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R&D Note: Data Representation for Binary and Multicomponent Gas Adsorption Equilibria

S. SIRCAR
Air Products and Chemicals, Inc., 7201 Hamilton Boulevard, Allentown, PA 18195-1501

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The true experimental variables for measuring the extent of equilibrium adsorption from a pure gas or a multicomponent gas mixture are the Gibbs surface excesses defined by (Sircar, 1985):

Pure Gas

$$n^{m0} = v^{a0}[\rho^{a0} - \rho^{0}] = n^{a0} - v^{a0} \cdot \rho^{0} \qquad (1)$$

$$n^{m0} = n^{m0}[P, T] \qquad (2)$$

Multicomponent Gas

$$n_i^m = v^a\left[\rho^a x_i^a - \rho y_i\right] = n_i^a - v^a \cdot \rho y_i \qquad (3)$$

$$n_i^m = n_i^m(P, T, y_i) \qquad (4)$$

$$n^m = \sum n_i^m = v^a[\rho^a - \rho] = n^a - v^a \cdot \rho \qquad (5)$$

For a pure gas adsorption, n^{m0} is the specific surface excess (moles/g) of the component in equilibrium with a gas phase at pressure P and at the system temperature T. The density of the equilibrium gas phase is ρ^0 (moles/cm^3). The quantities v^{a0} and ρ^{a0} are, respectively, the actual specific adsorbed phase volume (cm^3/g) and adsorbed phase density (moles/cm^3) in equilibrium with the pure gas at P and T. The quantity n^{a0} is the actual specific amount (moles/g) of the pure gas adsorbed at P and T. Equation (1) shows that $n^{m0} \sim n^{a0}$ only when $\rho^{a0} \gg \rho^0$. Otherwise n^{m0} and n^{a0} can be substantially different. Equation (1) also shows that n^{a0} can be calculated from the measured n^{m0} value at a given P and T only if v^{a0} can be independently estimated at that P and T. That is generally not possible without making extraordinary assumptions about the size of v^{a0} for a given P and T. The only correct way to represent the adsorption equilibria from a pure gas is to use the measured surface excess, n^{m0}, as functions of P and T (Eq. 2).

According to the Gibbsian model of a pure gas adsorption system (Sircar, 1985), the specific surface excess defined by Eq. (1) is also given by:

$$n^{m0} = v^{g0}[\bar{\rho}^{a0} - \rho^0] = v^0[\bar{\rho}^0 - \rho^0] \qquad (6)$$

where v^{g0} is the specific volume (cm^3/g) of the Gibbsian adsorbed phase defined by an arbitrarily chosen interface located within the bulk gas phase where the adsorbate density is equal to ρ^0. Figure 1(a) is a schematic diagram of the Gibbsian model for a pure gas-solid interface. The quantity $\bar{\rho}^{a0}$ is the corresponding Gibbsian adsorbed phase density (moles/cm^3) whose value depends on the location of the Gibbsian interface. The variable v^0 is the total specific helium volume (cm^3/g) of the entire adsorption system and the variable $\bar{\rho}^0$ is the total adsorbate density (moles/cm^3) of the entire system. The variables v^0, $\bar{\rho}^0$ and ρ^0 are experimental quantities (Sircar, 1985). Thus, n^{m0} can be experimentally measured as functions of P and T. On the other hand, v^{a0} and ρ^{a0} depend on the exact location of the actual adsorbed phase (ambiguous).

Adsorption takes place at every gas-solid interface due to intermolecular attractions between the gas and solid molecules. The extent of adsorption may be very small to large. Thus, ρ^{a0} or $\bar{\rho}^{a0}$ is always larger than ρ^0 except at very high pressures where ρ^0 can be equal to or greater than ρ^{a0} or $\bar{\rho}^{a0}$. Consequently, the

