Measurement of Gibbsian Surface Excess

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The Gibbsian Surface Excesses (GSE) are the true experimental variables for measurement of equilibria and kinetics for pure and multicomponent gas-solid adsorption. The gravimetric and volumetric methods, which are the most commonly used experimental procedures, are revisited. The common practice of ignoring helium adsorption during measurement of adsorbent density by helium pycnometry and measurement of void volumes in adsorption apparatus by helium expansion can lead to large errors in estimating GSE at high pressures and for less selectivity adsorbed components of a gas mixture. Methods to overcome these problems are described.

Introduction

The actual size and structure of the adsorbed phase, as well as the adsorbate density and composition profiles within that phase, cannot be measured by today's technology. Consequently, the actual amounts adsorbed for a pure gas or the components of a gas mixture are not meaningful experimental variables. This problem is resolved by using an elegant model of adsorption systems proposed by Gibbs (1928). It recommends that the extents of adsorption of the adsorbates be quantified by variables called Gibbsian Surface Excesses (GSE) which can be unambiguously measured (Gibbs, 1928; Sircar, 1999).

Figure 1 is a cartoon of the GSE model for adsorption (equilibrium or transient) from a multicomponent bulk gas mixture at pressure (P), temperature (T), and gas-phase mol fraction (y_i) of component i. The gas is in contact with a unit amount of a chemically inert adsorbent which can be porous or nonporous, physico-chemically homogeneous, or heterogeneous. The adsorbent is placed in a chamber of volume v^T.

The Gibbsian adsorbed phase is defined by an arbitrarily chosen interface which is located within the bulk gas phase characterized by P, T, and y_i. The volumes of the bulk gas and the Gibbsian adsorbed phases are, respectively, v and v^a. The total void volume (v^o) for the system of Figure 1 is given by

$$v^o = v + v^a \tag{1}$$

A mass balance for the component i of the gas mixture yields

$$n_i^o = n_i^m + v^o \rho y_i \tag{2}$$

$$n_i^m = n_i^a - v^a \rho y_i = v^a[\rho^a x_i^a - \rho y_i] \tag{3}$$

$$n_i^a = v^a \rho^a x_i^a;\ x_i^a = n_i^a/n^a;\ n^a = v^a \rho^a \tag{4}$$

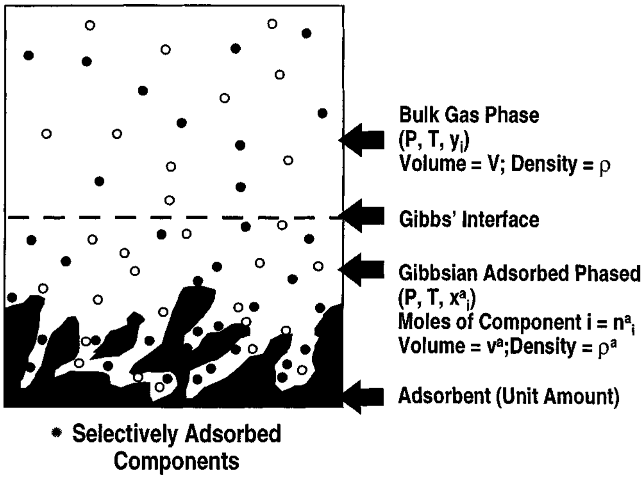

Figure 1. Gibbsian model for gas adsorption.

where n_i^o is the total moles of component i present in the adsorption system of Figure 1. ρ is the molar density of the bulk gas phase at P, T, and y_i. The variable n_i^m is called the GSE for component i of the gas mixture. n_i^a, n^a, ρ^a, and x_i^a are, respectively, the amount of component i adsorbed, the total amount of all components adsorbed, the molar density of the adsorbed phase, and the adsorbed phase mol fraction of component i.

Obviously, the properties of the Gibbsian adsorbed phase depend on the location of the Gibbs interface. Thus, they cannot be experimentally measured. On the other hand, the quantities n_i^o, v^o, ρ, and y_i in Eq. 2 can be experimentally measured. Thus, the GSE of component i (n_i^m) is independent of the location of the Gibbs interface and it can be unambiguously determined.

The quantity n_i^o can be estimated (a) by measuring the amounts of each adsorbate added to form the adsorption system of Figure 1, or (b) by completely desorbing the contents of the adsorption system and then measuring the amounts of each component desorbed. The total void volume of the system (v^o) can be (a) measured by helium expansion into the evacuated chamber of Figure 1 containing the regenerated (clean) adsorbent, and (b) by independently measuring the pure helium adsorption isotherms on the adsorbent. The bulk gas-phase properties (P, T, and y_i) can be measured by appropriately instrumenting the gas phase of the system.

