsorption of a single gas there two degrees of freedom and for adsorption of a binary gas mixture, there are three degrees of freedom, e.g. $\{T, P, y_1\}$.

5.2. **Properties of Bulk Gas Phase.** The driving force for adsorption of a gas is its chemical potential which it is convenient to quantify via the fugacity ($f_i$):

$$\mu_i = \mu_i^\circ(T) + RT \ln \frac{f_i}{f_i^\circ} \qquad \text{(const. } T\text{)} \qquad (5.1)$$

where $\mu_i$ is the chemical potential, $\mu_i^\circ$ refers to the chemical potential in the perfect-gas reference state at the same temperature and $f_i^\circ \equiv 1$ bar. The density of the gas phase and the fugacities of its components may be calculated from the Soave-Redlich-Kwong or Peng-Robinson equation of state, given the temperature, pressure, and composition of the gaseous mixture. Parameters needed for this calculation are the critical properties $\{T_c \text{ and } P_c\}$ and "acentric factor" ($\omega$) of each component; the calculation is described in thermodynamic textbooks [30]. The fugacity of a pure component is given by the pressure ($f = P$) and the fugacity of a component in a mixture is given by its partial pressure ($f_i = Py_i$) provided that $P < 2$ bar. A 2-bar limitation for applying the perfect-gas law is only a suggestion; the range of the perfect-gas law depends upon the system and the accuracy of the experimental data.

The properties (enthalpy, entropy, etc.) of the gas phase obey the perfect-gas law at low pressure or an equation of state at higher pressure. We assume the availability of a suitable equation of state when required for high pressure so that attention in this development is focused on the solid phase.

5.3. **Thermodynamics of the Solid Phase.** The fundamental thermodynamic equation for adsorption in a solid is:

$$dU = \quad TdS - PdV + \mu_s' dm_s + \sum \mu_i \, dn_i \qquad (5.2)$$

This equation applies to an open system with a differential amount $dn_i$ of adsorbate $i$ entering the solid phase. The summation is over the gas species present, one term for each gas. The equilibrium condition is that the chemical potential of the adsorbate in the solid phase ($\mu_i$) is equal to its chemical potential in the bulk gas phase. $\mu_s'$ in the chemical potential of the solid adsorbent and the prime symbol is intended to emphasize its mass basis of J/kg. $dm_s$ refers to differential mass of solid adsorbent. For adsorption, the solid phase is open to the adsorbates but closed to the solid material. $dm_s$ is zero but the term $\mu_s' dm_s$ is retained as a reminder that the chemical potential of the solid $\mu_s'$ is altered by adsorption. Mole numbers ($n_i$) refer to absolute adsorption in this and subsequent sections unless stated otherwise.

The extensive properties of the solid phase are energy $U$ in J, entropy $S$ in J/K, volume $V$ in m$^3$, mass of solid $m_s$ in kg, and *absolute* amount $n_i$ of $i$th gaseous component in moles. The extensive properties $(U, S, V)$ refer to the entire solid phase including the adsorbate. Since the function $U(S, V, m_s, n_1, n_2, \dots)$ is homogeneous first-order in the variables $S, V, m_s$, and amounts $n_i$, Eq. (5.2) may be integrated directly:

$$\text{internal energy:} \qquad U = TS - PV + \mu_s' m_s + \sum \mu_i n_i \qquad (5.3)$$

The summation term is over the gases; the solid is accounted for in the $\mu_s' m_s$ term.

For independent variables $V$, $T$, and $n$ in the solid phase, the Helmholtz free energy is:

$$\text{Helmholtz free energy:} \qquad F = U - TS = -PV + \mu_s' m_s + \sum \mu_i n_i \qquad (5.4)$$

| $P$, bar | $PV$, kJ/mol |
|:---:|:---:|
| 1 | 0.01 |
| 10 | 0.1 |
| 100 | 1.0 |

TABLE 2. Values for $PV$ product in solid phase for a typical zeolite.

The grand potential transforms the independent variables for the gases from mole numbers (in $F$) to chemical potentials (in $\Omega$):

$$\text{grand potential:} \qquad \Omega = F - \sum \mu_i n_i = -PV + \mu'_s m_s \qquad (5.5)$$

The differential equations for the auxiliary functions are:

$$dF = -SdT - PdV + \mu'_s dm_s + \sum \mu_i dn_i \qquad (5.6)$$

$$d\Omega = -SdT - PdV + \mu'_s dm_s - \sum n_i d\mu_i \qquad (5.7)$$

The natural thermodynamic functions for adsorption are the Helmholtz free energy and grand potential. Enthalpy and Gibbs free energy functions are less useful for the solid phase but they are well defined:

$$\text{enthalpy:} \qquad H = U + PV \qquad (5.8)$$

$$\text{Gibbs free energy:} \qquad G = F + PV \qquad (5.9)$$

Sample values of the $PV$ product are listed in Table 2 for a typical zeolite with a density of 2 kg/dm$^3$ and a loading of 5 mol/kg. Since values of energy and free energy are within the range of 10–30 kJ/mol, the approximations $H \approx U$ and $G \approx F$ are valid at pressures below 10 bar.

The special character of a gas-solid mixture allows a major simplication: the volume $V$ of the solid adsorbent is effectively constant. Although the solid may expand according to its temperature coefficient of expansion, contract according to its isothermal compressibility, or swell due to adsorption, changes in $V$ are normally negligible. If the volume of the solid varies significantly over the range of the experiment, the principles of phase equilibrium are still valid but with the complication that the volume of the solid phase must be included as a variable in the thermodynamic equations. This complication will not be pursued here, but to do so would be straightforward.

The volume of a porous solid must be defined. Here, $V$ is the volume of the solid including its pores, that is the skeletal volume plus its open and closed pores. This volume excludes interstitial void between the adsorbent particles. The density of the solid, which is the mass of the particle divided by this volume, is called the "effective particle density" in particle technology. If the solid is ordered and crystallographic data are available, the effective particle density is that of the unit cell. The effective particle density of a solid material is always greater than its bulk density, for which the volume includes the void space outside the particles.

Imposing the constancy of the solid volume and the fact that the system is closed for the solid material, the differential equations simplify to:

$$dU = \quad TdS + \sum \mu_i \, dn_i \qquad (5.10)$$

$$dF = -SdT + \sum \mu_i \, dn_i \qquad (5.11)$$

$$d\Omega = -SdT - \sum n_i \, d\mu_i \qquad (5.12)$$

Eqns. (5.10)–(5.12) exploit the advantage of the Helmholtz representation for systems of constant volume. The thermodynamic functions $(U, S, F, \Omega)$ refer to the entire solid phase consisting of the solid material and the gas adsorbed in its pores. What is striking about these equations is the absence of pressure and volume variables.

In preparation for a discussion of the Gibbs adsorption isotherm, Eq. (5.12) is compared term-by-term with the Gibbs-Duhem equation which plays a central role in vapor-liquid equilibrium:

$$\text{Gibbs-Duhem:} \quad SdT - VdP + \sum n_i d\mu_i = 0$$

$$\text{Eq. (5.12):} \quad SdT + d\Omega + \sum n_i d\mu_i = 0$$

For vapor-liquid equilibrium, the independent variables which define the standard states for the components of the mixture are $T$ and $P$. By analogy, the standard states for mixture adsorption are determined by $T$ and $\Omega$.

5.4. **Gibbs Adsorption Isotherm for Solid Phase.** In all equations that follow in this paper, unless stated otherwise, the extensive thermodynamic functions describing the solid phase are *specific* extensive functions per unit mass of solid adsorbent: $U, F$, and $\Omega$ in J/kg, $S$ in J/(kg-K), $V$ in m$^3$/kg, and $n_i$ in mol/kg. Eq. (5.12) is unchanged:

$$d\Omega = -SdT - \sum n_i \, d\mu_i \tag{5.13}$$

but the extensive variables have been converted to specific quantities per unit mass of solid adsorbent. At constant temperature:

$$d\Omega = -\sum n_i \, d\mu_i \tag{5.14}$$

This equation, which is called the *Gibbs adsorption isotherm*, provides a powerful basis for describing the properties of adsorbed mixtures. In calculations, it is convenient to introduce a reduced grand potential $(\psi)$

$$\psi \equiv -\frac{\Omega}{RT} \tag{5.15}$$

Using Eqs. (5.1) and (5.15), the Gibbs adsorption isotherm is written:

$$\boxed{d\psi = \sum n_i \, d\ln f_i} \tag{5.16}$$

The reduced grand potential $\psi$ has units of mol/kg.

5.5. **Massieu Grand Potential Function.** The grand potential in Eq. (5.13) is a double Legendre transformation of the internal energy:

$$\Omega = U - TS - \sum \mu_i n_i \tag{5.17}$$

The Massieu companion function[12] is a double Legendre transformation of the entropy:

$$-\left(\frac{\Omega}{T}\right) = S - \left(\frac{1}{T}\right)U + \sum \left(\frac{\mu_i}{T}\right) n_i \tag{5.18}$$

which generates the differential equation:

$$-d\left(\frac{\Omega}{T}\right) = -Ud\left(\frac{1}{T}\right) + \sum n_i \, d\left(\frac{\mu_i}{T}\right) \tag{5.19}$$

or, using Eq. (5.15):

$$R \, d\psi = -Ud\left(\frac{1}{T}\right) + \sum n_i \, d\left(\frac{\mu_i}{T}\right) \tag{5.20}$$

This equation is used to calculate the energy by differentiating chemical potential at constant $\psi$, in the same way that Eq. (5.13) yields the entropy by differentiating chemical potential at constant $\Omega$.

5.6. **Helmholtz Free Energy from Grand Potential.** From Eq. (5.5):

$$F = \sum \mu_i n_i + \Omega \tag{5.21}$$

For adsorption of a single gas:

$$F = \mu n + \Omega \tag{5.22}$$

Isothermal integration for $F$ and $\Omega$ using Eqs. (5.11) and (5.12) gives:

$$\int \mu \, dn = \mu n - \int n \, d\mu \tag{5.23}$$

Comparison of the two previous equations shows that the determination of $F$ in terms of $\Omega$ involves an integration by parts.

5.7. **Connection to Statistical Mechanics.** Switching from the gas constant $R$ and "moles" to the Boltzmann constant $k_B$ and "molecules", the Helmholtz free energy is related to the canonical partition function ($Q$):

$$F(V, T, N) = -k_B T \ln Q(V, T, N) \tag{5.24}$$

and the grand potential is related to the grand canonical partition function ($\Xi$):

$$\Omega(V, T, \mu) = -k_B T \ln \Xi(V, T, \mu) \tag{5.25}$$

The set of independent variables $(V, T, \mu)$ is matched to those of adsorption thermodynamics. Grand canonical Monte Carlo (GCMC) methods are especially well suited to molecular simulation of adsorption. These simulations can be carried out within a sample of the solid phase using periodic boundary conditions or for a sample of the solid phase in contact with the bulk fluid [23, 24]. The number of molecules adsorbed in the solid and the integral energy are obtained as ensemble averages.

Alternatively the above equations can be written interns of Massieu functions

$$-F(V, 1/T, N)/T = k_B \ln Q(V, 1/T, N) \tag{5.26}$$

and

$$-\Omega(V, 1/T, \mu/T)/T = k_B \ln \Xi(V, 1/T, \mu/T) \tag{5.27}$$

5.8. **Differential Properties of Solid Phase for Adsorption of Gaseous Mixtures.** The partial molar volume of a pure fluid is the same as its molar volume. Adsorption is distinguished from the thermodynamics of fluids in that molar integral functions for a single adsorbate are *not* equal to their differential values. For adsorption of amount $n$ of a pure gas, extensive properties ($Z$) such as $U$, $S$, and $F$ possess a molar integral value ($z$):

$$z = \frac{Z}{n} \tag{5.28}$$

and an associated differential property:

$$\bar{z} = \left[\frac{\partial Z}{\partial n}\right]_T \tag{5.29}$$

but $z \neq \bar{z}$. The integral quantity is obtained by isothermal integration of the associated differential property:

$$z = \frac{Z}{n} = \frac{1}{n} \int_0^n \left[\frac{\partial Z}{\partial n}\right]_T dn + z^\circ \qquad \text{(constant T)} \tag{5.30}$$

| type | energy | Helmholtz free energy | entropy |
|------|--------|----------------------|---------|
| integral | $U$ | $F$ | $S$ |
| molar integral | $u$ | F | $s$ |
| differential | $\overline{u}_i = \left[\frac{\partial U}{\partial n_i}\right]_{T,n_j}$ | $\mu_i = \left[\frac{\partial F}{\partial n_i}\right]_{T,n_j}$ | $\overline{s}_i = \left[\frac{\partial S}{\partial n_i}\right]_{T,n_j}$ |
| molar value, perfect gas | $u_i^\circ$ | $F_i^\circ$ | $s_i^\circ$ |

TABLE 3. Notation for differential and integral properties.

For multicomponent adsorption, each gaseous component has its own set of differential properties:

$$\overline{z}_i = \left[\frac{\partial Z}{\partial n_i}\right]_{T,n_j} \tag{5.31}$$

It is important to distinguish differential properties ($\overline{z}_i$) of the solid phase from *partial molar quantities* for bulk fluid phases such as, for example, the partial molar entropy of a component of a liquid mixture:

$$\overline{s}_i = \left[\frac{\partial S}{\partial n_i}\right]_{T,P,n_j}$$

for which the entropy of the fluid mixture is given by $S = \sum \overline{s}_i n_i$. Partial molar properties do not apply to adsorption of a gas in a porous solid material. For gases adsorbed in a solid, integral properties are the solution of a differential equation. For a binary mixture:

$$dZ = \left[\frac{\partial Z}{\partial n_1}\right]_{T,n_2} dn_1 + \left[\frac{\partial Z}{\partial n_2}\right]_{T,n_1} dn_2 \qquad \text{(constant T)} \tag{5.32}$$

A path for the integration must be specified, but since $Z$ is a state function, the value obtained for $Z$ is independent of the path. The enormous difficulty of integrating differential equations like Eq. (5.32) using experimental data is the motivation for using excess mixing functions and activity coefficients to describe mixture behavior.

Notation for integral and differential forms is summarized in Table 3. The reference state identified by the superscript $\circ$ is the pure, perfect gas at the same temperature and at a pressure of 1 bar.