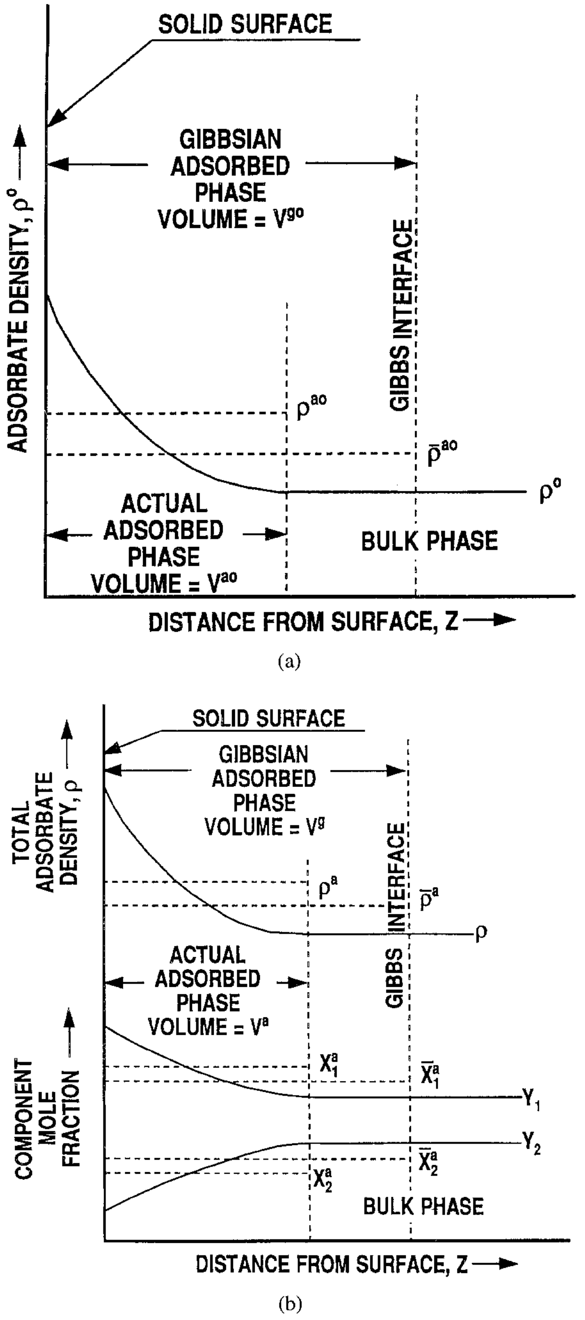

Figure 1. Schematic diagrams of Gibbsian gas-solid adsorption system: (a) pure gas, (b) binary gas mixture.

surface excess n^{m0} as a function P at constant T can go through a maximum value, pass through the value of zero ($\bar{\rho}^{a0} = \rho^0$) and finally become negative at larger values of ρ^0. This has been experimentally demonstrated (Michels et al., 1961). The surface excess (n^{m0}) is always positive at low pressures [ρ^{a0}, $\bar{\rho}^{a0} > \rho^0$]. It is equal to zero in the low pressure region only when $\rho^0 = 0$, which is the trivial case of no adsorption.

The surface excess variable is approximately equal to the actual amount adsorbed ($n^{m0} \sim n^{a0}$) only when the actual adsorbed phase density is much larger than the bulk phase gas density [$\rho^{a0} \gg \rho^0$]. The specific molar density of the Gibbsian adsorbed phase ($\bar{\rho}^{a0}$) can have any value depending on the location of the interface. The quantity [$v^{g0}\bar{\rho}^{a0}$] is not equal to the actual amount adsorbed (n^{a0}).

For a multicomponent gas adsorption, n_i^m is the specific surface excess (moles/g) of component i of a gas mixture in equilibrium with a gas phase at pressure P, system temperature T, and gas phase mole fraction $y_i[\Sigma y_i = 1]$ for component i. The density (moles/cm^3) of the equilibrium gas phase is ρ. The quantities v^a, ρ^a and x_i^a are, respectively, the specific actual adsorbed phase volume (cm^3/g), the adsorbed phase density (moles/cm^3) and the actual adsorbed phase mole fraction of component i in equilibrium with the gas mixture at P, T and y_i. The quantity n_i^a is the specific actual amount (moles/g) of component i adsorbed at P, T and y_i. Equation (3) shows that $n_i^m \sim n_i^a$ only when $\rho^a x_i^a \gg \rho y_i$. This requires that the criterion of $\rho^a \gg \rho$ alone is not sufficient for n_i^m to be equal to n_i^a. The adsorbed phase composition of component i must also be such that the inequality ($x_i^a \gg \rho y_i/\rho^a$) is satisfied (Sircar, 1985). Otherwise, n_i^m and n_i^a can be substantially different. Again, Eq. (3) shows that n_i^a can be calculated from the measured n_i^m values at a given P, T and y_i only if v^a can be independently estimated at that P, T and y_i. Since, that is not generally possible without making specific assumptions about the adsorbed phase size for a given P, T and y_i, the only correct way to represent the adsorption equilibria from a multicomponent gas mixture is to use the measured surface excess of component i, n_i^m, as functions of P, T and y_i (Eq. 4). The total specific surface excess n^m (moles/g) for adsorption from a multicomponent gas mixture is defined by Eq. (5). It shows that the total actual specific amount adsorbed, n^a (moles/g), from the gas mixture cannot be estimated from the measured n^m values unless v^a is known as functions of P, T and y_i. All specific quantities (surface excess and actual amount adsorbed) described above are based on unit weight of the adsorbent. The adsorbent is assumed to be inert.