Equation 3 shows that the actual amount of component i adsorbed (n_i^a) can be estimated from the experimentally measured GSE of that component (n_i^m) only if an assumption is made about v^a as a function of P, T, and y_i. For that case, it can be shown that the difference between n_i^m and n_i^a increases as the gas-phase pressure increases and the selectivity of adsorption of that component decreases (Sircar, 1999). Equations 3 and 4 also show that $n_i^m \sim n_i^a$ only when $\rho^a \gg \rho$ for a pure gas ($x_i^a = y_i = 1$), and $\rho^a x_i^a \gg \rho y_i$ for a mixed gas (Sircar, 1985). It follows that the GSE and the actual amount adsorbed of component i are approximately equal when (a) the pure gas adsorbed phase is much denser than the gas phase and (b) the mixed gas adsorbed phase is much denser than the gas phase and the component i is very selectively adsorbed ($x_i^a \gg y_i$). Thus, the general conclusion is that the actual amounts adsorbed should not be treated as bona fide variables for describing the adsorption phenomenon. Instead, the GSE should be used.

Experimental Measurement of Gibbsian Surface Excess

Numerous experimental techniques have been developed and used for measurement of pure and multicomponent gas adsorption equilibria and kinetics during the last 80 years. These include methods like (a) gravimetric, (b) volumetric, (c) piezometric, (d) gravimetric-volumetric, (e) total desorption, (f) column dynamic, (g) chromatographic, (h) closed-loop recycle, (i) isotope exchange, and so on. It has been shown that all of the these methods measure the equilibrium or transient GSE of a pure gas or those for the components of a gas mixture under the conditions of the experiments (Sircar, 1999). Methods (a) and (b) are most frequently used in practice (Rouquerol et al., 1999). They will be discussed in detail in the following.

Gravimetric Method

The simplest gravimetric experiment consists of exposing a clean adsorbent sample to a pure gas at constant P and T (mass density ρ_w, g/cm^3) or to a gas mixture at constant P, T and y_i (mass density, ρ_w, g/cm^3), and then measuring the change in the mass (weight) of the adsorbent sample with time (t) until equilibrium is reached. Various designs of spring and microbalances are used for this purpose. The adsorbent is placed in a pan which is suspended from the balance arm inside a thermostated tube, as shown by Figure 2. The mass of the pan (w^P) and the adsorbent (w^S) are independently measured under vacuum.

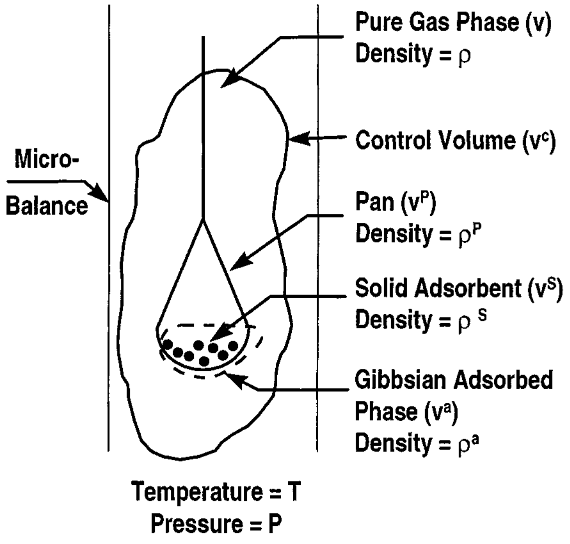

Figure 2. Gravimetric adsorption experiment.

The experiment measures the mass of a control volume (V^C) which includes the volume of the pan (V^P), the volume of the solid matter of the adsorbent (V^s), the transient volume of the adsorbed phase on the solid surface [$V^a(t)$], and the transient volume of the gas phase [$V(t)$]. Let $w(t)$ and w be the transient state and equilibrium state mass of the control volume, respectively.

Then, one can write

$$V^C = V^P + V^S + V^a(t) + V(t) \tag{5}$$

$$w(t) = V^P \rho^P + V^S \rho^s + V^a(t)\rho_w^a(t) + V(t)\rho_w - V^C \rho_w \tag{6}$$

where ρ^P and ρ^s are, respectively, the chemical (true) densities (g/cm^3) of the pan and the adsorbent materials. $\rho_w^a(t)$ is the transient mass density (g/cm^3) of the adsorbed phase. The last term on the righthand side of Eq. 6 accounts for the buoyancy correction. Equations 5 and 6 can be combined and rearranged to get

$$w(t) = w^P + w^S + w^S n^w(t) - (V^P + V^S)\rho_w \tag{7}$$

$$n^w(t) = V^a(t)[\rho_w^a(t) - \rho_w]/w^S \tag{8}$$

where $n^w(t)$ is the transient total specific mass surface excess (g/g) for the adsorbed phase per unit amount of the adsorbent. For a mixed gas system, $n^w(t) = \sum n_i^w(t)$, where $n_i^w(t)$ is the transient specific mass surface excess (g/g) of component i of the gas mixture. The equilibrium mass surface excess n^w can be obtained by replacing $w(t)$ with w in Eq. 7.

The mass surface excess (n^w, g/g) is related to the molar surface excess (n^m, mol/g) by

$$n^m = n^w/M \tag{9}$$

where M is the molecular weight of the adsorbed phase. For pure gas adsorption, M is simply the molecular weight of the adsorbate. For mixed gas adsorption, however, one does not know the composition and the molecular weights of the adsorbed phase. Thus, only the total mass GSE can be estimated gravimetrically.