From Eq. (5.11) for the chemical potential:

$$\mu_i = \left[\frac{\partial F}{\partial n_i}\right]_{T,n_j} \tag{5.33}$$

The bar signifying a differential variable was omitted for $\mu_i$ in Table 3 to indicate its dual status as a differential for the solid and partial molar variable for the bulk gas:

$$\mu_i = \left[\frac{\partial G}{\partial n_i}\right]_{T,P,n_j} \tag{5.34}$$

The differential energy is derived from Eq. (5.10):

$$\left[\frac{\partial U}{\partial n_i}\right]_{T,n_j} = T\left[\frac{\partial S}{\partial n_i}\right]_{T,n_j} + \mu_i \tag{5.35}$$

From the Maxwell equation for the Helmholtz free energy, Eq. (5.11):

$$\left[\frac{\partial S}{\partial n_i}\right]_{T,n_j} = -\left[\frac{\partial \mu_i}{\partial T}\right]_{n_i,n_j} \tag{5.36}$$

Substitution of Eq. (5.36) into Eq. (5.35) gives:

$$\left[\frac{\partial U}{\partial n_i}\right]_{T,n_j} = \mu_i - T\left[\frac{\partial \mu_i}{\partial T}\right]_{n_i,n_j} = -T^2\left[\frac{\partial}{\partial T}\left(\frac{\mu_i}{T}\right)\right]_{n_i,n_j} \tag{5.37}$$

From Eq. (5.1):

$$\mu_i = \mu_i^{\circ}(T) + RT\ln\left(\frac{f_i}{f_i^{\circ}}\right) \tag{5.38}$$

The reference fugacity $f_i^{\circ}$ is a constant equal to 1 bar. The reference chemical potential $\mu_i^{\circ}(T)$ refers to the pure, perfect-gas reference state at a pressure of 1 bar. In the perfect-gas reference state:

$$\mu_i^{\circ} = h_i^{\circ} - Ts_i^{\circ} \tag{5.39}$$

From Eq. (5.39), the Gibbs-Helmholtz equation for the perfect-gas reference state is:

$$h_i^{\circ} = -T^2\frac{d}{dT}\left(\frac{\mu_i^{\circ}}{T}\right) \tag{5.40}$$

Substituting Eq. (5.1) into Eq. (5.37) and using Eqs. (5.39) and (5.40):

$$\left[\frac{\partial U}{\partial n_i}\right]_{T,n_j} = -RT^2\left[\frac{\partial \ln f_i}{\partial T}\right]_{n_i,n_j} + h_i^{\circ} \tag{5.41}$$

The differential energy of adsorption is exothermic and negative. Eq. (5.41) applies to multicomponent adsorption from a real gas and provides a rigorous connection between adsorption isotherms and the differential energy of adsorption ("heats") measured in adsorption calorimetry (see Section 7).

An equation similar to Eq. (5.41) for the differential entropy is derived from Eq. (5.35):

$$T\left[\frac{\partial S}{\partial n_i}\right]_{T,n_j} = \left[\frac{\partial U}{\partial n_i}\right]_{T,n_j} - \mu_i \tag{5.42}$$

Substituting Eqs. (5.41) and (5.1) into (5.42) and using Eq. (5.39):

$$\left[\frac{\partial S}{\partial n_i}\right]_{T,n_j} = -RT\left[\frac{\partial \ln f_i}{\partial T}\right]_{n_i,n_j} - R\ln\left(\frac{f_i}{f^{\circ}}\right) + s_i^{\circ} \tag{5.43}$$

The differential entropy of adsorption relative to the perfect-gas reference state $(s_i^{\circ})$ is negative, as expected for a molecule going from the perfect-gas state to a confined state inside the pore of the adsorbent.

5.9. **Differential and Integral Properties of Solid for Single-Gas Adsorption.** The development to this point has been for multi-component adsorption. For a single gas, the subscript notation may be eliminated and from Eq. (5.41):

$$\overline{u} = -RT^2\left[\frac{\partial \ln f}{\partial T}\right]_n + h^{\circ} \tag{5.44}$$

where $\overline{u} \equiv (\partial U/\partial n)_T$. This equation is rigorous for single-gas adsorption. The enthalpy reference instead of energy is the consequence of using $\mu^{\circ} = (h^{\circ} - Ts^{\circ})$ as the perfect-gas reference state for the chemical potential. Similarly for the differential entropy of adsorption from Eq. (5.43):

$$\overline{s} = -RT\left[\frac{\partial \ln f}{\partial T}\right]_n - R\ln\left[\frac{f}{f^{\circ}}\right] + s^{\circ} \tag{5.45}$$

If the pressure does not exceed a few bars, the perfect gas approximation $f = P$ may be applied:

$$\overline{u} = -RT^2 \left[\frac{\partial \ln P}{\partial T}\right]_n + h^\circ \qquad (5.46)$$

This is arguably the most important equation of adsorption thermodynamics. $\overline{u}$ is the differential energy in the solid phase in J/kg and $n$ is specific absolute adsorption in mol/kg. $h^\circ$ is the molar enthalpy of the gas in its perfect-gas reference state at the same temperature $T$. The term containing the derivative is called *isosteric heat* in the adsorption literature:

$$q_{\text{st}} \equiv RT^2 \left[\frac{\partial \ln P}{\partial T}\right]_n \qquad (5.47)$$

Heats of adsorption are discussed in Section 9.

For the molar integral properties, we have:

$$u = \frac{U}{n} = \frac{1}{n}\int_0^n \overline{u}\,dn + \frac{U^\circ}{n} \qquad (5.48)$$

$$s = \frac{S}{n} = \frac{1}{n}\int_0^n \overline{s}\,dn + \frac{S^\circ}{n} \qquad (5.49)$$

$$F = \frac{F}{n} = \frac{1}{n}\int_0^n \mu\,dn + \frac{F^\circ}{n} \qquad (5.50)$$

The integrals are at constant temperature and the quantities $\{U^\circ, S^\circ, F^\circ\}$ refer to the clean solid under full vacuum. Note that the differential Helmholtz free energy ($\overline{F} = \overline{u} - T\overline{s}$) is equal to the chemical potential ($\mu$); see Table 7 in Section 6.

The integral properties are also given by Clapeyron-type equations. For the integral energy, it can be shown [26] that:

$$u = \frac{\int_0^n \overline{u}\,dn}{n} = -RT^2 \left[\frac{\partial \ln f}{\partial T}\right]_\psi + h^\circ \qquad (5.51)$$

This equation seems to provide a shortcut to the integral quantities in Eqs. (5.48)–(5.50). Since the grand potential is itself an integral, differentiation at constant reduced grand potential $\psi$ is awkward. For analysis of experimental data, it is easier to apply Eqs. (5.44) and (5.45) to the adsorption isotherm and then integrate for $u$ and $s$.

5.10. **Clapeyron Equation.** Eq. (5.46) is the adsorption version of the Clapeyron equation. Let $\Delta v = v_g - v_s$ and let $\lambda = h_g^\circ - \overline{u}$. Assume that the molar volume of the adsorbed gas $v_s$ is negligible compared to $v_g$ so that $\Delta v = RT/P$ . With these perfect-gas approximations, Eq (5.46) becomes:

$$\left[\frac{\partial P}{\partial T}\right]_n = \frac{\lambda}{T\Delta v} \qquad (5.52)$$

so the slope of the "vapor pressure" curve for adsorption at constant loading may be compared to the Clapeyron equation:

$$\frac{dP}{dT} = \frac{L}{T\Delta v} \qquad (5.53)$$

for the slope of a coexistence curve of specific latent heat $L$ and specific volume change $\Delta v$. Eq. (5.52) shows the association of Eq. (5.44) to the Clapeyron equation but is not intended for calculations because of its approximations.
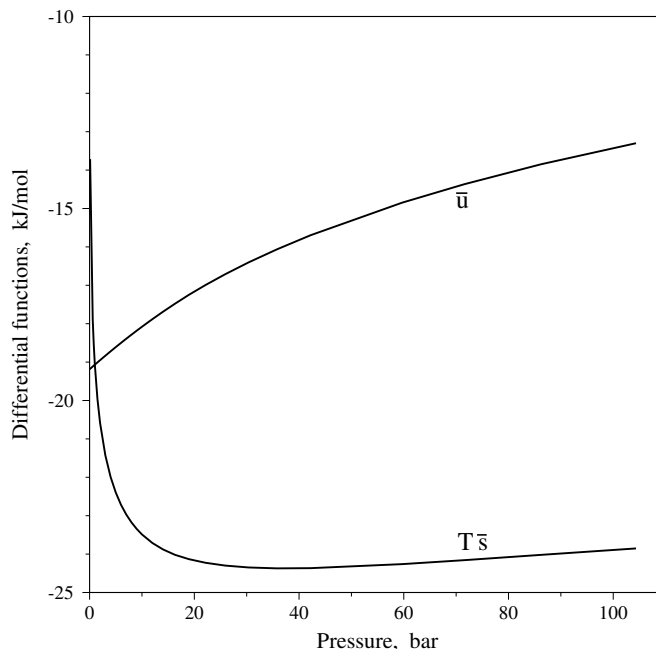
FIGURE 4. Absolute differential energy and differential entropy at 285 K for adsorption of $CH_4$ on 13X molecular sieve.

5.11. **Properties at High Pressure.** Eqs. (5.44) and (5.45) are valid up to high pressure of the order of 100 bar without making any approximations. An example is shown on Figure 4. Using the absolute isotherms in Figure 1, the differential energy ($\overline{u}$) was calculated from Eq. (5.44) and the differential entropy ($\overline{s}$) from Eq. (5.45). Fugacity was estimated from the Soave-Redlich-Kwong equation of state. The differential energy is relative to the enthalpy ($h^{\circ}$) in the perfect-gas state at 285 K. The differential entropy of the adsorbed gas, which is measured relative to the entropy in the perfect-gas state at 285 K, has a limit of infinity at zero pressure. The differential energy and differential entropy intersect at a pressure of 1 bar where the chemical potential of the gas is zero ($\mu = \overline{U} - T\overline{s}$). $T\overline{s}$ has a minimum of -24.4 kJ/mol, which at 285 K corresponds to an entropy of vaporization of 86 J/mol-K. A rule of thumb estimate for the entropy of vaporization of a liquid at its NBP is 88 J/mol-K (the Trouton constant). Even though the adsorbed methane gas is supercritical, its entropy of vaporization from a micropore at high pressure is comparable to the entropy of vaporization from its liquid state at 112 K.

## 6. IDEAL ADSORBED SOLUTIONS

At the time when the theory of ideal adsorbed solutions (IAS) was developed [13], the Gibbs excess formalism was the standard approach to adsorption, as it is today. The physical picture most commonly used in thinking about such systems was quasi two-dimensional adsorption at a planar surface rather than adsorption in a three-dimensional pore network. The standard state for the definition of an ideal adsorbed solution was taken to be the pure adsorbed components at the same spreading pressure (or solid-fluid interfacial tension) as the mixture.

The application of solution thermodynamics to adsorption in microporous materials leads to equations similar to those for vapor-liquid equilibria. Surface area and spreading pressure variables are eliminated. The proposed definition of an ideal solution for adsorption in

porous materials is:

$$\mu_i(T, \Omega, x) \equiv \mu_i^*(T, \Omega) + RT \ln x_i \tag{6.1}$$

for the chemical potential of the $i$th component. This is the simplest expression for the composition dependence of the chemical potential that is consistent with the known results in the Henry's law (low pressure or adsorbed ideal gas) limit. It is equivalent to the definition of an ideal solution in the bulk. We will show that all results for IAS follow from this.

The chemical potential of the pure gas in its standard state ($\mu_i^*$) is determined by temperature ($T$) and grand potential ($\Omega$). Alternatively, based on the reduced grand potential $\psi$ from Eq. (5.15) for the standard state:

$$\mu_i(T, \psi, x) = \mu_i^*(T, \psi) + RT \ln x_i \tag{6.2}$$

From Eq. (5.13):

$$d\Omega = -SdT - \sum n_i \, d\mu_i \tag{6.3}$$

From this we can write for the molar entropy:

$$s = -\sum x_i \left(\frac{\partial \mu_i}{\partial T}\right)_{\Omega, x} \tag{6.4}$$

and for IAS:

$$s^{id} = \sum x_i s_i^* - R \sum x_i \ln x_i \tag{6.5}$$

Eq. (5.20) is based on the Massieu formulation for the grand potential:

$$R \, d\psi = -U d\left(\frac{1}{T}\right) + \sum n_i d\left(\frac{\mu_i}{T}\right) \tag{6.6}$$

From this the molar energy is:

$$u = \sum x_i \left(\frac{\partial(\mu_i/T)}{\partial(1/T)}\right)_{\psi, x} \tag{6.7}$$

and for IAS:

$$u^{id} = \sum x_i u_i^* \tag{6.8}$$

The Helmholtz free energy for IAS is:

$$\mathrm{F}^{id} = u^{id} - Ts^{id} = \sum x_i \mathrm{F}_i^* + RT \sum x_i \ln x_i \tag{6.9}$$

with $\mathrm{F}_i^* = (u_i^* - Ts_i^*)$.

Finally the total amount adsorbed ($n$) is calculated from the Gibbs adsorption isotherm, Eq. (5.14):

$$-\sum n_i d\mu_i = d\Omega \tag{6.10}$$

or

$$-\sum x_i d\mu_i = \frac{1}{n} d\Omega \tag{6.11}$$

and

$$-\sum x_i \left(\frac{\partial \mu_i}{\partial \Omega}\right)_{T,x} = \frac{1}{n} \tag{6.12}$$

For an ideal solution and using the pure component version of Eq. (6.10):

$$-\sum x_i \left(\frac{\partial \mu_i}{\partial \Omega}\right)_{T,x} = \sum \frac{x_i}{n_i^*} \tag{6.13}$$

so that for IAS:

$$\boxed{\frac{1}{n} = \sum \frac{x_i}{n_i^*}} \tag{6.14}$$

Referring the chemical potential to its standard state $\mu_i^*$ instead of the perfect-gas reference state as in Eq. (5.1):

$$\mu_i = \mu_i^* + RT \ln \frac{f_i}{f_i^*} \tag{6.15}$$

Comparison of Eqs. (6.15) and (6.1) gives:

$$\boxed{f_i = f_i^* x_i} \tag{6.16}$$

Eqs. (6.16) and (6.14) are the working equations for an ideal adsorbed solution. In the special (and usual) case of a perfect gas, the fugacity in the bulk gas phase $f_i = Py_i$ and Eq. (6.16) becomes Raoult's law. $1/n$ is the mass of solid adsorbent required to adsorb one mole of the gas mixture of composition $x$. The reciprocal relationship in Eq. (6.14) is simply the requirement that, for an ideal solution, the mass of adsorbent needed to adsorb a mixture is the same mass required to adsorb the individual components separately in their standard states.

6.1. **Statement of the Adsorption Equilibrium Problem for Mixtures.** For a system of $N_c$ gases plus the solid adsorbent, there are $N_c + 1$ components, two phases (solid and gas) and $N_c + 1$ degrees of freedom according to the Gibbs phase rule. The system is therefore fully specified by the temperature and $N_c$ values of fugacity. These $N_c$ fugacities in the bulk gas phase are given by $f_i = Py_i\phi_i$, where the fugacity coefficient $\phi_i(P, y_i)$ is calculated from an equation of state for the gaseous mixture, e.g., Soave-Redlich-Kwong or Peng-Robinson, as discussed in section 5.2. The approximation $\phi_i = 1$ and $f_i = Py_i$ may be used for $P < 2$ bar.

6.2. **Simultaneous Solution of Equilibrium Equations.** We focus on a binary mixture of gases ($N_c = 2$) with specified variables $f_1$, $f_2$, and $T$. From Eq. (6.16), the phase equilibrium equations are:

$$f_1^*(\psi)\, x_1 = f_1 \tag{6.17}$$
$$f_2^*(\psi)\, x_2 = f_2 \tag{6.18}$$

The gas-phase fugacities ($f_1, f_2$) at temperature $T$ are the input variables. The mole fractions sum to unity:

$$x_1 + x_2 = 1 \tag{6.19}$$

Since $x_2 = (1 - x_1)$, there are two equations, (6.17) and (6.18), and two unknowns ($\psi$, $x_1$).