According to the Gibbsian model of a multicomponent adsorption system (Sircar, 1985), the specific surface excess of component i of the mixture, defined by Eq. (3), is also given by:

$$n_i^m = v^g\left[\bar{\rho}^a \bar{x}_i^a - \rho y_i\right] = \bar{v}[\bar{\rho}\bar{y}_i - \rho y_i] \qquad (7)$$

where v^g is the specific volume (cm^3/g) of the Gibbsian adsorbed phase for the multicomponent adsorption system defined by an arbitrarily chosen interface located within the bulk gas phase where the adsorbate density and mole fraction of component i are respectively ρ and y_i. Figure 1(b) is a schematic diagram of the Gibbsian model for a binary gas-solid interface. The quantities $\bar{\rho}^a$ and $\bar{x}_i^a$ are, respectively, the corresponding Gibbsian adsorbed phase density and mole fraction of component i whose values depend on the location of the Gibbsian interface. The variable $\bar{v}$ is the total specific helium volume (cm^3/g) of the entire multicomponent adsorption system. The quantities $\bar{\rho}$ and $\bar{y}_i$ are the total adsorbate density and mole fraction of component i in the entire system. The quantities $\bar{v}, \bar{\rho}, \rho, \bar{y}_i$ and y_i can be experimentally measured (Sircar, 1985). Thus, n_i^m can be estimated as functions of P, T and y_i even though the variables v^a, ρ^a, x_i^a, $v^g\bar{\rho}^a$, $\bar{x}_i^a$ cannot be estimated unambiguously.

The experimentally measured surface excesses (pure and multicomponent) are often loosely called amounts adsorbed in the adsorption literature and a measured selectivity of adsorption (S_{ij}^m) for component i over component j is defined for multicomponent gas system as:

$$S_{ij}^m = \frac{n_i^m \cdot y_j}{n_j^m \cdot y_i} = \frac{x_i^m \cdot y_j}{x_j^m \cdot y_i} \qquad (8)$$

$$S_{ij}^m = S_{ij}^m(P, T, y_i) = S_{ij}^m\left(n_i^m, T\right) \qquad (9)$$

The variable x_i^m [$=n_i^m/n^m$; $\sum x_i^m = 1$] in Eq. (8) is loosely called the adsorbed phase mole fraction of component i in equilibrium with the gas phase at P, T and y_i. The actual selectivity, $S_{ij}^a[=x_i^a y_j/x_j^a y_i]$ is not equal to the measured selectivity S_{ij}^m and it cannot generally be estimated for reasons given earlier. The measured selectivity is a function of P, T and y_i or n_i^m and T (Eq. 9).

The definition of the equilibrium selectivity of adsorption in terms of the apparent mole fractions of the components in the adsorbed phase and those in the gas phase (Eq. 8) is analogous to that of relative volatility used for describing vapor-liquid equilibria (VLE). Thus, a common practice, following the VLE tradition, is to represent binary ($i = 1, 2$) gas adsorption equilibria in terms of x_1^m as a function of y_1 for a given P and T (Valenzuela and Myers, 1989). That alone, however, does not completely define the binary adsorption system (like VLE), and a plot of the total surface excess (n^m) as a function of y_1 for a given P and T is frequently used (Valenzuela and Myers, 1989) to complement the $x_1^m - y_1$ plot.

These two plots are often used to compare the experimentally measured binary adsorption equilibrium data with those calculated by a correlative or predictive model (Valenzuela and Myers, 1984). Unfortunately, the following analysis will show that such comparison can be very misleading because the errors in calculating x_1^m and n^m from the fundamental variables for a binary system (n_1^m and n_2^m as functions of y_1 at a given P and T) can be significantly suppressed compared to the errors in the measurement or prediction of the base variables (n_i^m).

A conventional error analysis using Eqs. (5) and (8) and the definition of the variable x_i^m for a binary system shows that:

$$\frac{dx_1^m}{x_1^m} = \frac{y_2}{\left(S_{12}^m y_1 + y_2\right)}\left[\frac{dn_1^m}{n_1^m} - \frac{dn_2^m}{n_2^m}\right] \qquad (10)$$

$$\frac{dn^m}{n^m} = \left[\frac{S_{12}^m y_1}{S_{12}^m y_1 + y_2}\right]\left[\frac{dn_1^m}{n_1^m}\right] + \frac{y_2}{\left(S_{12}^m y_1 + y_2\right)}\left[\frac{dn_2^m}{n_2^m}\right] \qquad (11)$$

Equations (10) and (11), respectively, describe the errors in calculating x_1^m and n^m for a given set of values of y_1 and S_{12}^m (apparent selectivity of adsorption of component 1 over component 2) and a specified set of errors in measuring or predicting n_i^m ($=dn_i^m/n_i^m$). According to Eqs. (10) and (11), the limiting errors in calculating x_1^m and n^m at the infinite dilutions of component 1 ($y_1 \to 0$) and component 2($y_1 \to 1$) are:

$$y_1 \to 0 \quad \frac{dx_1^m}{x_1^m} = \left[\frac{dn_1^m}{n_1^m} - \frac{dn_2^m}{n_2^m}\right]; \quad \frac{dn^m}{n^m} = \frac{dn_2^m}{n_2^m} \qquad (12)$$

$$y_1 \to 1 \quad \frac{dx_1^m}{x_1^m} = 0; \quad \frac{dn^m}{n^m} = \frac{dn_1^m}{n_1^m} \qquad (13)$$