We now carry out a similar experiment using the same gravimetric apparatus where the adsorbent sample is replaced by a nonporous, nonpolar reference material of extremely low surface area like borosilicate glass having the same volume (V^S) as that of the adsorbent solid matter of the previous experiment. The clean mass of the reference sample is $w^g(=w^S\rho^g/\rho^s)$, where ρ^g is the chemical density of the reference solid. The reference sample is then exposed to a very weakly adsorbing reference gas at a temperature of T_R and pressure P_R where the mass density of the gas is ρ_w. The weight of this reference system (w^R) is measured. It follows that

$$w^R = w^P + w^g + w^g n_R^w - (V^P + V^S)\rho_w \tag{10}$$

where n_R^w is the specific mass surface excess of the reference gas on the reference solid (g/g) at P_R and T_R (or ρ_w and T_R).

Equations 7 and 10 can be combined to get

$$\left\{n^w(t) - \left[w^g/w^S\right]n_R^w\right\} = \left[\left\{w(t) - w^S\right\} - \left\{w^R - w^g\right\}\right]/w^S \tag{11}$$

Equation 11 shows that if $n^w(t) \gg [w^g/w^S]n_R^w$, then $n^w(t)$ can be unambiguously estimated by measuring $w(t)$, w^R, w^g, and w^S using a gravimetric apparatus. The quantity n_R^w cannot be estimated. The quantity $w^g/w^S(=\rho^g/\rho^s)$ is generally between 0.8–1.5, because the chemical densities of many practical adsorbents are similar to that of the reference material like borosilicate glass ($\rho^s = 1.9$–3.5 g/cm^3, $\rho^g = 2.3$ g/cm^3).

It is generally accepted that the inequality $[n^w(t) \gg n_R^w]$ for the same gas-phase density (ρ^w) is satisfied because:

(a) The surface area of the reference solid (~ 10 cm^2/g) is negligible compared to that of a practical adsorbent (~ 100–$1{,}500$ m^2/g).

(b) The reference solid and the reference gases are nonpolar and, therefore, there are no specific adsorption forces between them. Helium is often used as the reference gas.

(c) The temperature of the reference experiment (T_R) can be substantially higher than that of the base experiment (T) which will further minimize the relative adsorption of the reference gas on the reference solid.

Criterion (a) alone should be sufficient. For example, the ratio of the surface area of nonporous, spherical particles (radius = 0.1 cm) of borosilicate glass and that of a practical adsorbent (area of at least 50 m^2/g) of equal solid volume is only $\sim 2.8\times10^{-5}$.

It follows from Eqs. 9 and 11 that the transient rate of change of GSE of a pure gas (mass or molar) at constant P and T or the transient rate of change of total GSE (mass only) from a gas mixture at constant P, T and y_i can be easily obtained from the gravimetric experiment

$$\frac{dn^w(t)}{dt} = \frac{1}{w^S}\cdot\frac{dw(t)}{dt} \tag{12}$$

Measurement of Helium Adsorption by Gravimetric Method

The gravimetric experiments outlined earlier can be used to obtain the surface excess of pure helium (n_{He}^m) as functions of P and T on any practical adsorbent whose surface area is much larger than that of the reference solid. Consequently, the Henry's Law constant $[K_{\mathrm{He}}(T)]$ for helium can be obtained from the linear Henry's Law region of the surface excess isotherm (n_{He}^m as a function of P at constant T) at low to moderate pressures

$$n_{\mathrm{He}}^m = K_{\mathrm{He}}(T)\cdot P = \bar{K}_{\mathrm{He}}(T)\cdot\rho \qquad \text{Henry's Law region} \tag{13}$$

The helium Henry's Law constant $[\bar{K}_{\mathrm{He}}(T)]$ written in terms of the gas density is related to $K_{\mathrm{He}}(T)$ by $[\bar{K}_{\mathrm{He}} = K_{\mathrm{He}}RT]$ when the gas phase is ideal.

Chemical density of the adsorbent

The chemical (true) densities of the adsorbent (ρ^s) and the reference solid (ρ^g) must be known in order to use the previously described gravimetric experiment protocol for measuring the surface excess. The exact quantity of the reference solid ($w^g = w^S\rho^g/\rho^s$) having the same volume as the adsorbent (V^s) can then be estimated.

The chemical density of a nonporous reference solid can be measured by using a pycnometer or a mercury porosimeter (Lowell, 1979). The chemical density of a microporous crystalline adsorbent can be estimated by crystallography (Breck, 1984). The chemical density of a mesoporous amorphous adsorbent can be measured using a mercury porosimeter (Lowell, 1979). However, the common method to estimate the chemical density of a micro-mesoporous amorphous adsorbent or that of a pelletized crystalline adsorbent is helium pycnometry (Lowell, 1979). It is generally assumed that helium penetrates all pores of the solid and it is not adsorbed at the conditions of the test (low pressure and moderate temperature). Thus, the helium density of the adsorbent (ρ_{He}^s) is assumed to be equal to its chemical density (ρ^s).

The exact relationship between ρ^s and ρ_{He}^s is given by (Sircar, 1999)

$$\frac{1}{\rho^s} = \frac{1}{\rho_{\mathrm{He}}^s} + \bar{K}_{\mathrm{He}}(T_R) \tag{14}$$

where $\bar{K}_{\mathrm{He}}\,(T_R)$ is the Henry's Law constant for helium (density domain) on the adsorbent at the temperature (T_R) of helium density measurement. Equation 14 assumes that the helium adsorption isotherm is linear under the conditions of the pycnometer test.