The simultaneous solution of these equations obviously requires the standard-state fugacity functions $f_i^*(\psi)$. If the adsorption isotherm is based upon fugacity (or pressure) for the independent variable, integration for $\psi$ yields the function $\psi(f_i^*)$, which must be inverted to solve the fugacity equations. The model isotherm in Appendix A has $n$ as independent variable so its integration yields $\psi(n_i^*)$, which is inverted to obtain $n_i^*(\psi)$ as described in Appendix C. The function required to solve the fugacity equations is then the composite function $f_i^*[n_i^*(\psi)]$. Solution of Eqs. (6.17) and (6.18) by Newton's method for $\psi$ and $x_1$ is described in Appendix B. For multicomponent mixtures beyond binary solutions, each additional component adds one additional composition unknown ($x_i$) and one additional fugacity equation.

Solution of the phase equilibrium equations for $\psi$ and the composition variables $x_i$ yields as a bonus the standard-state amounts adsorbed $n_i^*$. Eq. (6.14) gives the total amount adsorbed $n$ and the individual amounts adsorbed are:

$$n_i = n x_i \tag{6.20}$$

**Note.** Substitution of the fugacity equations into Eq. (6.19) for a binary mixture gives:

$$\frac{f_1}{f_1^*(\psi)} + \frac{f_2}{f_2^*(\psi)} = 1$$

which is a single equation in a single unknown ($\psi$). Numerical solution of this equation is problematic because of its high degree of nonlinearity. Attempting to solve for $\psi$ with this equation is not recommended. Simultaneous numerical solution of the fugacity equations is robust and less likely to stray outside the physical domain of $\psi > 0$ and $0 < x_i < 1$.

---

6.3. **Energy and Entropy Functions.** Expressions for the molar integral properties of an ideal adsorbed solution ($u^{id}$, $s^{id}$, $F^{id}$) have been given in terms of the corresponding properties of the components in their standard state.

For differential energy, the task is to relate $\overline{u}_i^{id}$ in the mixture to its value in the standard state ($\overline{u}_i^*$) It can be shown [26] that for an ideal solution:

$$\boxed{n_i^*(\overline{u}_i^{id} - u_i^*) = \frac{\sum x_j \mathcal{G}_j^* n_j^* (\overline{u}_j^* - u_j^*)}{\sum x_j \mathcal{G}_j^*}} \tag{6.21}$$

Specifically, the differential energy of component 1 in a mixture of components 1 and 2 is:

$$\overline{u}_1^{id} = u_1^* + \frac{1}{n_1^*}\left[\frac{x_1 \mathcal{G}_1^* n_1^* (\overline{u}_1^* - u_1^*) + x_2 \mathcal{G}_2^* n_2^* (\overline{u}_2^* - u_2^*)}{x_1 \mathcal{G}_1^* + x_2 \mathcal{G}_2^*}\right] \tag{6.22}$$

All of the quantities on the R.H.S. of Eq. (6.22) are evaluated in the standard state (same $T$ and $\psi$ as the mixture). $\overline{u}$ means differential energy and $u$ means integral energy. The standard-state quantity $\mathcal{G}_i^*$ is given by:

$$\mathcal{G}_i^* = \frac{1}{(n_i^*)^2}\left[\frac{\partial \ln n_i^*}{\partial \ln f_i^*}\right]_T \tag{6.23}$$

The derivative is the dimensionless slope of the adsorption isotherm of the $i$th component in its standard state, or $(\partial \ln n / \partial \ln P)_T$ for a perfect gas. Specifically, for Eq. (A.1), the reciprocal of the dimensionless slope is given by Eq. (A.15).

In the limit of pure adsorbate no. 1, its differential energy is the value for the standard state:

$$\lim_{x_1 \to 1} \overline{u}_1^{id} = u_1^* + (\overline{u}_1^* - u_1^*) = \overline{u}_1^* \tag{6.24}$$

as required. In the Henry's law region as $n \to 0$, the integral and differential energy functions in the mixture and in the standard state ($u_i$, $\overline{u}_i$, $u_i^*$, $\overline{u}_i^*$) are equal.

Having calculated the differential energy of adsorption ($\overline{u}_i^{id}$) by Eq. (6.21), the differential entropy is given by Eq. (5.42):

$$\overline{s}_i^{id} = \frac{\overline{u}_i^{id} - \mu_i}{T} \tag{6.25}$$

6.4. **Numerical Example for Ideal Adsorbed Solution.** This calculation uses Eq. (A.1) to fit the single-gas isotherms. Equations for standard-state properties based upon Eq. (A.1) are explicit in terms of loading ($n$). Eq. (A.12) provides the standard state $\psi(n)$ and its inverse function $n(\psi)$ generates composite functions $u[n(\psi)]$, $s[n(\psi)]$, $f[n(\psi)]$ etc. for calculating standard-state properties as functions of $\psi$. The use of Newton's method to invert the function $\psi(n)$ is covered in Appendix C.

For a binary solution, given the input variables ($T$, $f_1$, $f_2$), the phase equilibrium equations (6.17) and (6.18) are solved for $\psi$ and $x_1$. The numerical solution of the fugacity equations by Newton's method is given in Appendix B.
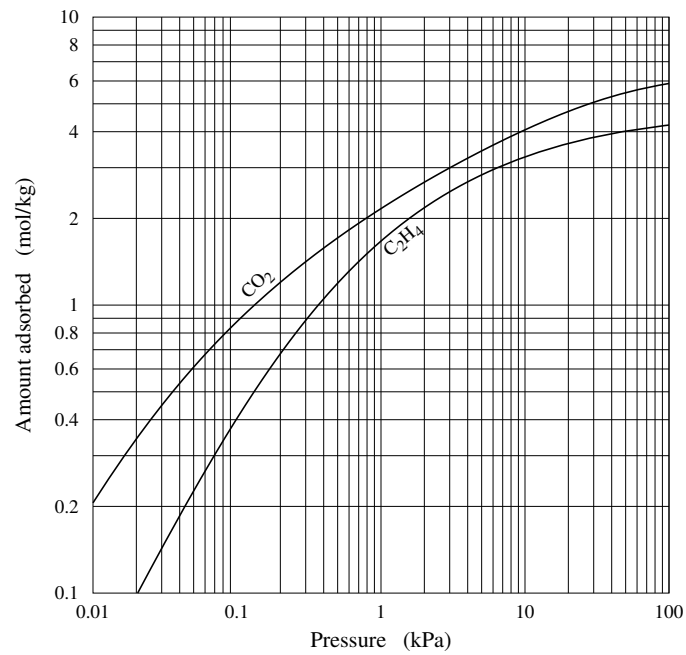
FIGURE 5. Single-gas adsorption isotherms of $CO_2$ and $C_2H_4$ on zeolite FAU at 293.15 K [26].
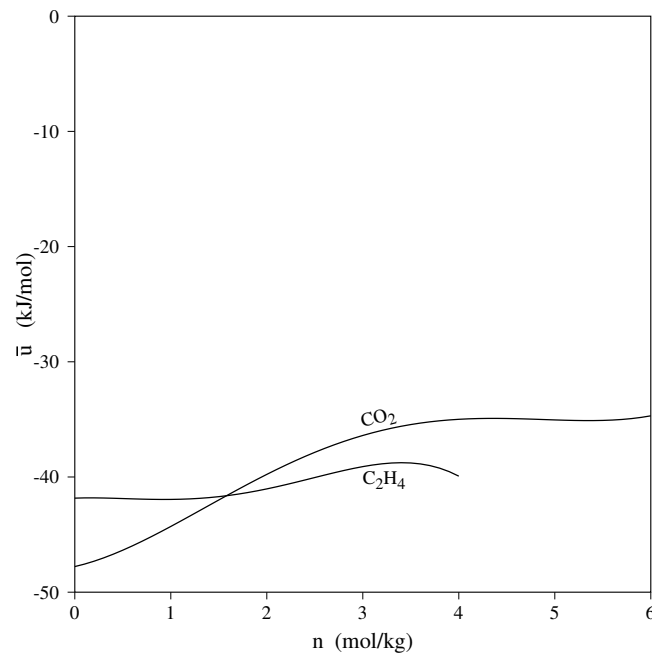


FIGURE 6. Differential energies ($\overline{u}$) of adsorption of $CO_2$ and $C_2H_4$ on zeolite FAU at 298.15 K [26].

The system chosen here is a binary mixture of $CO_2$ and $C_2H_4$ adsorbed on zeolite FAU. The experimental single-gas adsorption isotherms [26] are plotted on Fig. 5 and the differential energies obtained by calorimetry [26] are shown on Fig. 6. Constants of Eq. (A.1) for these plots are in Tables 4, 5 and 6.

Consider specifically the set of input variables $T = 293.15$ K, $f_1 = 50$ kPa, $f_2 = 50$ kPa. In this case, the temperature of the isotherm is chosen to be the reference temperature $T_\circ$ in Eq. (A.1). Based on the perfect gas law, $P = 100$ kPa and $y_1 = y_2 = 0.5$ but the input variables are the fugacities, not the pressure. Solution of equations (6.17) and (6.18) gives $x_1 = 0.7889$ and $\psi = 20.82$ mol/kg. The solution procedure based on Newton's method is described in Appendix B. Here, Eq. (A.1) for $f_i(n_i)$ and Eq. (A.12) for $\psi(n_i)$ are used. However, the function $\psi(n_i)$ for the standard states must be inverted to $n_i(\psi)$ as described in Appendix C.

Standard-state properties are given in Table 7 and the results for the mixture are listed in Table 8. The reference states for energy, entropy, and free energy are enthalpy $(h^\circ)$, entropy $(s^\circ)$, and chemical potential $(\mu^\circ)$, respectively, in the perfect-gas state at 293.15 K.

| No. | Gas | $K_\circ$, mol/(kg-kPa) | m, mol/kg | $T_\circ$, K |
|-----|-----|------|------|------|
| 1 | $CO_2$ | 27.253 | 6.4674 | 293.15 |
| 2 | $C_2H_4$ | 5.2039 | 4.5341 | 293.15 |

TABLE 4. Constants of Eq.(A.1) for zeolite FAU.

| No. | Gas | $C_1$ | $C_2$ | $C_3$ | $C_4$ |
|-----|-----|------|------|------|------|
| 1 | $CO_2$ | 1.2338 | -0.1241 | 0.0038 | 0.0 |
| 2 | $C_2H_4$ | 0.3850 | 0.0075 | 0.0012 | 0.0012 |

TABLE 5. Grand potential power series for zeolite FAU. For $n$ in units of mol/kg, the coefficients $C_i$ yield the dimensionless function $C(n)$ in Eq. (A.4).

| No. | Gas | $D_0$ | $D_1$ | $D_2$ | $D_3$ | $D_4$ |
|-----|-----|------|------|------|------|------|
| 1 | $CO_2$ | -47.776 | 1.8994 | 2.2273 | -0.7006 | 0.0562 |
| 2 | $C_2H_4$ | -41.836 | 0.3215 | -1.2203 | 0.9452 | -0.1576 |

TABLE 6. Differential energy power series for zeolite FAU. For $n$ in units of mol/kg, the coefficients $D_i$ yield the function D(n) in Eq. (A.5) in units of kJ/mol.

In Table 8, $T$, $f_1$ and $f_2$ are input variables. $\psi$ and $x_1$ are obtained by simultaneous solution of the fugacity equations. $x_2 = (1 - x_1)$. $n$, $n_1$ and $n_2$ are from Eqs. (6.14) and (6.20). The differential and integral energies and entropies are from Eqs. (A.5) – (A.8). $\mu_i = \overline{u}_i - T\overline{s}_i$ and $F = u - Ts$.

Eq. (5.21) provides an overall check of the mixture properties in Table 8:

$$F = \sum x_i \mu_i - RT\psi/n$$
$$= (0.5)(-1.69) + (0.5)(-1.69) - (0.0083145)(293.15)(20.82)/(5.301)$$
$$= -11.26 \text{ kJ/mol}$$

which agrees with $F = u - Ts$ from Table 8.

| No. | Gas | $n$ | $f$ | $\overline{u}$ | $T\overline{s}$ | $\mu$ | $u$ | $Ts$ | F |
|-----|-----|-----|-----|------|------|------|------|------|------|
| | | mol/kg | kPa | kJ/mol | kJ/mol | kJ/mol | kJ/mol | kJ/mol | kJ/mol |
| 1 | $CO_2$ | 5.624 | 63.38 | -35.05 | -33.94 | -1.112 | -38.86 | -28.73 | -10.13 |
| 2 | $C_2H_4$ | 4.364 | 236.8 | -42.28 | -44.38 | 2.102 | -40.67 | -31.15 | -9.52 |
| Equations | | | (A.1) | (A.5) | (A.7) | (5.1) | (A.6) | (A.8) | |

TABLE 7. Standard-state properties for zeolite FAU at 293.15 K and $\psi = 20.82$ mol/kg. The standard-state loadings ($n$) were obtained from the inversion of Eq. (A.12) and the other properties were obtained as explicit functions of loading using the equations listed. Note that $\mu = \overline{u} - T\overline{s}$ and F $= u - Ts$.

| Property | Value | | Property | Value |
|----------|-------|---|----------|-------|
| $T$ | 293.15 K | | $\mu_1$ | -1.69 kJ/mol |
| $\psi$ | 20.82 mol/kg | | $\mu_2$ | -1.69 kJ/mol |
| $f_1$ | 50.0 kPa | | $\overline{u}_1$ | -35.62 kJ/mol |
| $f_2$ | 50.0 kPa | | $\overline{u}_2$ | -36.49 kJ/mol |
| $x_1$ | 0.7889 | | $T\overline{s}_1$ | -33.93 kJ/mol |
| $x_2$ | 0.2111 | | $T\overline{s}_2$ | -34.80 kJ/mol |
| $n_1$ | 4.182 mol/kg | | $u$ | -39.24 kJ/mol |
| $n_2$ | 1.119 mol/kg | | $Ts$ | -27.98 kJ/mol |
| $n$ | 5.301 mol/kg | | F | -11.26 kJ/mol |

TABLE 8. Mixture point for ideal solution of $CO_2$ (1) and $C_2H_4$ (2) adsorbed in zeolite FAU.
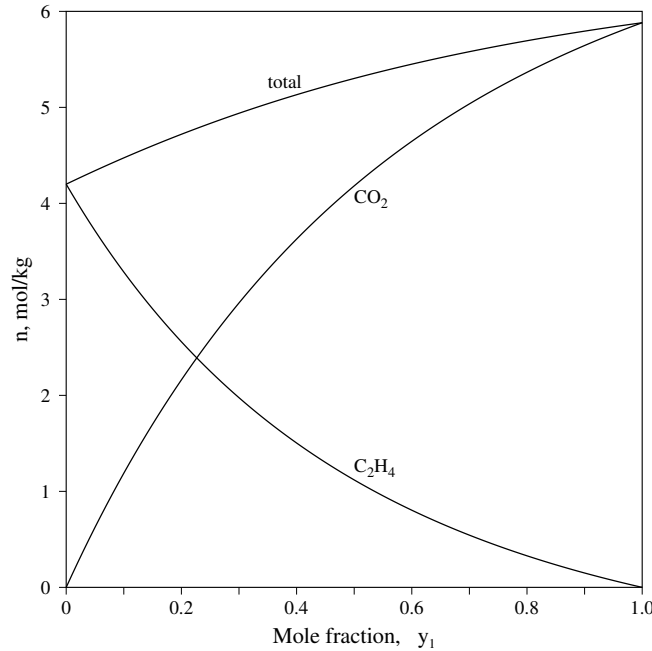