Equations (12) and (13) show that the errors in the variable x_1^m vary between the sum of the errors in measuring or predicting the base variables at the limit of $y_1 \to 0$ to zero at the limit of $y_1 \to 1$. On the other hand, the error in the variable n^m vary between the error in measuring or predicting the base variable n_2^m at the limit of $y_1 \to 0$ to the error in measuring or predicting the base variable n_1^m at the limit of $y_1 \to 1$. The errors in the variables x_1^m and n^m for a specific value of y_1 depend on the errors in measuring or predicting the base variables (n_i^m) at that value of y_1 as well as on the apparent selectivity of adsorption of component 1 over component 2 at the appropriate values of P, T and y_1.

Typically the errors in measuring or predicting the surface excess of the more selectively adsorbed component (n_1^m) of a binary system are much less than those for the less selectively adsorbed component (n_2^m). Specifically, the errors in measuring or predicting n_2^m can be very large when S_{12}^m is high due to the relatively smaller values of n_2^m. Furthermore, the errors in measuring or predicting n_1^m and n_2^m at the limits of infinite dilutions of these components (respectively $y_1 \to 0$ and $y_1 \to 1$) are generally large.

Table 1 shows the errors in calculating x_1^m and n^m by Eqs. (10) and (11) for different values of S_{12}^m when the relative errors in predicting n_1^m and n_2^m are, respectively, ±5% and ±20% at all values of y_1. It may be seen from Table 1 that the errors in the variables x_1^m and n^m are very low and they do not reflect the true errors in the base variables (n_i^m) in the region of moderate to large values of y_1 (≥ 0.2). The effect is much more pronounced when S_{12}^m is large. For example, the errors in calculating x_1^m and n^m are less than ±10% even at small values of y_1 (≥ 0.05) when S_{12}^m is large (≥ 50). It can be shown that this behavior is exhibited even when the errors in the base variables (n_i^m) are functions of y_1.

Table 1. Error in calculating x_1^m and n^m for relative errors of ±5% and ±20% in predicting n_1^m and n_2^m, respectively.

	% error in estimating x_1^m and n^m					
	$S_{12}^m = 5$		$S_{12}^m = 10$		$S_{12}^m = 50$	
y_1	x_1^m	n^m	x_1^m	n^m	x_1^m	n^m
0.00	25.0	20.0	25.0	20.0	25.0	20.0
0.05	19.8	16.8	16.4	14.8	6.9	9.1
0.10	16.1	14.6	11.8	12.1	3.8	7.3
0.20	11.1	11.7	7.1	9.3	1.8	6.1
0.30	7.9	9.7	4.7	7.8	1.1	5.7
0.50	4.2	7.5	2.3	6.4	0.5	5.3
0.70	1.9	6.2	1.0	5.6	0.2	5.1
0.90	0.5	5.4	0.3	5.2	0.0	5.0
1.00	0.0	5.0	0.0	5.0	0.0	5.0

The above discussion clearly shows that the binary equilibrium adsorption data predicted or correlated by a model should not be compared with the experimental data in terms of $x_1^m - y_1$ and $n^m - y_1$ plots. The differences between the experimental and the theoretically calculated values of the base variables (n_i^m) will be underestimated. It is recommended that the accuracy of prediction or correlation of equilibrium adsorption data by a model for a multicomponent system should be tested by comparing (a) n_i^m values as functions of P for isothermal data at constant y_i, or (b) n_i^m values as functions of y_i for isothermal data at constant P. Data for case (a) can be represented by a two dimensional plot for a multicomponent system. Data for case (b) can be represented by a two dimensional plot only for a binary system or for a multicomponent system where the gas phase mole fractions of all components except two are held constant.

References

Michels, A., P.G. Menon, and C.A. ten Seldam, "Adsorption at High Pressures," *Recl. Trav. Chim. Pays-Bas.*, **80**, 483 (1961).

Valenzuela, D.P. and A.L. Myers, "Gas Adsorption Equilibria," *Sep. Purif. Methods*, **13**, 153 (1984).

Valenzuela, D.P. and A.L. Myers, *Adsorption Equilibrium Data Book*, Prentice Hall, New Jersey, 1989.

Sircar, S., "Excess Properties and Thermodynamics of Multicomponent Gas Adsorption," *J. Chem. Soc. Faraday Trans I.*, **81**, 1541 (1985).