It can be shown by combining Eqs. 7, 8, 10, 11 and 14 that, if one uses helium density of the adsorbent instead of its true density for obtaining $w^g(=w^S\rho^s/\rho_{\mathrm{He}}^s)$, then Eq. 11 should be corrected to give

$$\left\{n^w(t) - \left(w^g/w^S\right)n_R^w\right\} = \left[\left\{w(t) - w^S\right\} - \left\{w^R - w^g\right\}\right]/w^S + \bar{K}_{\mathrm{He}}(T_R)\cdot\rho_w \tag{15}$$

The argument that $n^s(t) \gg (w^g/w^S)n_R^w$ is still valid. However, Eq. 15 shows that the second term on the righthand side of that equation can significantly contribute to the value of $n^w(t)$ in the high-pressure region even though $\overline{K}_{\mathrm{He}}(T_R)$ can be very small. Thus, the surface excess estimated by Eq. 11 by assuming $\rho^s \sim \rho_{\mathrm{He}}^s$ will be an apparent mass surface excess $[n^{wa}(t)]$ at ρ_w and T. The true mass surface excess $[n^w(t)]$ will be given by

$$n^w(t) = n^{wa}(t) + \overline{K}_{\mathrm{He}}(T_R) \cdot \rho_w \tag{16}$$

A relationship identical to Eq. 16 can be written for the apparent and true molar surface excesses of a pure gas at ρ and T by dividing each term of Eq. 16 with the molecular weight of the gas.

Equation 16 shows that the knowledge of pure helium adsorption isotherm on the adsorbent at T_R is needed for estimating the true surface excess of a gas by the gravimetric experiment when the assumption of $\rho^s = \rho_{\mathrm{He}}^s$ is made. n^w (or n^m) will be approximately equal to n^{wa} (or n^{ma}) only in the low to moderate pressure region.

It follows from Eq. 16 that for adsorption of pure helium in the Henry's Law region at temperature T, one can write

$$\overline{K}_{\mathrm{He}}(T) = \overline{K}_{\mathrm{He}}^a(T) + \overline{K}_{\mathrm{He}}(T_R) \tag{17}$$

where $\overline{K}_{\mathrm{He}}^a$ is the apparent Henry's Law constant for helium in ρ domain at T

$$n_{\mathrm{He}}^{ma} = \overline{K}_{\mathrm{He}}^a \cdot \rho \tag{18}$$

The isosteric heat of adsorption of helium (q_{He}^o) in the Henry's Law region is given by (Sircar, 1999)

$$\frac{d \ln K_{\mathrm{He}}(T)}{dT} = -\frac{q_{\mathrm{He}}^o}{RT^2} \qquad R = \text{Gas Constant} \tag{19}$$

Equation 19 can be integrated by assuming that q_{He}^o is independent of T to get

$$\frac{K_{\mathrm{He}}(T)}{K_{\mathrm{He}}(T_R)} = \exp\left[\frac{q_{\mathrm{He}}^o}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right)\right] \tag{20}$$

Equations 13, 17, 19, and 20 can be combined to get

$$\frac{d \ln \overline{K}_{\mathrm{He}}^a(T)}{dT} = \frac{-\left[q_{\mathrm{He}}^o - RT\right]/RT^2}{\left[1 - \frac{T_R}{T}\exp\left\{\frac{q_{\mathrm{He}}^o}{R}\left(\frac{1}{T_R} - \frac{1}{T}\right)\right\}\right]} \tag{21}$$

$$\overline{K}_{\mathrm{He}}(T) = \frac{-\left(\frac{d\overline{K}_{\mathrm{He}}^a}{dT}\right)}{\left[\left(q_{\mathrm{He}}^o - RT\right)/RT^2\right]} \tag{22}$$

Equation 21 shows that q_{He}^o can be estimated by measuring $\overline{K}_{\mathrm{He}}^a(T)$ using Eq. 18 and the apparent surface excess isotherm for helium at different temperatures. Equation 22 can then be used to estimate the actual Henry's Law constant for helium $[\overline{K}_{\mathrm{He}}(T)]$ as a function of T. Subsequently, $\overline{K}_{\mathrm{He}}(T_R)$ can be estimated. Thus, it is possible to estimate the true Henry's Law constant for helium adsorption by gravimetrically measuring the apparent surface excess isotherms for helium at different temperatures with the assumption of $\rho_{\mathrm{He}}^s = \rho^s$ if the true chemical density of the adsorbent is not known.