FIGURE 7. Individual adsorption isotherms predicted for ideal solution of mixtures of $CO_2$ (1) and $C_2H_4$ (2) on zeolite FAU at 293.15 K and 1 bar.
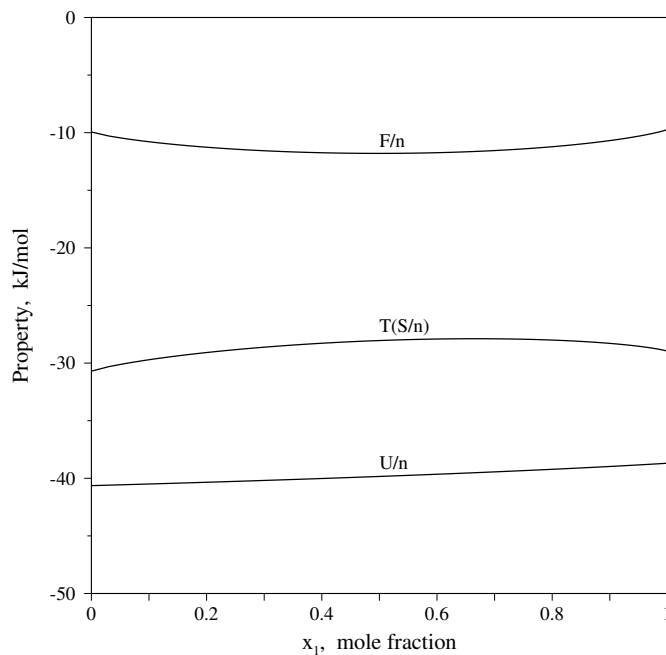
FIGURE 8. Energy, entropy, and Helmholtz free energy for ideal adsorption of $CO_2$ (1) and $C_2H_4$ (2) mixtures on zeolite FAU at 293.15 K and 1 bar.
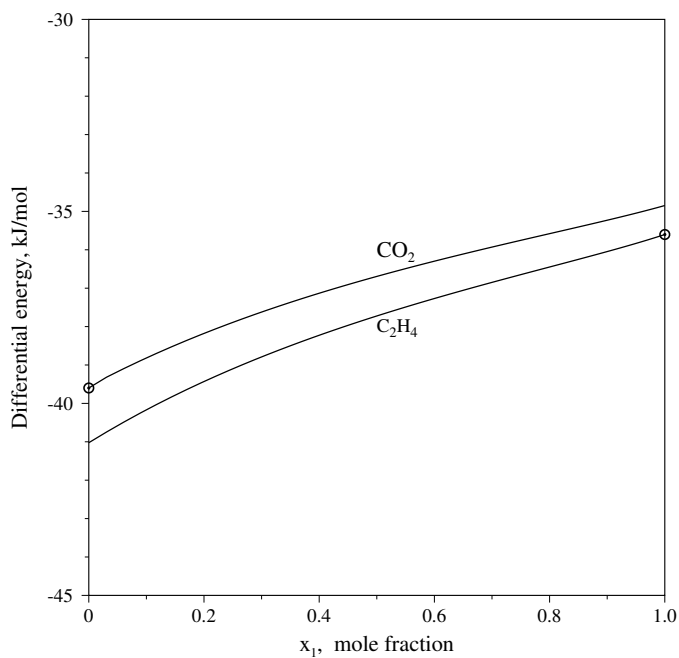


FIGURE 9. Differential energies of adsorption of $CO_2$ (1) and $C_2H_4$ (2) on zeolite FAU at 293.15 K and 1 bar predicted for an ideal solution. The points labeled $\odot$ are values at infinite dilution.

The calculation in Table 8 is for the point at $T = 293.15$ K, $P = 1$ bar, and $y_1 = 0.5$. Fig. 7 shows an isobar ($P = 1$ bar) for individual and total amounts adsorbed at 293.15 K. Fig. 8 is a plot of the isobaric energy and entropy properties for the same conditions, 293.15 K and 1 bar.

Fig. 9 shows the isobaric differential energies ("heats") relative to $h°$ at 293.15 K and 1 bar calculated from Eq. (6.22). The points identified by $\odot$ are "infinite dilution heats", which could be measured with a calorimeter after pre-loading the other component to its equilibrium value.

## 7. Excess Mixing Functions

*Excess* in this section refers to the difference between a thermodynamic variable (e.g. energy) for a real solution and the same variable for an ideal solution. This kind of excess function for mixtures is completely unrelated to the Gibbs *excess* of adsorption in Chapter 4.

Experiments [26] and simulations [1] show that most adsorbed mixtures show negative deviations from ideality, which means that adsorbed-phase activity coefficients are less than unity. The cause of this behavior is understood [15] but it is still not possible to predict the magnitude of the deviations, although attempts have been made [18]. Here, procedures are described for using experimental data to calculate thermodynamic properties by accounting for the effects of temperature, loading, and composition on activity coefficients.

Most binary liquid mixtures show positive deviations from ideality, which means that activity coefficients are greater than unity and the free energy of the solution is *greater* (more positive) than for an ideal solution. For sufficiently large and positive values of activity coefficients, the homogeneous solution becomes thermodynamically unstable and splits into two immiscible liquid phases. Other binary liquid mixtures exhibit negative deviations from ideality when mixture pairs form weak bonds such as hydrogen bonds; a classic example is chloroform and acetone.

For adsorption, one might expect a correlation between activity coefficients of adsorbed and liquid solutions. As it turns out, there is no correlation because the binary adsorbate interactions are overwhelmed by the stronger energy of their interactions with the solid. For adsorption in micropores, activity coefficients are either unity (ideal solution) or *negative* deviations from ideality.

The explanation for negative deviations from ideality (activity coefficients less than unity) for adsorbed mixtures is the segregation of components into different regions of the pore space where the local composition differs from the overall composition. Imagine an extreme case in which the adsorbent is a mixture of two different microporous materials. Suppose that each adsorbent (by itself) forms an ideal adsorbed solution but with different compositions, for example $x_1 = 0.2$ on one adsorbent and $x_1 = 0.4$ on the other adsorbent. If this heterogeneous mixture of adsorbents is treated (incorrectly) as a single adsorbent with a single (averaged) adsorbed-phase composition, then the composite system will *appear* to generate large negative deviations from ideality. It can be shown [1] that segregation into regions of different composition (e.g., in different micropores) always generates negative deviations from ideality if the mixture is falsely assumed to be homogeneous.

7.1. **Activity Coefficients.** Following the practice for vapor-liquid equilibria, activity coefficients ($\gamma_i$) for adsorption in porous materials are defined by

$$\mu_i(T, \Omega, x) \equiv \mu_i^*(T, \Omega) + RT \ln x_i + RT \ln \gamma_i \tag{7.1}$$

for the chemical potential. Expressions for all excess mixing functions follow from Eq. (7.1), which reduces to Eq. (6.1) for an ideal solution ($\gamma_i = 1$).

The chemical potential of the pure adsorbate in its standard state ($\mu_i^*$) is determined by temperature ($T$) and grand potential ($\Omega$). Alternatively, based on the reduced grand potential $\psi$ from Eq. (5.15) for the standard state:

$$\mu_i(T, \psi, x) \equiv \mu_i^*(T, \psi) + RT \ln x_i + RT \ln \gamma_i \tag{7.2}$$

In terms of fugacity, Eqs. (7.1) and (7.2) are written:

$$\mu_i = \mu_i^* + RT \ln \frac{f_i}{f_i^*} \tag{7.3}$$

or

$$f_i = f_i^* \gamma_i\, x_i \tag{7.4}$$

$f_i$ is the fugacity in the bulk gas phase and $f_i^*$ is the fugacity of the gas in the solid phase at the standard state.

An excess Helmholtz free energy function for the mixture is defined by:

$$\boxed{\mathrm{F}_\gamma^E \equiv RT \sum x_i \ln \gamma_i} \tag{7.5}$$

and an *excess mass* $m^E$ is defined by:

$$\boxed{m^E \equiv \frac{1}{n} - \sum \frac{x_i}{n_i^*}} \tag{7.6}$$

The name *excess mass* is appropriate because reciprocal loading ($1/n$) has units of kg/mol. The pore volume of an adsorbent is directly proportional to its mass, so Eq. (7.6) is the adsorption equivalent of $v^E = v - \sum x_i v_i^*$ for the excess volume of a liquid mixture.

The terminology and notation for excess functions like $m^E$ and $F^E$ is copied from excess functions for liquid mixtures and has no relation to excess adsorption notation such as $n_e$ for the Gibbs surface excess discussed in Section 4. Here, excess notation refers to the difference between the actual mixture and an ideal solution. For example, the excess energy is defined by

$$\boxed{u^E = u(\text{actual adsorbed mixture at } \{T, \psi, x\}) - u(\text{ideal solution at same } \{T, \psi, x\})} \tag{7.7}$$

Similar definitions hold for excess entropy $s^E$, excess Helmholtz free energy $\mathrm{F}^E$, and excess mass $m^E$.

As will be shown, the excess Helmholtz free energy function in Eq. (7.5) contains complete thermodynamic information about the mixture, not only activity coefficients but also excess mass, energy, entropy, etc. The natural independent variables of this "master" function are temperature ($T$), composition ($x$), and either grand potential ($\Gamma$) or reduced grand potential ($\psi$).

The integral entropy of the mixture is obtained from Eq. (6.4):

$$s = - \sum x_i \left( \frac{\partial \mu_i}{\partial T} \right)_{\Omega, x} \tag{7.8}$$

Using Eqs. (5.13), (7.1), and (7.5):

$$s = \sum x_i s_i^* - R \sum x_i \ln x_i - \left( \frac{\partial \mathrm{F}_\gamma^E}{\partial T} \right)_{\Omega, x} \tag{7.9}$$

Substituting Eq. (6.5), the excess entropy is:

$$\boxed{s^E = s - s^{id} = - \left( \frac{\partial \mathrm{F}_\gamma^E}{\partial T} \right)_{\Omega, x}} \tag{7.10}$$

The integral energy of the mixtures is obtained from Eq. (6.7):

$$u = \sum x_i \left( \frac{\partial(\mu_i/T)}{\partial(1/T)} \right)_{\psi,x} \tag{7.11}$$

Using Eqs. (5.20), (7.2), and (7.5):

$$u = \sum x_i u_i^* + \left( \frac{\partial(\mathrm{F}_\gamma^E/T)}{\partial(1/T)} \right)_{\psi,x} \tag{7.12}$$

Substituting Eq. (6.8), the excess energy is:

$$\boxed{u^E = u - u^{id} = \left( \frac{\partial(\mathrm{F}_\gamma^E/T)}{\partial(1/T)} \right)_{\psi,x}} \tag{7.13}$$

Recalling that $\Gamma = -RT\psi$, it is noteworthy that entropy is obtained by differentiation with respect to $T$ at constant $\Omega$, but energy is obtained by differentiation with respect to $T$ at constant $\psi$. We have

$$\mathrm{F}^E = u^E - Ts^E \tag{7.14}$$

but $\mathrm{F}^E \neq \mathrm{F}_\gamma^E$. The function $\mathrm{F}_\gamma^E$ is merely the definition in Eq. (7.5). The direct determination of $\mathrm{F}^E$ is from Eq. (5.21):

$$F = \sum n_i \mu_i + \Omega \tag{7.15}$$

for which the single component version is:

$$F_i^* = n_i^* \mu_i^* + \Omega \tag{7.16}$$

where the superscript $^*$ refers to a single adsorbate in its standard state at the same value of $T$ and $\Omega$ as the mixture. Inserting the chemical potential from Eq. (7.1) into (7.15) and using (7.16):

$$\mathrm{F} = \sum x_i \mathrm{F}_i^* + RT \sum x_i \ln x_i + RT \sum x_i \ln \gamma_i + \Omega \left[ \frac{1}{n} - \sum_i \frac{x_i}{n_i^*} \right] \tag{7.17}$$

where $\mathrm{F} \equiv F/n$ and $\mathrm{F}_i^* = F_i^*/n_i^*$. Using Eq. (6.9) and the definitions from Eqs. (7.5) and (7.6):

$$\boxed{F^E = F_\gamma^E + \Omega\, m^E} \tag{7.18}$$

where

$$F^E = F - F^{id} \tag{7.19}$$

An expression for the excess mass $(m^E)$ is derived from the Gibbs adsorption isotherm, Eq. (5.14).

$$d\Omega = -\sum n_i d\mu_i \tag{7.20}$$

and for single components in their standard states:

$$d\Omega = -n_i^* d\mu_i^* \tag{7.21}$$

The remainder of the derivation is at constant $T$ and $x$. From Eq. (7.1):

$$d\mu_i = d\mu_i^* + RT d\ln \gamma_i \tag{7.22}$$

From Eq. (7.5):

$$d\mathrm{F}_\gamma^E = RT \sum x_i d\ln \gamma_i \tag{7.23}$$

Combination of the last four equations at constant $T$ and $x$ gives:

$$d\text{F}_\gamma^E = - \left[ \frac{1}{n} - \sum \frac{x_i}{n_i^*} \right] d\Omega \tag{7.24}$$

which may be written using Eq. (7.6):

$$m^E = - \left[ \frac{\partial \text{F}_\gamma^E}{\partial \Omega} \right]_{T,x} \tag{7.25}$$

Alternatively in terms of $\psi = -\Omega/RT$:

$$m^E = \left[ \frac{\partial \text{F}_\gamma^E / RT}{\partial \psi} \right]_{T,x} \tag{7.26}$$

We have seen that excess functions $(u^E, s^E, \text{F}^E, m^E)$ are calculable from Eq. (7.5) by differentiation. It can be shown from Eq. (5.13) that activity coefficients are related to the $\text{F}_\gamma^E$ function by:

$$RT \ln \gamma_i = \left[ \frac{\partial \, n\text{F}_\gamma^E}{\partial n_i} \right]_{T,\psi,n_j} \tag{7.27}$$

## 7.2. Adsorption Analog of Gibbs-Helmholtz Equation.
The Gibbs-Helmholtz equation for excess mixing functions of liquid mixtures is:

$$H^E = \left[ \frac{\partial (G^E / T)}{\partial (1/T)} \right]_{P,x} \tag{7.28}$$

The adsorption equivalent for a binary mixture is:

$$U^E = \left[ \frac{\partial (F^E / T)}{\partial (1/T)} \right]_{n_1,n_2} \tag{7.29}$$

which is derived from Eqs. (5.4) and (5.10).

Holding the absolute adsorption of each component of a mixture fixed while varying the temperature, either experimentally or theoretically, is awkward. For adsorption, $F^E = U^E - TS^E$ but the independent variables for activity coefficients are $\{\psi, x, T\}$, not $\{n_1, n_2, T\}$.

## 7.3. Model for Activity Coefficients and Excess Functions.
In order to proceed, a model for activity coefficients and excess functions is needed. The excess functions are all zero for ideal solutions. For nonideal solutions, the simplest equation for activity coefficients [26] which has the proper limits and takes into account the set of independent variables $\{T, \psi, x\}$ is:

$$\text{F}_\gamma^E = (A + BT)x_1 x_2 [1 - e^{-C\psi}] \tag{7.30}$$

There are three constants $\{A, B, C\}$ for a binary mixture of gases. At the limit of low loading, $\psi \to 0$ and $\text{F}_\gamma^E \to 0$. This limit enforces ideal solution behavior in the Henry's law region. The absolute values of the excess functions reach a maximum as $\psi \to \infty$. The quadratic composition dependence satisfies the boundary condition that $\text{F}_\gamma^E \to 0$ for the pure adsorbates. More complex asymmetrical behavior can be introduced into $\text{F}^E$ at the expense of additional constants. The linearity of the excess free energy with temperature predicts a temperature-independent energy of adsorption, which is the usual approximation for adsorption over a limited range of temperature.

From Eq. (7.27) for activity coefficients:

$$\ln \gamma_1 = \frac{(A + BT)}{RT}(1 - e^{-C\psi})x_2^2 \tag{7.31}$$

$$\ln \gamma_2 = \frac{(A + BT)}{RT}(1 - e^{-C\psi})x_1^2 \tag{7.32}$$

The excess mass from Eq. (7.26) is:

$$m^E = \frac{C(A + BT)}{RT}x_1 x_2 e^{-C\psi} \tag{7.33}$$

The value of the excess mass at the limit of zero loading ($\psi \to 0$) has the form ($\infty - \infty$) as shown by Eq. (7.6). Although the limiting value of $m^E$ from Eq. (7.33) is finite, Eq. (7.6) reduces to Eq. (6.14) as $\psi \to 0$, as required for an ideal solution. From Eqs. (7.13), (7.10) and (7.18)

$$u^E = u - u^{id} = Ax_1 x_2[1 - e^{-C\psi}] \tag{7.34}$$

$$s^E = s - s^{id} = -Bx_1 x_2[1 - e^{-C\psi}] + \frac{C(A + BT)}{T}x_1 x_2 \psi e^{-C\psi} \tag{7.35}$$

$$\mathrm{F}^E = \mathrm{F} - \mathrm{F}^{id} = (A + BT)x_1 x_2[1 - (1 + C\psi)e^{-C\psi}] \tag{7.36}$$

Differential properties for nonideal mixtures depend upon temperature coefficients of the activity coefficients. It can be shown [26] that the differential energy for a binary mixture is:

$$\overline{u}_i = (u_i^* + d_{Ai}) + \left[\frac{1}{n_i^*} + d_{Bi}\right]\left[\frac{\left[\sum x_j \mathcal{G}_j^* n_j^*(\overline{u}_j^* - u_j^*)\right] + d_C}{\left[\sum x_j \mathcal{G}_j^*\right] + d_D}\right] \tag{7.37}$$

where

$$d_{Ai} = RT^2\left[\frac{\partial \ln \gamma_i}{\partial T}\right]_{\psi,x} \qquad d_{Bi} = \left[\frac{\partial \ln \gamma_i}{\partial \psi}\right]_{T,x}$$

$$d_C = RT^2\left[\frac{\partial m^E}{\partial T}\right]_{\psi,x} \qquad d_D = -\left[\frac{\partial m^E}{\partial \psi}\right]_{T,x}$$

$\mathcal{G}_i^*$ is defined by Eq. (6.23). The set of derivatives $\{d_A, d_B, d_C, d_D\}$ vanishes for an ideal solution. For a single component, the limit from Eq. (7.37) is

$$\lim_{x_1 \to 1} \overline{u}_1 = \overline{u}_1^*$$

which means that in the limit of single-component adsorption, the differential energy of the $i$th component of a mixture is equal to its differential energy in the standard state, as required.

In terms of the model from Eqs. (7.31), (7.32), and (7.33):

$$RT^2\left[\frac{\partial \ln \gamma_1}{\partial T}\right]_{\psi,x} = -A(1 - e^{-C\psi})x_2^2$$

$$RT^2\left[\frac{\partial \ln \gamma_2}{\partial T}\right]_{\psi,x} = -A(1 - e^{-C\psi})x_1^2$$

$$\left[\frac{\partial \ln \gamma_1}{\partial \psi}\right]_{T,x} = \frac{(A + BT)}{RT}Ce^{-C\psi}x_2^2$$

$$\left[\frac{\partial \ln \gamma_2}{\partial \psi}\right]_{T,x} = \frac{(A + BT)}{RT}Ce^{-C\psi}x_1^2$$

$$RT^2 \left[ \frac{\partial m^E}{\partial T} \right]_{\psi,x} = -ACe^{-C\psi} x_1 x_2$$

$$\left[ \frac{\partial m^E}{\partial \psi} \right]_{T,x} = -\frac{(A+BT)}{RT} C^2 e^{-C\psi} x_1 x_2$$

Note the minus signs so that $d_D = \frac{(A+BT)}{RT} C^2 e^{-C\psi} x_1 x_2$.

7.4. **Extraction of Constants from Experimental Data.** Consider a set of $N$ experimental points for a binary mixture. For each point, the input variables are temperature and fugacities $(T, f_1, f_2)$ and the measured variables are the loadings $(n_1, n_2)$. *Activity coefficients must be calculated indirectly.* From Eq. (7.4), the activity coefficient $\gamma_i = f_i/(f_i^* x_i)$ but the standard-state fugacity $(f_i^*)$ is unknown because $\psi$ is unknown. The extraction of the constants $\{A,B,C\}$ is a three-parameter optimization problem for which the objective function is the summation of error in loadings for the $N$ data points.

The constants derived from experimental data will not fit the experimental data exactly for two reasons. First, the actual behavior of the mixture may be more complex than the three-constant model described here. Second, the experimental data may be thermodynamically inconsistent and thus incapable of being fit.

7.5. **Solution Procedure.** Given the constants for Eq. (7.30), the calculation is similar to that for an ideal solution. The condition for equilibrium is equality of chemical potentials of the gases in the solid and gas phases, which is equivalent to equality of fugacities in both phases. For a binary mixture of gases $(N_c = 2)$ the specified variables are $f_1$, $f_2$, and $T$. Using Eq. (7.4) for the solid phase, the conditions for equilibrium are:

$$f_1^*(\psi)\gamma_1(\psi, x_1)x_1 = f_1 \tag{7.38}$$
$$f_2^*(\psi)\gamma_2(\psi, x_2)x_2 = f_2 \tag{7.39}$$

The gas-phase fugacities $(f_1, f_2)$ at temperature $T$ are the input variables. The mole fractions sum to unity:

$$x_1 + x_2 = 1 \tag{7.40}$$

Since $x_2 = (1 - x_1)$, there are two equations, (7.38) and (7.39), and two unknowns $(\psi, x_1)$. Solution of the fugacity equations (7.38) and (7.39) by Newton's method for $\psi$ and $x_1$ is described in Appendix B. The total amount adsorbed from Eq. (7.6) is:

$$\frac{1}{n} = \sum_i \frac{x_i}{n_i^*} + m^E \tag{7.41}$$

with $m^E$ from Eq. (7.33). Individual amounts adsorbed are:

$$n_1 = nx_1 \tag{7.42}$$
$$n_2 = nx_2 \tag{7.43}$$

Eqs. (7.34) and (7.35) give the molar integral functions $u$ and $s$ in terms of the corresponding excess functions $u^E$ and $s^E$ and the expressions for ideal solutions, Eqs. (6.8) and (6.5). The differential energies $\bar{u}_i$ are calculated from Eq. (7.37). Finally, the differential entropy follows from the differential energy according to Eq. (6.25).

| No. | Gas | $n$ | $f$ | $\overline{u}$ | $T\overline{s}$ | $\mu$ | $u$ | $Ts$ | F |
|---|---|---|---|---|---|---|---|---|---|
|  |  | mol/kg | kPa | kJ/mol | kJ/mol | kJ/mol | kJ/mol | kJ/mol | kJ/mol |
| 1 | $CO_2$ | 5.670 | 68.11 | -35.02 | -34.09 | -0.936 | -38.83 | -28.77 | -10.06 |
| 2 | $C_2H_4$ | 4.377 | 259.9 | -42.39 | -44.72 | 2.328 | -40.68 | -31.19 | -9.49 |
| Equations |  |  | (A.1) | (A.5) | (A.7) | (5.1) | (A.6) | (A.8) |  |

TABLE 9. Standard-state properties for zeolite FAU at $T = 293.15$ K and $\psi = 21.23$ mol/kg. The standard-state loadings $n$ were obtained from Eq. (A.12) inverted as described in Appendix C.

| Property | Value | Property | Value |
|---|---|---|---|
| $T$ | 293.15 K | $n$ | 5.362 mol/kg |
| $\psi$ | 21.23 mol/kg | $\mu_1$ | -1.69 kJ/mol |
| $f_1$ | 50.0 kPa | $\mu_2$ | -1.69 kJ/mol |
| $f_2$ | 50.0 kPa | $\overline{u}_1$ | -34.27 kJ/mol |
| $\gamma_1$ | 0.9740 | $\overline{u}_2$ | -33.45 kJ/mol |
| $\gamma_2$ | 0.7812 | $T\overline{s}_1$ | -32.58 kJ/mol |
| $x_1$ | 0.7537 | $T\overline{s}_2$ | -31.76 kJ/mol |
| $x_2$ | 0.2463 | $u$ | -39.86 kJ/mol |
| $n_1$ | 4.042 mol/kg | $Ts$ | -28.52 kJ/mol |
| $n_2$ | 1.320 mol/kg | F | -11.34 kJ/mol |

TABLE 10. Mixture point for $CO_2$ (1) and $C_2H_4$ (2) adsorbed in zeolite FAU.

7.6. **Numerical Example.** Consider a binary mixture of $CO_2$ and $C_2H_4$ adsorbed on zeolite FAU, the same system used in the calculation for an ideal solution in Section 6. The constants of Eq. (A.1) for the single-gas isotherms are tabulated in Tables 4 – 6. For the mixture, the constants determined experimentally [26] for Eq. (7.30) are: $A = -6.5$ kJ/mol, $B = 0.0145$ kJ/mol-K, $C = 0.030$ kg/mol.

The numerical calculation is reproduced for the input variables $T = 293.15$ K and $f_1 = f_2 = 50$ kPa. Based upon the perfect-gas law, $P = 100$ kPa and $y_1 = y_2 = 0.5.$, but the input variables are the fugacities, not the pressure. Solution of the fugacity equations (7.38) and (7.39) by Newton's method as described in Appendix B gives $x_1 = 0.7537$ and $\psi = 21.23$ mol/kg. The standard-state properties for this value of $\psi$ are given in Table 9.

The mixture point calculation summarized in Table 10 is based on standard state properties in Table 9. Input variables are $T$, $f_1$ and $f_2$. $\psi$ and $x_1$ are obtained by simultaneous solution of the fugacity equations (7.38) and (7.39). $x_2 = (1 - x_1)$. $n$, $n_1$ and $n_2$ are from Eqs. (7.41) – (7.43). Activity coefficients $\gamma_i$ are from Eqs. (7.31) and (7.32). Integral properties $u$ and $s$ are from Eqs. (7.34) and (7.35). Differential energies $\overline{u}_i$ are from Eq. (7.37) and differential entropies $\overline{s}_i$ from Eq. (6.25). Note that $\mu_i = \overline{u}_i - T\overline{s}_i$ and $F = u - Ts$.

Eq. (5.21) provides an overall check of the calculations in Table 10:

$$\text{F} = \sum x_i \mu_i + \Gamma/n = \sum x_i \mu_i - RT\psi/n$$

$$= 0.5(-1.69) + 0.5(-1.69) - (8.3145 \cdot 10^{-3})(293.15)(21.23)/5.362 = -11.34 \text{ kJ/mol}$$

which agrees with the value for $F = u - Ts$ in Table 10.

This example is for the point at $T = 293.15$ K, $P = 1$ bar and $y_1 = 0.5$. Fig. 10 shows individual and total amounts for an isobar ($P = 1$ bar). The solid lines are from experimental data as fit by Eq. (7.30) and the dashed lines are the prediction for an ideal solution from Fig. 7.

The differential energies ("heats") are plotted on Fig. 11. Comparison with the values predicted for an ideal solution on Fig. 9 show that the differential properties are sensitive to deviations from Raoult's law. The experimental values at infinite dilution identified by an $\odot$ on Figs. 9 and 11 are about 8 percent lower (absolute values) than the values predicted for an ideal solution (Table 11). The dominant coefficient $D_{Ai}$ in Eq. (7.37) is always positive in sign so that experimental differential heats should generally be less negative (smaller in absolute value) than IAS predictions, as is the case for this mixture.

|        | $CO_2$  | $C_2H_4$ |
|--------|---------|----------|
| IAS    | -39.56  | -35.60   |
| exper. | -36.92  | -32.63   |

TABLE 11. Differential energy at infinite dilution for mixtures of $CO_2$ and $C_2H_4$ adsorbed on zeolite FAU.
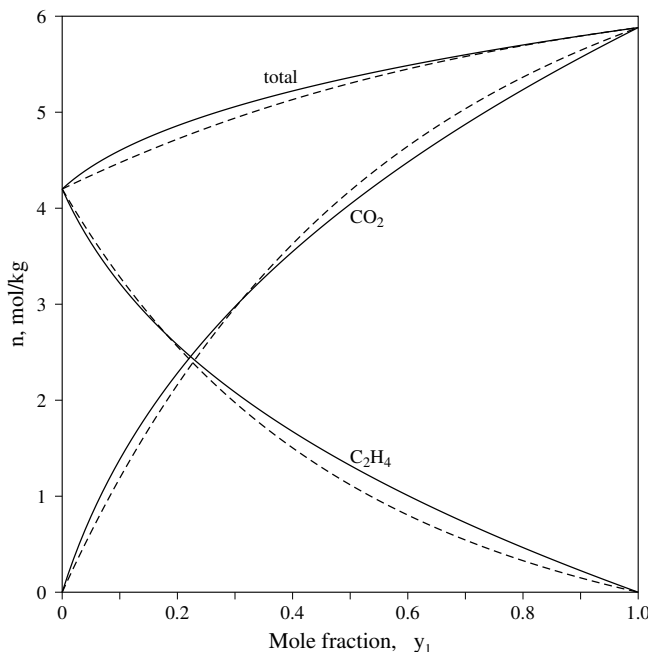


FIGURE 10. Adsorption of $CO_2$ and $C_2H_4$ on zeolite FAU at 293.15 K and 1 bar. Solid lines: from experimental data fit by Eqs. (7.31) and (7.32). Dashed lines: prediction for ideal adsorbed solution.