Experimental example of gravimetric helium isotherm

We used a commercial Cahn microbalance [Model 1000] for measurement of helium adsorption on a porous alumina sample produced by Alcoa, Inc. The BET N_2 surface area of the adsorbent sample was 113.0 m^2/g. Its chemical density (gamma alumina) was assumed to be 3.45 g/cm^3 (Dean, 1985). The reference material consisted of a mixture of nonporous beads of quartz glass (diameter = 0.40 cm, $\rho^g = 2.203$ g/cm^3) and tungsten (diameter = 0.048 cm, $\rho^g = 19.16$ g/cm^3). The volumes of the adsorbent and the reference solid were identical. The total weights of the alumina sample and the reference put in the pan of the micro-balance were, respectively. 2.0 and 2.85 g. The average surface area of the mixed reference solid was 6.62×10^{-4} m^2/g. Thus, the surface area ratio between the reference solid and the adsorbent was 5.8×10^{-6}. The helium surface excess isotherms were evaluated at 77 K and 186 K on the alumina and the reference solid. Figure 3 shows the measured experimental data at 77 K. It plots the difference between the equilibrium weight (w) of the adsorption system of Figure 2 at gas pressure P (molar density = ρ) and temperature T (constant), and the weight (w_o) of the adsorption system under vacuum ($\rho = 0$) divided by the weight of the clean adsorbent (w^S) as a function of gas density ρ. The plots for both the adsorbent and the reference solid are shown.

For adsorption in the Henry's Law region, Eqs. 6, 10, and 13 can be combined to get

$$\left[(w - w_o) - \left(w^R - w_o^R\right)\right]/w^S \cdot M_{\mathrm{He}} = \overline{K}_{\mathrm{He}} \cdot \rho\left[1 - \frac{w^g}{w^S} \cdot \frac{\overline{K}_{\mathrm{He}}^R}{\overline{K}_{\mathrm{He}}}\right] \tag{23}$$

where M_{He} is the molecular weight of helium and $\overline{K}_{\mathrm{He}}^R$ $[\ll \overline{K}_{\mathrm{He}}]$ is the Henry's Law constant for helium on the reference

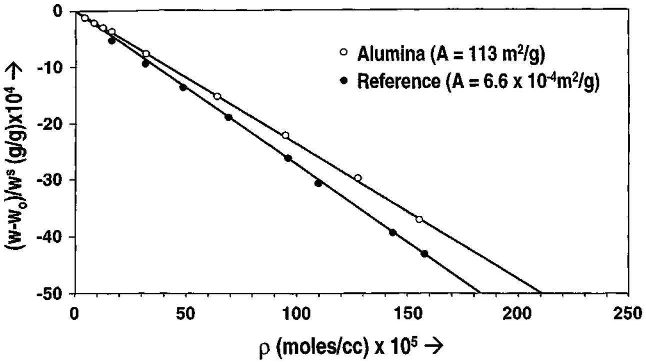

Figure 3. Helium adsorption (gravimetric) on alumina at 77 K.

Table 1. Henry's Law Constants for Helium on Alumina*

T (K)	K_{He} (mol/g/atm)	$\bar{K}_{\mathrm{He}}$ (cm^3/g)
77.0	1.3982×10^{-5}	0.0883
186.1	0.0940×10^{-5}	0.0143
600.0 (Est.)	0.0252×10^{-5}	0.0124
298.0 (Est.)	0.0459×10^{-5}	0.0112

*BET area 113 m^2/g.

solid at T. The superscript R represents quantities for the reference solid. Equation 23 shows that the Henry's Law constant for helium on the adsorbent $[\bar{K}_{\mathrm{He}}]$ at temperature T can be estimated from the slopes of the lines in Figure 3. The straight line plots of Figure 3 prove that the helium adsorption on both substrates are in the Henry's Law region.

Table 1 summarizes the estimated Henry's Law constants for helium adsorption on the alumina. The data of Table 1 gave a q^o_{He} value of 0.705 kcal/mol for the alumina by Eq. 19. Equations 13 and 19 were then used to obtain $\bar{K}_{\mathrm{He}}$ at different temperatures. The values of $\bar{K}_{\mathrm{He}}$ on the alumina at 298 K and 600 K were calculated to be 0.0112 and 0.0124 cm^3/g, respectively. It should be emphasized that these values are sensitive to the value of the chemical density of the alumina. The purpose here is to demonstrate that $\bar{K}_{\mathrm{He}}$ may not be negligible at ambient or elevated temperatures.

The following sections will show that the knowledge of $\bar{K}_{\mathrm{He}}(T)$ is critical in estimating void volumes of adsorption systems by helium expansion, especially when measuring the surface excess isotherms at high pressures and temperatures and when the adsorbate of interest is the less selectively adsorbed component from a gas mixture.

Volumetric Method

The simplest volumetric method consists of expanding a pure gas or a multicomponent gas mixture from a reservoir of known volume (V^R) into an evacuated sample chamber containing a known amount (w^S,g) of the clean adsorbent. The void volume of the sample side (empty volume-volume of adsorbent solid) is V^o. The entire system is thermostated. Figure 4 shows the volumetric apparatus.