The integral properties are insensitive to deviations from ideal solution behavior. The experimental integral properties ($u$,$s$,$_F$) for a non-ideal mixture are nearly indistinguishable from the ideal values plotted on Fig. 8. Table 12 compares integral properties for the experimental data with those for an ideal solution. Note that the experimental standard state for $\psi$ differs slightly from the standard state for an ideal adsorbed solution in Table 8. Having specified the independent variables $\{f_1, f_2, T\}$, the standard state ($\psi$) for the point depends upon the nonideality of the mixture. Excess functions for a nonideal mixture are defined by Eq. (7.7), or $\psi = 21.23$ kJ/mol for this particular point.
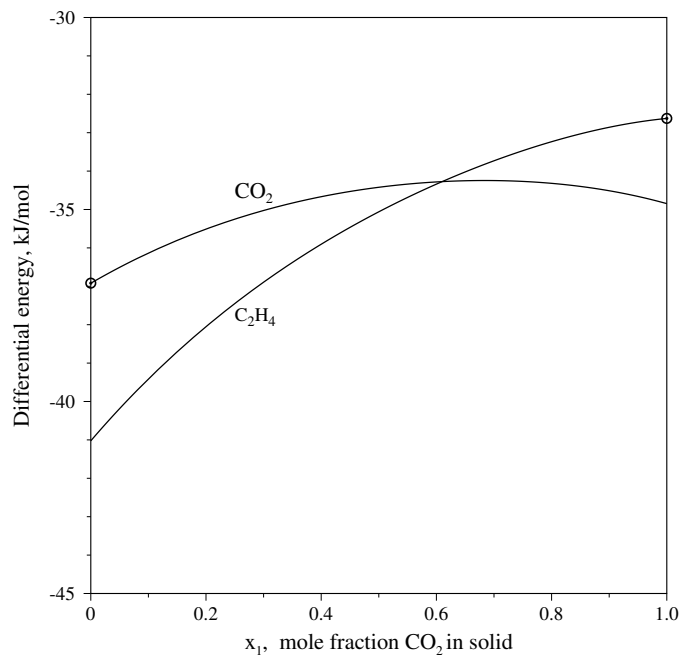
FIGURE 11. Differential energy of adsorption of $CO_2$ and $C_2H_4$ on zeolite FAU at 293.15 K and 1 bar from calorimetric data. Compare with Fig. 9 for ideal solution. The points labeled $\odot$ are values at infinite dilution.
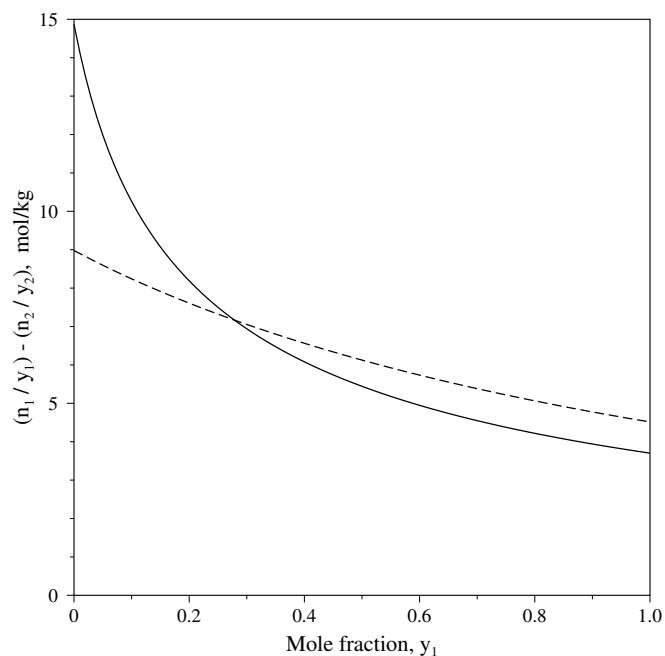


FIGURE 12. Integration of Gibbs adsorption isotherm for binary mixture of $CO_2$ (1) and $C_2H_4$ (2) at 1 bar and 293.15 K. Dashed line is for ideal solution and solid line is for experimental data. The integral for both curves is $\Delta\psi = 6.325$ mol/kg.
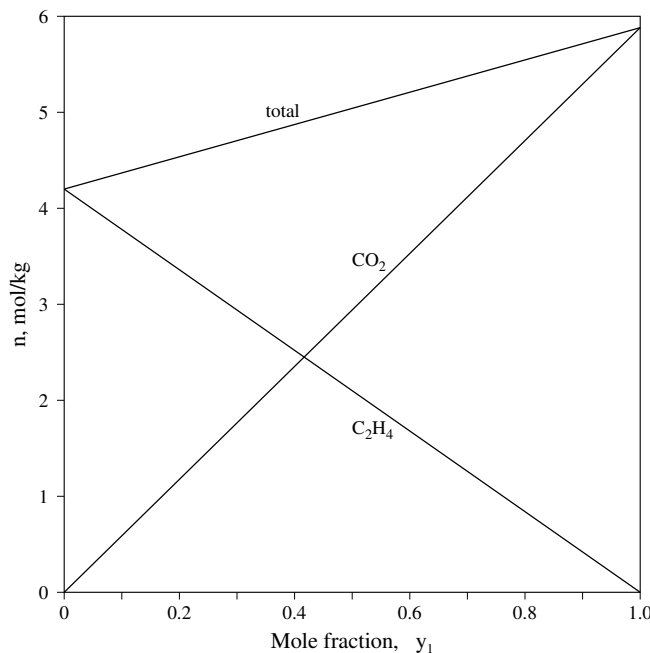
FIGURE 13. Hypothetical (and incorrect) linear adsorption isotherms for $CO_2$ and $C_2H_4$ on zeolite FAU at 293.15 K and 1 bar. These individual isotherms violate the Gibbs adsorption isotherm.

| | $u$ | $Ts$ | F | $\psi$ (mol/kg) |
|---|---|---|---|---|
| exper. | -39.86 | -28.52 | -11.34 | 21.23 |
| ideal | -39.24 | -27.98 | -11.26 | 20.82 |
| excess | -0.568 | -0.512 | -0.056 | 21.23 |

TABLE 12. Integral properties (kJ/mol) for $CO_2$ (1) and $C_2H_4$ (2) in zeolite FAU for point $f_1 = f_2 = 50$ kPa, $T = 293.15$ K.

The isobar shown on Fig. 10 must satisfy the Gibbs adsorption isotherm Eq. (5.16) integrated from $y_1 = 0$ to $y_1 = 1$. Assuming a perfect gas so that $f_1 = Py_1$ and $f_2 = Py_2$:

$$\Delta\psi = \psi_1 - \psi_2 = \int_{y_1=0}^{1} \left[ \frac{n_1}{y_1} - \frac{n_2}{y_2} \right] dy_1 \tag{7.44}$$

For the single gas isotherms at 1 bar, $\psi_1 = 23.450$, $\psi_2 = 17.125$, and $\Delta\psi = 6.325$ mol/kg. The integrands for Eq. (7.44) are plotted on Fig. 12. Both integrals are 6.325 mol/kg so both the ideal solution and the experimental data satisfy the consistency test.

Obviously adsorption data can be both thermodynamically consistent and incorrect. The consistency test is most useful when it fails. For example, Figure 13 shows linear individual isotherms for a hypothetical isobar at 1 bar and 293.15 K. (Individual isotherms are linear at low pressure). The pure component loadings agree with experiment for the $CO_2$–$C_2H_4$ mixture but the integral of Eq. (7.44) is $\Delta\psi = 1.68$ mol/kg compared to the value of 6.325 mol/kg obtained from the single-gas adsorption isotherms. Thus the linear individual isotherms at 1 bar plotted on Figure 13 are thermodynamically inconsistent and erroneous.

## 8. Adsorption from Liquid Mixtures

Immersion of a microporous material in a pure liquid causes pore filling but the amount of liquid in the pores at equilibrium is difficult to measure. However the *heat of immersion* or integral energy change associated with immersion of a solid in a liquid can be measured with a calorimeter.

Consider equilibrium between a microporous solid material and a binary liquid mixture. Contact of clean adsorbent with a binary liquid mixture generates a change in the composition of the liquid $(\Delta x_1)$ from its initial value $x_1^\circ$ to the equilibrium value $(x_1^\ell)$. This preferential adsorption of one component over another has been applied commercially to adsorptive separation of close-boiling liquid mixtures such as xylene isomers. $\Delta x_1$ can be related to the adsorbed liquid by a mass balance as follows:

$$n^\circ = n^\ell + n^a \qquad \text{(total amount)} \tag{8.1}$$

$$n_i^\circ = n_i^\ell + n_i^a \qquad \text{(component } i) \tag{8.2}$$

$n^\circ$ is the total amount before contact with the adsorbent; $n^\ell$ is the amount in the liquid phase at equilibrium; $n^a$ is the absolute amount in the solid phase at equilibrium.

Mole fractions are defined by:

$$n_i^\circ = n^\circ x_i^\circ \qquad \text{(before contact)} \tag{8.3}$$

$$n_i^\ell = n^\ell x_i^\ell \qquad \text{(in liquid phase)} \tag{8.4}$$

$$n_i^a = n^a x_i^a \qquad \text{(in solid phase)} \tag{8.5}$$

Using the mass balance for a binary liquid mixture, a quantity called excess adsorption $(n_i^e)$ is defined:

$$n_1^e = n^\circ(x_1^\circ - x_1^\ell) = n^a(x_1^a - x_1^\ell) = n_1^a x_2^\ell - n_2^a x_1^\ell \tag{8.6}$$

$$n_2^e = n^\circ(x_2^\circ - x_2^\ell) = n^a(x_2^a - x_2^\ell) = n_2^a x_1^\ell - n_1^a x_2^\ell \tag{8.7}$$

This definition of excess by a superscript $^e$ for adsorption from a liquid mixture is unrelated to the Gibbs excess adsorption from a gas $(n_e)$ discussed in Section 2. It is apparent that $n_1^e + n_2^e = 0$ and the preferentially adsorbed component has a positive excess. The quantity $n^\circ \Delta x$ is measured by experiment without knowing either $n^a$ or $x_1^a$. The excess terminology is appropriate because $n_1^e$ is the amount of component no. 1 in the pores $(n_1^a)$ minus the hypothetical amount $n^a x_1^\ell$ that would be present in the pores if the composition were the same as the liquid phase.

The liquid phase is governed by the Gibbs-Duhem equation for a binary liquid mixture:

$$v\,dP = x_1^\ell d\ln f_1 + x_2^\ell d\ln f_2 \qquad \text{(const. } T) \tag{8.8}$$

and the liquid in the pores obeys the Gibbs adsorption isotherm, Eq. (5.16):

$$d\psi = n_1^a d\ln f_1 + n_2^a d\ln f_2 \qquad \text{(const. } T) \tag{8.9}$$

Assuming that the $v\,dP$ term in the Gibbs-Duhem equation is negligible, as is the practice in vapor-liquid equilibrium:

$$d\psi = n_1^a d\ln f_1 - \frac{x_1^\ell}{x_2^\ell} n_2^a d\ln f_1 = \frac{n_1^a x_2^\ell - n_2^a x_1^\ell}{x_2^\ell} d\ln f_1 \qquad \text{(const. } T) \tag{8.10}$$

Using Eq. (8.6):

$$d\psi = \frac{n_1^e}{x_2^\ell} d\ln f_1 \qquad \text{(const. } T) \tag{8.11}$$

Since temperature is fixed, the fugacity in the liquid may be replaced by activity:

$$d\psi = \frac{n_1^{\mathrm{e}}}{x_2^{\ell}} d\ln a_1^{\ell} = \frac{n_1^{\mathrm{e}}}{x_2^{\ell} a_1^{\ell}} da_1^{\ell} \qquad (\text{const. } T) \tag{8.12}$$

where the activity in the liquid is $a_i^{\ell} = \gamma_i^{\ell} x_i^{\ell}$ and $\gamma_i^{\ell}$ is the activity coefficient in the liquid phase.

Given isothermal measurements of $n_1^{\mathrm{e}}$ as a function of liquid-phase composition, Eq. (8.12) may be integrated for the difference $\Delta\psi$:

$$\boxed{\psi_1^s - \psi_2^s = \int_0^1 \frac{n_1^{\mathrm{e}}}{x_2^{\ell} a_1^{\ell}} da_1^{\ell}} \tag{8.13}$$

$\psi_i^s$ is the reduced grand potential for immersion of the solid in pure liquid, so the integral in Eq. (8.13) can be verified [14] by integrating the absolute adsorption isotherms of pure $i$ vapors from zero pressure to the vapor pressure according to Eq. (A.11). Alternatively, Eq. (8.13) provides a basis for a thermodynamic consistency test which can be applied to three binary pairs of three liquids: the three differences $(\psi_1^s - \psi_2^s)$, $(\psi_2^s - \psi_3^s)$ and $(\psi_3^s - \psi_1^s)$ obtained by integrating Eq. (8.13) must sum to zero [28].

It is interesting that Eq. (8.13) for *excess* adsorption from a liquid mixture was derived from a mass balance based on *absolute* adsorption in the solid phase.
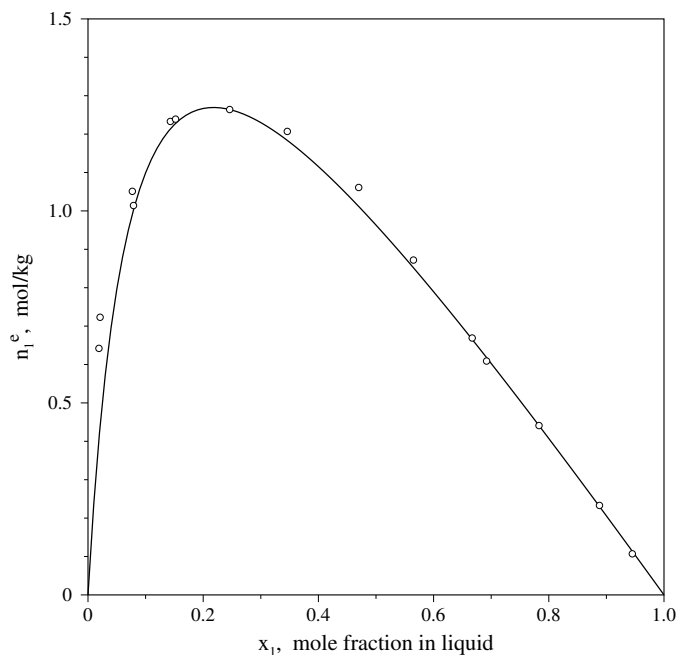


FIGURE 14. Excess adsorption of benzene from liquid mixture of benzene and cyclohexane on BPL activated carbon at 303.15 K. Points are experimental data [32]. Solid line is Eq. (8.14) with $m = 2.25$ mol/kg and $s = 12.9$.

Excess adsorption from liquids can be predicted from single-gas adsorption isotherms and vapor-liquid equilibrium data (activity coefficients) for the binary system. Given the temperature and liquid composition, the pair of fugacities in the liquid phase are given by $f_i = f_i^s \gamma_i x_i^{\ell}$. This pair of fugacities combined with the temperature provides the input data for predicting the amounts of each component adsorbed $(n_1^a, n_2^a)$ for an ideal adsorbed

solution. The individual amounts adsorbed combined with the known liquid composition yield $n_1^E$ from Eq. (8.6).

Usually single-gas adsorption isotherms for vapors are unavailable for such calculations and the standard procedure is to measure excess adsorption directly from liquid-phase measurements of $n°\Delta x^\ell$ according to Eq. (8.6). It can be shown that for the case of ideal solutions in both the liquid and adsorbed phase and for molecules with identical saturation capacities $(m)$:

$$n_1^e = \frac{m x_1^\ell x_2^\ell (s - 1)}{s x_1^\ell + x_2^\ell} \qquad (s > 1) \qquad (8.14)$$

Substitution of Eq. (8.14) in (8.13) gives $\Delta\psi = m \ln s$. The quantity $s$ is a ratio defined by the fugacity of pure saturated liquid $(f_i^s)$ and adsorption Henry constant $(K_i)$:

$$s = \frac{f_1^s K_1}{f_2^s K_2}$$

The skewed quadratic Eq. (8.14) generates a maximum in $n_1^e$ at

$$x_1^\ell = \frac{\sqrt{s} - 1}{s - 1}$$

In spite of the drastic approximations required for its derivation, Eq. (8.14) provides a qualitative fit of experimental data for ideal or nearly ideal mixtures. An example is shown on Figure 14.