The experiment consists of monitoring the gas-phase P, T and y_i of the sample chamber and the reservoir as a function of time (t). The initial gas conditions inside the reservoir are P^R and T for the pure gas and P^R, y_i^R, and T for the mixed gas. A transient molar balance for component i using Eq. 2 yields

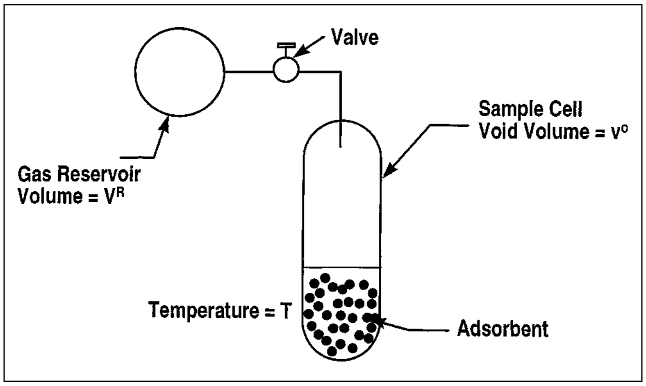

Figure 4. Volumetric adsorption experiment: pure and multicomponent gas.

$$V^R\rho^R y_i^R = V^R\rho(t)y_i(t) + w^S n_i^m(t) + V^o\rho(t)y_i(t) \quad (24)$$

where ρ^R is the initial gas density in the reservoir and $\rho(t)$ is the transient gas density in the entire system (assuming instantaneous gas mixing). Equation 24 shows that the specific transient molar GSE for component i [$n_i^m(t)$, mol/g] can be measured by knowing V^R, ρ^R, y_i^R, $y_i(t)$, w^S, $\rho(t)$ and V^o, which are experimental variables for the volumetric test. Furthermore the rate of change of molar GSE of component i is given by

$$\frac{dn_i^m(t)}{dt} = -\frac{1}{w^S}(V^o + V^R)\frac{d[\rho(t)y_i(t)]}{dt} \quad (25)$$

The equilibrium GSE (n_i^m for component i at P, T, and y_i) can be calculated using Eq. 24 and the final equilibrium gas density (ρ) and composition (y_i). The same equations can be used for a pure gas [$y_i(t) = 1$].

Equations 24 and 25 show that V^o must be measured accurately in order to use the volumetric method for estimation of GSE.

Estimation of Void Volume

An experiment similar to that described above can be carried out at a temperature T_R using a very weakly adsorbing gas like helium in the reservoir side (P^R_{He}, T_R) at the start of the experiment and measuring the final equilibrium pressure P at T_R (density = ρ_{He}). Then according to Eqs. 13 and 24, one has

$$V^o = V^R[\rho^R_{\mathrm{He}} - \rho_{\mathrm{He}}]/\rho_{\mathrm{He}} - w^S\bar{K}_{\mathrm{He}}(T_R) \quad (26)$$

It is assumed that the helium expansion experiment is done at a sufficiently low starting pressure and at a relatively high temperature so that the helium GSE isotherm is linear (Eq. 13). Equation 26 shows that V^o can be accurately measured if [$\bar{K}_{\mathrm{He}}(T_R)$] is independently measured.

It is customary, in the published adsorption literature, to assume that helium at low pressures (near or below ambient) and moderate temperatures ($>$ 500 K) is not adsorbed on practical adsorbents (Maggs et al., 1960; Fernbacher and Wenzel, 1972; Suzuki et al., 1987). Thus, the second term on the righthand side of Eq. 26 can be neglected. The quantity $[V^R(\rho^R_{\mathrm{He}} - \rho_{\mathrm{He}})/\rho_{\mathrm{He}}w^S]$ is called the specific helium void volume [v^o_{He}, (cm^3/g)] of the sample side. It is then assumed that (V^o/w^S) is approximately equal to v^o_{He} in order to calculate $n_i^m(t)$ from the volumetric experimental data using Eq. 24.

Actually, Eqs. 24 and 26 can be combined to get

$$n_i^m(t) = [V^R\{\rho^R y_i^R - \rho(t)y_i(t)\}]/w^S - v^o_{\mathrm{He}}\rho(t)y_i(t) + \bar{K}_{\mathrm{He}}(T_R)\rho(t)y_i(t) \quad (27)$$

Equation 27 shows that the last term on the righthand side can be neglected only when $\rho(t)$ is relatively small. That term may be comparable with $n_i^m(t)$ at high gas-phase pressures even though $\overline{K}_{\mathrm{He}}(T_R)$ is very small. This is precisely the situation at very high pressures (large ρ), and for the case of the less selectively adsorbed component of a gas mixture since n_i^m for that component is small. This point has been well recognized by several researchers (Malbrunot et al., 1997) who recommended correction of the conventionally measured (volumetric method) surface excess isotherms of pure gases at high pressures by introducing the last term on the righthand side of Eq. 27. This correction, however, needs the knowledge of helium adsorption isotherm at the temperature (T_R) of void volume estimation.

The previous sections showed that $\overline{K}_{\mathrm{He}}(T_R)$ can be estimated by gravimetric adsorption experiments. The following section shows that the same protocol can be used for obtaining $\overline{K}_{\mathrm{He}}(T_R)$ by volumetric adsorption experiments.

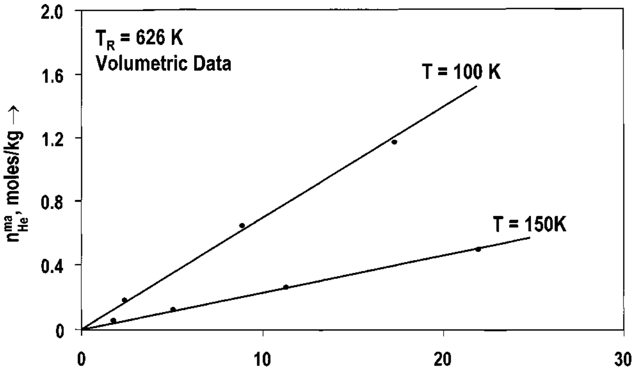

Figure 5. Apparent helium adsorption (volumetric) on BPL carbon at 100 and 150 K.