## 9. HEATS OF ADSORPTION

The key equation of adsorption thermodynamics is Eq. (5.41)

$$\overline{u}_i = -RT^2 \left[ \frac{\partial \ln f_i}{\partial T} \right]_{n_i, n_j} + h_i° \qquad (9.1)$$

This exact Clapeyron-type equation for multicomponent adsorption connects the differential energy with the adsorption isotherm. The differential energy is:

$$\overline{u}_i \equiv \left[ \frac{\partial U}{\partial n_i} \right]_{T, n_j} \qquad (9.2)$$

For binary adsorption at constant temperature, we have from the calculus and Eq. (9.2):

$$dU = \overline{u}_1 \, dn_1 + \overline{u}_2 \, dn_2 \qquad (\text{const. } T) \qquad (9.3)$$

which provides immediately a consistency test for binary mixtures:

$$\left( \frac{\partial \overline{u}_1}{\partial n_2} \right)_{T, n_1} = - \left( \frac{\partial \overline{u}_2}{\partial n_1} \right)_{T, n_2} \qquad (9.4)$$

Eq. (9.3) was used to make calorimetric measurements of differential energies in binary mixtures [2]. Focusing upon adsorption of a single pure gas, Eq. (9.1) simplifies to:

$$\overline{u} = -RT^2 \left[ \frac{\partial \ln f}{\partial T} \right]_n + h° \qquad (9.5)$$

The perfect-gas enthalpy reference $(h°)$ for the differential energy is the consequence of using $\mu° = h° - Ts°$ as the reference state for the chemical potential.

For calorimetry, the *differential heat* of adsorption is defined by:

$$q_d = u_g - \overline{u}_a \qquad (9.6)$$

where $\overline{u}_a$ is the differential energy in the adsorbed phase and $u_g$ is the molar energy of the equilibrium gas phase. The subscript notation is needed to distinguish the adsorbed phase $(a)$ from the gas phase $(g)$.

For energy balances in adsorption columns, the *isosteric heat* of adsorption is defined by:

$$q_{st} = h_g - \overline{h}_a \tag{9.7}$$

The differential enthalpy and differential energy in the adsorbed phase are related by:

$$\overline{h}_a = \overline{u}_a + \frac{V_s}{(\partial n/\partial P)_T} \tag{9.8}$$

where $(\partial n/\partial P)_T$ is the slope of the adsorption isotherm. Combining Eqs. (9.5), (9.7) and (9.8):

$$q_{st} = RT^2 \left[ \frac{\partial \ln f}{\partial T} \right]_n + h_g^R - \frac{V_s}{(\partial n/\partial P)_T} \tag{9.9}$$

where $h_g^R = (h_g - h_g^\circ)$ is the residual enthalpy of the gas phase, usually calculated from a PVT equation of state for the bulk gas.

The volume of the solid $(V_s)$ is of order $1 \ \mathrm{dm^3/kg}$ and equations for the heats simplify considerably at pressures at or below 2 bar where $\overline{h}_a \approx \overline{u}_a$ and the perfect gas approximations $h_g = h_g^\circ$ and $u_g = u_g^\circ = (h_g^\circ - RT)$ are valid:

$$\boxed{q_{st} = RT^2 \left[ \frac{\partial \ln P}{\partial T} \right]_n = q_d + RT} \tag{9.10}$$

The nomenclature of heats ($q_{st}$ and $q_d$) is a misnomer because heats depend upon the path and both of these quantities are the difference between state functions. The isosteric heat $q_{st}$ is an enthalpy difference $\Delta h$, but the heat terminology is firmly established in the adsorption literature.

The isosteric and differential heats of adsorption are *defined* as positive quantities. Since heats of adsorption are exothermic and therefore negative in the standard thermodynamic sign convention, confusion about the sign of the heat of adsorption is unavoidable.

## 10. Remarks on Applications to Adsorption Column Dynamics

The choice of variables affects the basic equations for the dynamics of adsorption columns. These equations include the mass balances for each gaseous component and the energy balance for the packed column. Which variables should be used in the equations of transport which determine column dynamics: absolute or excess? Textbooks on adsorption [21] ignore the difference between absolute and excess variables for heat and mass transfer.

We recommend the use of absolute variables for column design. Mass transfer between the solid and the gas is proportional to the difference between the absolute amount adsorbed in the micropores at time $t$ and the amount that would be adsorbed at equilibrium for the prevailing temperature and fugacities (partial pressures) in the bulk gas phase.

The heat capacity needed for the accumulation term of the energy equation is the sum of the heat capacity of the bulk gas (per unit volume) and the heat capacity of the solid (per unit volume). The heat capacity of the solid phase, which includes the gas in its micropores, is the sum of the heat capacity of the clean adsorbent under full vacuum and the heat capacities of the gases in their perfect-gas state. The isosteric heat accounts for gas-gas and gas-solid interactions.

It has been argued that excess properties are suitable for the equations of adsorption column dynamics [27]. However, at high pressure, the excess approach collapses because of the singularity in the isosteric heat when the excess amount adsorbed passes through a

maximum. Even at low pressure where it makes no difference, the use of absolute variables is more intuitive than excess variables for modeling of heat and mass transport.

## 11. Summary and Conclusions

In this paper we have discussed the thermodynamics of adsorption in porous materials. We have highlighted the difficulties with the Gibbs excess formalism for these systems and have argued that an approach based on absolute properties is simpler while providing a rigorous basis for high pressure studies of microporous adsorbents. Solution thermodynamics based on absolute adsorption provides a complete description of equilibrium adsorption of pure fluids and their mixtures in porous materials without any reference to surface area, dividing surfaces, or excess variables.

## Acknowledgment

## *Notation*

| | |
|---|---|
| A,B,C | constants in Eq. (7.30) |
| $C_i$ | power series coefficients for grand potential, Eq. (A.4) |
| $D_i$ | power series coefficients for energy, Eq. (A.5) |
| $f$ | fugacity of gas, Pa |
| $f^\circ$ | fugacity in perfect-gas reference state (= 1 bar) |
| F | molar integral Helmholtz free energy, J/mol |
| $F^\circ$ | molar Helmholtz free energy in perfect-gas state, J/mol |
| $F^E$ | excess Helmholtz free energy for nonideal solution, Eq. (7.18), J/mol |
| $F^E_\gamma$ | excess Helmholtz free energy for activity coefficients, Eq. (7.5), J/mol |
| $F$ | Helmholtz free energy of solid phase, J/kg; J in Section 3.3 |
| $G$ | Gibbs free energy of solid phase, J/kg; J in Section 3.3 |
| $\mathcal{G}_i^*$ | standard-state factor for $i$th component, Eq. (6.23), $(kg/mol)^2$ |
| $h^\circ$ | molar enthalpy in perfect-gas state, J/mol |
| $\overline{h}$ | differential enthalpy, J/mol |
| $H$ | enthalpy of solid phase, J/kg ; J in Section 3.3 |
| $k_B$ | Boltzmann constant, $1.3806 \times 10^{-23}$ J/K |
| $K$ | Henry constant, mol/(kg-Pa) |
| $K_\circ$ | Henry constant at ref. temp. $T_\circ$ |
| $m$ | adsorbent capacity, mol/kg, Eq. (A.1) |
| $m_s$ | mass of adsorbent, kg |
| $\Delta m$ | weighed increase in mass of adsorbent, kg |
| $m^E$ | "excess mass" from Eq. (7.6), kg/mol |
| $M$ | molecular weight of gas, kg/mol |
| $n$ | total absolute amount of adsorbate, mol/kg |
| $n_a$ | specific absolute adsorption, mol/kg |
| $n_e$ | specific excess adsorption, mol/kg |
| $n_i$ | absolute amount of $i$th component, mol/kg; mol in Section 3.3 |
| $n_n$ | specific net adsorption, mol/kg |
| $n_t$ | total amount of gas introduced to sample cell, mol |
| $n_{He}$ | mole of He gas used for dead-space calibration, mol |
| $N$ | number of molecules |
| $P$ | pressure in gas phase, Pa |
| $P^\circ$ | reference pressure in perfect gas state, 1 bar |
| $P_\circ$ | pressure for helium calibration, Eq. (4.2), Pa |
| $q_d$ | differential heat, J/mol |
| $q_{st}$ | isosteric heat, J/mol |
| $Q$ | canonical partition function |
| $R$ | gas constant, 8.3145 J/(mol-K) |
| $s^\circ$ | entropy in perfect-gas state, J/(mol-K) |
| $s$ | molar integral entropy of solid phase, J/(mol-K) |
| $\overline{s}$ | differential entropy of gas in solid, J/(mol-K) |
| $S$ | entropy of solid phase, J/(kg-K); J/K in Section 3.3 |
| $S_s^\circ$ | entropy of degassed solid under full vacuum, J/(kg-K) |
| $T$ | temperature, K |
| $T_\circ$ | reference temperature for Eq. (A.1) or temperature for helium calibration, Eq. (4.2) , K |
| $u^\circ$ | molar energy in perfect-gas state, J/mol |
| $u$ | molar integral energy of solid phase, J/mol |
| $\overline{u}$ | differential energy in solid, J/mol |
| $U$ | energy of solid phase, J/kg; J in Section 3.3 |
| $V$ | volume of solid phase, $m^3$/kg; $m^3$ in Section 3.3 |
| $v_p$ | specific pore volume, $m^3$/kg |
| $v_s$ | specific volume of solid, $m^3$/kg |
| $v_{sk}$ | specific skeletal volume of solid, $m^3$/kg |
| $V_a$ | volume of adsorbed phase, $m^3$ |
| $V_d$ | volume of dead space, $m^3$ |

| | |
|---|---|
| $V_g$ | volume of bulk gas phase, m$^3$ |
| $V_p$ | pore volume, m$^3$ |
| $V_s$ | volume of solid, m$^3$ |
| $V_{sk}$ | skeletal volume of adsorbent, m$^3$ |
| $V_t$ | volume of sample cell, m$^3$ |
| $x_i$ | mole fraction of $i$th component in pores of solid |
| $y_i$ | mole fraction of $i$th component in gas phase |
| $z$ | molar extensive property ($u$, $s$, etc.) |
| $\overline{z}$ | differential property ($\overline{u}$, $\overline{s}$, etc.) |
| $Z$ | specific extensive property ($U$, $S$ etc.) |
| $\gamma_i$ | activity coefficient of $i$th component in adsorbed phase |
| $\Gamma$ | Gibbs excess adsorption per unit area, mol/m$^2$ |
| $\mu$ | chemical potential, J/mol |
| $\mu^\circ$ | chemical potential of adsorbate in perfect-gas state, J/mol |
| $\mu'_s$ | chemical potential of solid, J/kg |
| $\Xi$ | grand canonical partition function |
| $\rho$ | molecular density, m$^{-3}$, Eq. (3.4) |
| $\rho_g$ | molar density of bulk gas, mol/m$^3$ |
| $\rho_p$ | pore density, mol/m$^3$ |
| $\psi$ | reduced grand potential ($-\Omega/RT$), mol/kg |
| $\Omega$ | grand potential, J/kg; J in Section 3.3 |
| | *Subscript* |
| $i$ | refers to $i$ component |
| | *Superscript* |
| $*$ | refers to standard state for pure gas at same value of $T$ and $\Omega$ |
| $id$ | refers to function for an ideal adsorbed solution |
| e | refers to excess adsorption from liquid mixtures |
| $E$ | refers to excess function for deviation from ideal adsorbed solution |
| $\circ$ | refers to state of perfect gas |

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## Appendix A. Illustrative Calculations Based on a Mathematical Model for Absolute Adsorption in Microporous Adsorbents

Complete thermodynamic information on the adsorption of a single gas is provided either by a series of adsorption isotherms, or by a single adsorption isotherm coupled with calorimetric measurement of its differential energy. Eq. (A.1) provides a quantitative fit of data for adsorption in microporous materials (see Fig. 15) and is therefore suitable for calculating energy and entropy.
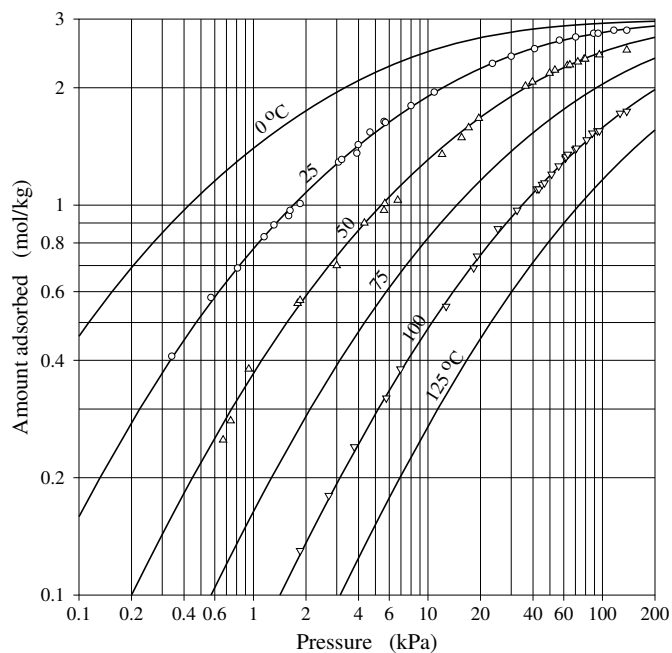
FIGURE 15. Points are experimental data for adsorption of ethylene on 13X molecular sieve at 25°, 50°, and 100°C [32]. Solid lines are Eq. (A.1) with constants from Table 13.
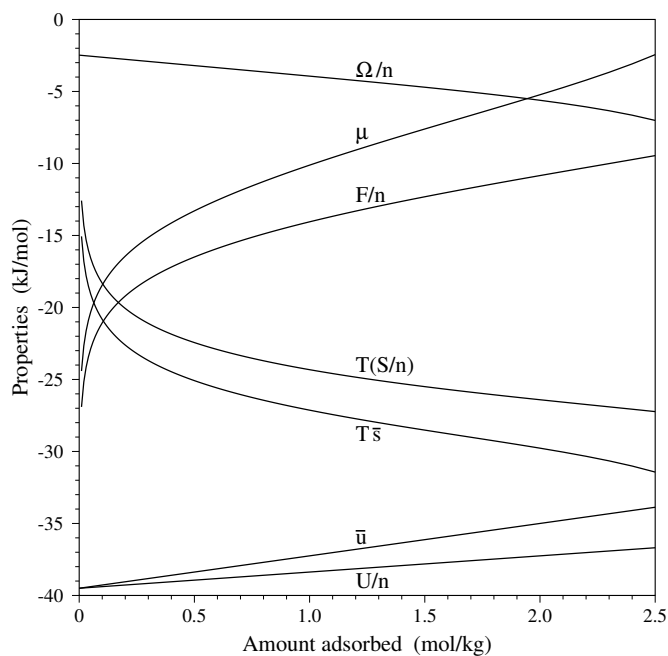


FIGURE 16. Properties for adsorption of ethylene on 13X molecular sieve at 298.15 K derived from experimental adsorption isotherms plotted on Figure 15. Values of energy and entropy relative to perfect-gas state for gases and fully evacuated adsorbent for solid, both at 298.15 K. $\mu = \overline{u} - T\overline{s}$. $F = U - TS = \mu n + \Omega$.