Courtesy of Fernbacher and Wenzel (1972).

Measurement of Helium Adsorption by Volumetric Method

The conventional practice to measure helium adsorption isotherm by the volumetric method is to measure the specific helium void volume (v_{He}^o) of the sample side at several temperatures. Generally, v_{He}^o decreases with increasing temperature due to decreased helium adsorption and then its value appears to be insensitive to increasing temperature (Maggs et al., 1960; Malbrunot et al., 1997). It is assumed that helium is not adsorbed at the high temperature range so that $v^o \sim v_{\mathrm{He}}^o$ in that range. The exact relationship between the actual (v^o) and helium void volumes (v_{He}^o) of the sample side per unit amount of the adsorbent is given by Eq. 26

$$v^o = v_{\mathrm{He}}^o - \overline{K}_{\mathrm{He}}(T_R) \tag{28}$$

Equation 28 shows that $\overline{K}_{\mathrm{He}}(T_R)$ can be very small at high values of T_R giving the impression that $v^o \sim v_{\mathrm{He}}^o$. This does not imply that the last term on the righthand side of Eq. 27 can be neglected when calculating n_i^m.

The apparent helium surface excess isotherm ($n_{\mathrm{He}}^{\mathrm{ma}}$ as a function of P at constant T) on an adsorbent can be measured using Eq. 27 by assuming that $\overline{K}_{\mathrm{He}}(T_R) \sim 0$ or $(v^o \sim v_{\mathrm{He}}^o)$. The apparent isotherm will also be linear in the Henry's Law region (Eq. 18).

Figure 5 shows examples of such linear apparent helium adsorption isotherms on BPL activated carbon measured by the volumetric adsorption method and by assuming that $v^o \sim v_{\mathrm{He}}^o$ at 350°C (Fernbacher and Wenzel, 1972).

It follows from Eqs. 13, 18, and 27 that in the Henry's Law region

$$\overline{K}_{\mathrm{He}}(T) = \overline{K}_{\mathrm{He}}^a(T) + \overline{K}_{\mathrm{He}}(T_R) \tag{29}$$

where T_R is the temperature of measurement of helium void volume of the adsorption system and $\overline{K}_{\mathrm{He}}(T_R)$ is the actual Henry's Law constant for helium at that temperature.

Equation 29 is identical to Eq. 17. Thus, the procedure described before can be used to estimate true Henry's Law constants for helium as functions of T by volumetrically measuring the apparent surface excess isotherms of helium at different values of T with the assumption of $(v^o = v_{\mathrm{He}}^o)$.

The above discussions demonstrate that the Henry's Law constant for helium adsorption on the adsorbent of interest at the temperature of helium void volume measurement is needed for correct estimation of GSE of other adsorbates (pure or mixture) by the volumetric method. Such information can be obtained by both gravimetric and volumetric helium adsorption measurements and by using the protocol for data analysis described in this work. The assumption of negligible helium adsorption during void volume estimation of the adsorption system can lead to serious errors in measurement of GSE at high pressures, and for the estimation of GSE of a less selectively adsorbed component of a gas mixture.

Example of Error in GSE Estimation

Figure 6 (closed circles) shows the experimental surface excess isotherm for adsorption of N_2 at 298°K on a porous alumina (BET N_2 surface area = 120 m^2/g) measured by piezometric method (Michels et al., 1961). The surface excess of N_2 increases with increasing pressure in the low-pressure region, goes through a maximum value, and then it decreases with increasing pressure, as expected from the definition of surface excess for a pure gas (Sircar, 1999). The free volume

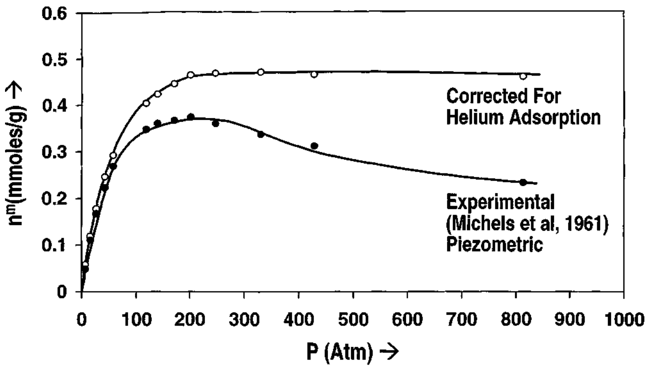

Figure 6. Adsorption of N_2 on alumina at 298 K: BET area, 120 m^2/g.