Isotherms for adsorption of pure gases are usually in the form $n(P)$ for loading as a function of pressure. The calculation of thermodynamic properties requires a more general function $n(P,T)$ for loading as a function of both pressure and temperature. It is apparent from Eq. (5.44) that an inverted form more useful for calculating thermodynamic properties would replace the independent variables $P$ and $T$ by $n$ and $T$, with fugacity as the dependent variable:

$$f = \frac{n}{K_\circ}\left[\frac{m}{m-n}\right]\exp\left[\frac{D(n)}{R}\left(\frac{1}{T}-\frac{1}{T_\circ}\right)\right]\exp\left[C(n)\right] \tag{A.1}$$

For $C(n)=0$, $D(n)=0$, and $f=P$, this reduces to the (inverted) Langmuir equation. $m$ is the saturation capacity parameter of the Langmuir equation corresponding to pore filling.

**Henry Constant.** $K$ is the Henry constant:

$$K = \lim_{P\to 0}\frac{n}{P} \tag{A.2}$$

and $K_\circ$ in Eq. (A.1) is the Henry constant at reference temperature $T_\circ$. From Eqs. (A.1) and (A.2):

$$K = K_\circ\exp\left[\frac{-D_\circ}{R}\left(\frac{1}{T}-\frac{1}{T_\circ}\right)\right] \tag{A.3}$$

The Henry constant $K$ decreases exponentially with increasing temperature.

**Energy and Entropy Properties.** The Langmuir equation accounts for molecules adsorbed singly in identical micropores and thus neglects entirely gas-gas interactions and variations in gas-solid interaction energy. The function $C(n)$ in the exponential of Eq. (A.1) is a power series:

$$C(n) = C_1 n + C_2 n^2 + C_3 n^3 + \cdots \tag{A.4}$$

The exponential factor $e^{C(n)}$ in the adsorption equation modifies the grand potential by adding a truncated power series to the Langmuir result, as shown in Eq. (A.12). $C(n)$ is dimensionless and its $C_i$ coefficients are measured at the reference temperature $T_\circ$. This series converges rapidly; typically termination after 3 or 4 coefficients provides quantitative agreement with experiment. Application of Eq. (5.44) to Eq. (A.1) yields the power series $D(n)$ for the differential energy:

$$\overline{u} = D(n) = D_\circ + D_1 n + D_2 n^2 + D_3 n^3 + \cdots \tag{A.5}$$

$D(n)$, like the differential energy, is negative in sign with units of J/mol. The constant $D_\circ$ is the differential energy at the limit of zero pressure. The assumption that the coefficients $C_i$ and $D_i$ in the power series are constants is equivalent to neglecting sensible heat in comparison to latent heat for the solid phase over a limited range of temperature. The energy $\overline{u}$ is relative to $h^\circ$ in the perfect-gas state at the reference temperature $T_\circ$.

The integral energy from Eq. (5.48) and the differential and integral entropies from Eqs. (5.45) and (5.49) are:

$$u = D_{\text{int}}(n) \tag{A.6}$$

$$\frac{\overline{s}}{R} = -\ln\left[\frac{m}{P^\circ K}\right] - \ln\left[\frac{n}{m-n}\right] + \frac{D(n)}{RT_\circ} - C(n) \tag{A.7}$$

$$\frac{s}{R} = -\ln\left[\frac{m}{P^\circ K}\right] - \ln\left[\frac{n}{m-n}\right] + \frac{m}{n}\ln\left[\frac{m}{m-n}\right] + \frac{D_{\text{int}}(n)}{RT_\circ} - C_{\text{int}}(n) \tag{A.8}$$

where

$$D_{\text{int}}(n) = \frac{\int D(n)dn}{n} = D_{\circ} + \frac{D_1}{2}n + \frac{D_2}{3}n^2 + \frac{D_3}{4}n^3 + \cdots \tag{A.9}$$

$$C_{\text{int}}(n) = \frac{\int C(n)dn}{n} = \frac{C_1}{2}n + \frac{C_2}{3}n^2 + \frac{C_3}{4}n^3 + \cdots \tag{A.10}$$

$C_{\text{int}}(n)$, like $C(n)$, is dimensionless. $D_{\text{int}}$, like $D(n)$, is a negative quantity with units of J/mol. The molar energy $u$ is relative to the perfect-gas enthalpy $h^{\circ}$ and the molar entropy $s$ is relative to the perfect-gas entropy $s^{\circ}$, both at the reference temperature $T_{\circ}$ in Eq. (A.1). The reference pressure $P^{\circ} = 1$ bar in Eqs. (A.7) and (A.8).

**Grand Potential.** Standard states for mixture equilibria are fixed by the reduced grand potential ($\psi$), which is obtained by integrating Eq. (5.16):

$$\psi = \int_0^f n\, d\ln f = \int_0^n \frac{d\ln f}{d\ln n} dn \qquad (\text{constant } T) \tag{A.11}$$

Substituting for the fugacity $f$ from Eq. (A.1) followed by integration yields:

$$\psi = m\ln\left(\frac{m}{m-n}\right) + \frac{D_{\psi}(n)}{R}\left(\frac{1}{T} - \frac{1}{T_{\circ}}\right) + C_{\psi}(n) \tag{A.12}$$

where the power series for $\psi$ are:

$$C_{\psi}(n) = \int_0^n nC'(n)dn = \frac{1}{2}C_1 n^2 + \frac{2}{3}C_2 n^3 + \frac{3}{4}C_3 n^4 + \cdots \tag{A.13}$$

$$D_{\psi}(n) = \int_0^n nD'(n)dn = \frac{1}{2}D_1 n^2 + \frac{2}{3}D_2 n^3 + \frac{3}{4}D_3 n^4 + \cdots \tag{A.14}$$

$C_{\psi}(n)$ has units of mol/kg and $D_{\psi}(n)$ has units of J/kg. The domain of $\psi$ is $0 \le n < m$ and the limit at low loading is:

$$\lim_{n\to 0} \frac{\psi}{n} = 1$$

**Slope of Adsorption Isotherm.** The calculation of differential energy or heat of adsorption of individual components of mixtures requires the slope of the adsorption isotherm evaluated at its standard state. From Eq. (A.1), the reciprocal of the dimensionless slope of an adsorption isotherm for a single gas is:

$$\left[\frac{\partial \ln f}{\partial \ln n}\right]_T = \frac{m}{m-n} + \frac{D_s(n)}{R}\left(\frac{1}{T} - \frac{1}{T_{\circ}}\right) + C_s(n) \tag{A.15}$$

The standard state notation is simplified by writing $f_i^*$ is written as $f$ and $n_i^*$ as $n$. $T_{\circ}$ is the reference temperature for the determination of the $C_i$ coefficients in Eq. (A.1). The power series for Eq. (A.15) are:

$$C_s(n) = C_1 n + 2C_2 n^2 + 3C_3 n^3 + \cdots \tag{A.16}$$

$$D_s(n) = D_1 n + 2D_2 n^2 + 3D_3 n^3 + \cdots \tag{A.17}$$

$C_s(n)$ is dimensionless and $D_s(n)$ has units of J/mol. The limit at zero loading is:

$$\lim_{n\to 0} \left[\frac{\partial \ln f}{\partial \ln n}\right]_T = 1 \tag{A.18}$$

| Constant | Value | Units |
|----------|-------|-------|
| $K_\circ$ | 1.9155 | $mol\ kg^{-1}\ kPa^{-1}$ |
| $m$ | 2.9997 | $mol\ kg^{-1}$ |
| $T_\circ$ | 298.15 | K |
| $C_1$ | 0.841 | $(mol/kg)^{-1}$ |
| $C_2$ | -0.06311 | $(mol/kg)^{-2}$ |
| $C_3$ | -0.009415 | $(mol/kg)^{-3}$ |
| $D_\circ$ | -39.5 | $(kJ/mol)$ |
| $D_1$ | 2.25 | $(kJ/mol)\ (mol/kg)^{-1}$ |

TABLE 13. Constants for adsorption of $C_2H_4$ on 13X molecular sieve.

**Example.** The first step is to select an isotherm measured at a reference temperature ($T_\circ$) suitable for extracting the constants $m$, $K_\circ$, and the $C_i$ coefficients. Eq. (6.21) written in the form:

$$\bar{u} = R\left[\frac{\partial \ln f}{\partial(1/T)}\right]_n \tag{A.19}$$

exploits the near-linearity of $\ln f$ versus $1/T$ at constant $n$ to determine values of the differential energy, which are fit with the $D_i$ coefficients. An example is shown in Figure 15, which compares Eq. (A.1) with adsorption isotherms measured at 25°, 50° and 100°C. The other isotherms at 0°, 75°, and 125°C are interpolations and extrapolations.

Having fit the adsorption isotherms with Eq. (A.1), the thermodynamic functions are given by explicit equations. On Figure 16 are plotted the integral and differential functions calculated from the equations in this Appendix. The functions $\{S,U,F\}$ are integrals with respect to $n$ of the differential functions $\{\bar{s},\bar{u},\mu\}$. In addition, $F = U - TS$, $\mu = \bar{u} - T\bar{s}$, and $(F/n) = \mu + (\Omega/n)$.

The $\mu$ function is the adsorption isotherm at 298.15 K. Eq. (A.1) is based upon the simplification that $U$ and $S$ are independent of temperature, an approximation justified for the temperature range of the experimental data on Figure 15.

All functions are negative in sign. Entropy and free energy functions are undefined at the limit of zero loading. The energy is finite at zero loading corresponding to the energy of a single molecule interacting with the solid. The grand potential ($\Omega$) has a finite value ($-nRT$) at zero loading, where $(\Omega/n) = -RT = -2.48$ kJ/mol.

APPENDIX B. SIMULTANEOUS SOLUTION OF FUGACITY EQUATIONS

B.1. **Ideal Solution.** The objective is the solution of the fugacity equations (6.16) for $\psi$ and composition $x$. For an ideal binary mixture with $x_2 = (1-x_1)$, we seek the simultaneous solution of the pair of fugacity equations at temperature $T$:

$$\begin{bmatrix} F_1(x_1, \psi) \\ F_2(x_2, \psi) \end{bmatrix} = \begin{bmatrix} \ln(f_1^* x_1/f_1) \\ \ln(f_2^* x_2/f_2) \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{B.1}$$

for which the Jacobian is:

$$\begin{bmatrix} \left(\frac{\partial F_1}{\partial x_1}\right)_\psi & \left(\frac{\partial F_1}{\partial \psi}\right)_{x_1} \\ \left(\frac{\partial F_2}{\partial x_1}\right)_\psi & \left(\frac{\partial F_2}{\partial \psi}\right)_{x_1} \end{bmatrix} = \begin{bmatrix} \frac{1}{x_1} & \frac{1}{n_1^*} \\ -\frac{1}{x_2} & \frac{1}{n_2^*} \end{bmatrix} \tag{B.2}$$

The size of the Jacobian is equal to the number of gaseous components. Solution of the linear equations:

$$\begin{bmatrix} \frac{1}{x_1} & \frac{1}{n_1^*} \\ -\frac{1}{x_2} & \frac{1}{n_2^*} \end{bmatrix} \begin{bmatrix} \Delta x_1 \\ \Delta \psi \end{bmatrix} = \begin{bmatrix} F_1 \\ F_2 \end{bmatrix} \tag{B.3}$$

gives successive iterations according to Newton's method:

$$(x_1)_{i+1} = (x_1)_i - \Delta x_1 \tag{B.4}$$

$$\psi_{i+1} = \psi_i - \Delta \psi \tag{B.5}$$

If the single-gas isotherms obey Eq. (A.1), a suitable first guess is:

$$x_i = \frac{K_i f_i}{\sum_i [K_i f_i]} \tag{B.6}$$

$$\psi = \frac{\sum_i [f_i m_i \ln(1 + K_i f_i/m_i)]}{\sum_i f_i} \tag{B.7}$$

$K_i$ is the Henry constant for the $i$th component from Eq. (A.3) .

Two pure-component functions are needed: $n_i^*(\psi)$ (see Appendix C) and the composite function $f_i^*[n_i^*(\psi)]$ .

B.2. **Activity Coefficients.** Insertion of activity coefficients into Eq. (B.1) gives:

$$\begin{bmatrix} F_1(x_1, \psi) \\ F_2(x_2, \psi) \end{bmatrix} = \begin{bmatrix} \ln(f_1^* \gamma_1 x_1/f_1) \\ \ln(f_2^* \gamma_2 x_2/f_2) \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{B.8}$$

Using Eqs. (7.31), (7.32) and (7.33), the Jacobian is:

$$\begin{bmatrix} \left(\frac{\partial F_1}{\partial x_1}\right)_\psi & \left(\frac{\partial F_1}{\partial \psi}\right)_{x_1} \\ \left(\frac{\partial F_2}{\partial x_1}\right)_\psi & \left(\frac{\partial F_2}{\partial \psi}\right)_{x_1} \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \tag{B.9}$$

where:

$$a_{11} = \frac{1}{x_1} - \frac{(A + BT)}{RT}(1 - e^{-C\psi})2x_2$$

$$a_{21} = -\frac{1}{x_2} + \frac{(A + BT)}{RT}(1 - e^{-C\psi})2x_1$$

$$a_{12} = \frac{1}{n_1^*} + \frac{(A + BT)}{RT}Ce^{-C\psi}x_2^2$$

$$a_{22} = \frac{1}{n_2^*} + \frac{(A + BT)}{RT}Ce^{-C\psi}x_1^2$$

Except for the more complicated form of the Jacobian, Eqs. (B.3)–(B.7) are unchanged.

APPENDIX C. INVERSION OF GRAND POTENTIAL FUNCTION FOR MIXTURE EQUILIBRIA.

Eq. (A.12) is the function $\psi(n)$ for single-gas adsorption but its inverse function is needed to fix the standard state. Define $\mathcal{P}(n) \equiv \psi(n)$ and find the solution of the function $\mathcal{H}(n) = 0$:

$$\mathcal{H}(n) = \mathcal{P}(n) - \psi = 0 \tag{C.1}$$

Solve Eq. (C.1) by Newton's method using:

$$n_{j+1} = n_j - \frac{\mathcal{H}}{\mathcal{H}'} \tag{C.2}$$

with

$$\mathcal{H}' = \psi'(n) = \frac{m}{m-n} + (C_1 n + 2C_2 n^2 + 3C_3 n^3 + \cdots) \tag{C.3}$$
$$+ \frac{1}{R}\left(\frac{1}{T} - \frac{1}{T^\circ}\right)(D_1 n + 2D_2 n^2 + 3D_3 n^3 + \cdots)$$

A suitable first guess is $n = m(1 - e^{-\psi/m})$. $\psi$ increases monotonically with $n$ and the iterative solution for the inverse function $n(\psi)$ converges rapidly. The above notation for $n$ is a simplification for $n_i^*$, the standard-state loading of single gas $i$. $\psi$ and its standard-state properties $(f_i^*, u_i^*, s_i^*)$ are all explicit functions of $n_i^*$.