Table 2. Estimated Henry's Law Constants for Helium at 600°K*

Adsorbent	$\bar{K}_{\mathrm{He}}$ at 600 K ($\mathrm{cm^3/g}$)	q^o_{He} (kcal/mol)
5A Zeolite	0.0334	1.39
13X Zeolite	0.0319	1.11
SXC Carbon (1,670 $\mathrm{m^2/g}$)	0.0551	1.18
BPL Carbon (1,120 $\mathrm{m^2/g}$)	0.1720	0.74
Alumina (113 $\mathrm{m^2/g}$)	0.0124	0.70

*Extrapolated from data at various temperatures using Eqs. 13 and 19.

of the piezometer, in this case, was calculated by measuring the empty system volume and the helium density of the adsorbent. It was assumed that helium was not adsorbed on the alumina at temperatures of 0–50°C during the density measurements. This assumption was justified by the observation that the helium density of the adsorbent did not change appreciably when measured at 0°, 25°, and 50°C.

The data of Table 1, on the other hand, shows that the adsorption of helium on alumina (similar surface area as that for the data of Figure 6) is not negligible. The Henry's Law constant [$\bar{K}_{\mathrm{He}}$] for helium at 25°C is 0.01123 $\mathrm{cm^3/g}$. This means that the last term on the righthand side of Eq. 27 can be significant in the high pressure range. Figure 6 shows the corrected surface excess isotherm of N_2 on the alumina (open circles). It may be seen that the absolute surface excess values and the isotherm shape change dramatically in the high-pressure region due to the correction. The surface excess isotherm in the low-pressure region is only moderately changed due to the correction.

There are sporadic publications on helium adsorption isotherms over practical adsorbents (Springer et al., 1969; Fernbacher and Wenzel, 1972; Malbrunot et al., 1997]. Approximate values of the isosteric heat of adsorption of helium (q^o_{He}) and the Henry's Law constant for helium at 600 K [$\bar{K}_{\mathrm{He}}$] were extracted from these published (often very scattered) data. Table 2 reports the findings. It may be seen from the table that $\bar{K}_{\mathrm{He}}$ at 600 K is in the range of 0.03–0.06 $\mathrm{cm^3/g}$ for most practical adsorbents. Thus, the correction terms in Eqs. 15 and 27 for the gravimetric and the volumetric data can be significant in the high pressure region even if the helium void is measured at 600 K.

Summary

Both the gravimetric and the volumetric adsorption techniques directly produce the Gibbsian Surface Excesses (equilibrium and transient) as the primary experimentally measured variables for pure or multicomponent gas adsorption. This is also true for all other conventional experimental methods (Sircar, 1999). The gravimetric and the volumetric methods require the knowledge of helium adsorption isotherm on the adsorbent at the temperature of (a) adsorbent density measurement by helium pycnometry, and (b) void volume estimation for the sample side of the apparatus by helium expansion in order to unambiguously estimate GSE at high pressures and GSE for less selectively adsorbed components of a gas mixture. Experimental protocols are described for estimating pure helium adsorption isotherms.

There is no need to calculate actual amounts adsorbed from the measured GSE. The surface excess can be used to describe adsorption thermodynamics, adsorption kinetics, adsorption column dynamics, as well as mass and heat balances in adsorption columns for adsorptive process designs without introducing additional complexity (Sircar, 1999).

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Notation

K = Henry's Law constant in P domain
$\bar{K}$ = Henry's Law constant in ρ domain
$\bar{K}^a$ = apparent Henry's Law constant in ρ domain
$\bar{K}^R$ = Henry's Law constant on reference solid
M = molecular weight
n_i^o = total moles of component i in system
n_i^{ma} = apparent Gibbs surface excess for component i (molar)
n_i^m = Gibbs surface excess for component i (molar)
n^m = total Gibbs surface excess (molar)
n_i^w = Gibbs surface excess for component i (mass)
n_R^w = total Gibbs surface excess (mass) on reference solid
n^w = total Gibbs surface excess (mass)
n^{wa} = apparent Gibbs surface excess (mass)
n_i^a = moles of component i in adsorbed phase
n^a = total moles in adsorbed phase
P = gas pressure
q^o = isosteric heat of adsorption in Henry's Law region
R = gas constant
v = gas phase volume per unit mass of adsorbent
v^a = adsorbed phase volume per unit mass of adsorbent
v^o = void volume per unit mass of adsorbent
v^o_{He} = helium void volume per unit mass of adsorbent
w = mass of control volume
w^g = mass of reference solid
w^s = mass of adsorbent
w^P = mass of pan
w_o = mass under vacuum
w^R = mass of control volume for reference solid
x_i^a = mol fraction of component i in adsorbed phase
y_i = mol fraction of component i in gas phase

Greek letters

ρ = mol density of gas
ρ^a = mol density of adsorbed phase
ρ^g = chemical density of reference solid
ρ^p = chemical density of pan
ρ_w = mass density of gas
ρ^s = chemical density of adsorbent
ρ_w^a = mass density of adsorbed phase
t = time
T = temperature
T_R = temperature of helium void measurement
V = volume of gas phase in V^c
V^a = volume of Gibbsian adsorbed phase in V^c
V^c = control volume in gravimetric experiment
V^o = void volume of sample side of volumetric apparatus
V^P = volume of pan
V^R = volume of reservoir side of volumetric apparatus
V^s = volume of adsorbent

Subscripts and superscripts

i = component i
He = helium
R = initial conditions at the reservoir side of volumetric apparatus
(t) = transient property at time t

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