

Gravimetric measurement of adsorption from binary gas mixtures

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Abstract – A precise experimental method for studying binary vapor-liquid equilibrium is to measure total pressure (P) as a function of the mole fraction in the liquid phase (x). The mole fraction in the vapor (y) is calculated from isothermal P - x experimental data using the Gibbs-Duhem equation. A similar procedure for adsorption is to measure total mass (m) of gas adsorbed as a function of the mole fraction in the vapor phase (y). Then the composition of the adsorbed phase is calculated from isothermal m - y experimental data using the Gibbs isotherm. Only a few experimental points are needed for the mixture. The method is rigorous even when the adsorbed phase is nonideal.

INTRODUCTION

The standard experimental procedure for equilibrium adsorption from a binary gas mixture is to report two measured variables: total amount adsorbed per unit mass of adsorbent (n_i) and mole fraction of component number 1 in the adsorbed phase (x_1). Independent variables for each experimental point are temperature (T), total pressure (P), and mole fraction of component number 1 in the gaseous phase (y_1). The volumetric method used to measure adsorption of pure gases is less successful for mixtures because the rate of counterdiffusion of different species within the pores is very slow. Equilibration is accelerated by recirculating the gas mixture through the adsorbent. The composition of the adsorbed phase is determined by desorption into an evacuated space followed by analysis.

Measuring the composition of the adsorbed phase is actually unnecessary. x_1 can be calculated from experimental data on the total amount adsorbed $n_i(T, P, y_1)$ using rigorous thermodynamic equations. Data on the total mass adsorbed $m_i(T, P, y_1)$ obtained with a gravimetric apparatus provide sufficient information to calculate x_1 . The gravimetric method is more convenient and easier to automate than the volumetric method. This paper describes a new procedure for calculating adsorbed-phase composition from gravimetric data.

THERMODYNAMICS

The thermodynamic principles can be clarified by reference to a similar method that is well established for vapor-liquid equilibrium (VLE) measurements. Barker¹ proposed a thermodynamic procedure, which was refined and applied to a series of binary and ternary mixtures by Van Ness and coworkers², for calculating vapor-phase composition from total pressure measurements as a function of liquid-phase composition. The vapor space of the equilibrium cell is made very small so that the composition of the liquid is very nearly equal to the composition of the charge to the cell. Degassing of the liquid phase before the experiment is essential. Experimental data for a binary mixture are isothermal measurements of the total pressure as a function of liquid-phase composition, $P(x_1)$. The numerical procedure is to optimize values for constants in an equation for liquid-phase activity coefficients using as objective function the sum of squares of deviations ΔP between the calculated and experimental points on the $P(x_1)$ curve. The equation for activity coefficients must be sufficiently flexible to account for the nonideality of the liquid phase, as judged by a statistical test of whether the deviations ΔP lie within the estimated experimental error.

The thermodynamic procedure for VLE is based on the Gibbs-Duhem equation, which is a differential equation connecting the variables P , x_1 , and y_1 . For adsorption the situation is complicated by an additional independent variable: the spreading pressure Π in the adsorbed phase. In the following, spreading pressure will be written in terms of the variable $\psi = \Pi A/RT$, which has the same units as n , the specific amount adsorbed (mol/kg). The Gibbs adsorption isotherm is:

$$d\psi = n_1[x_1 d \ln(Py_1) + x_2 d \ln(Py_2)] \quad (1)$$

for which the only assumption is that the fugacity coefficient $\phi_i = 1$ in the equation for gas-phase fugacity $f_i = Py_i\phi_i$. Extension of the method to imperfect gases is readily accomplished if necessary. The important point is that Eq. (1) is correct even when the adsorbed phase is nonideal.

Gravimetric measurements are the total mass of gas m_i adsorbed per unit mass of adsorbent as a function of pressure P and gas-phase composition y_i . The total amount adsorbed n_i depends on the molecular weights of the adsorbates:

$$n_i = \frac{m_i}{M_1 x_1 + M_2 (1 - x_1)} \quad (2)$$

The partial derivatives of Eq. (1) are:

$$\begin{aligned} \left[\frac{\partial \psi}{\partial y_i} \right]_P &= n_i \left[\frac{x_1}{y_i} - \frac{(1 - x_1)}{(1 - y_i)} \right] \\ \left[\frac{\partial \psi}{\partial P} \right]_{y_i} &= \frac{n_i}{P} \end{aligned} \quad (3)$$

Substitution of Eq. (2) into (3) gives a set of first-order partial differential equations that can be solved for the two unknowns, ψ and x_1 . Boundary conditions are the function $\psi(P)$ for the pure gases at $y_i = 0$ and $y_i = 1$, and $\psi = 0$ at $P = 0$ for $0 \leq y_i \leq 1$.

This procedure was used to calculate adsorbed-phase compositions from gravimetric data for adsorption of binary gas mixtures of benzene and cyclohexane on graphitized carbon and on activated carbon³. However the integration required about 100 experiment points for the function $m_i(P, y_i)$. A simpler procedure requiring less data is needed.

SOLUTION THERMODYNAMICS IN ADSORBED PHASE

The VLE procedure is based on an accurate equation for activity coefficients in the liquid phase. For example, the excess Gibbs free energy for the Wilson equation⁴ is:

$$\frac{g^e}{RT} = -\sum_i x_i \ln \left[\sum_j (x_j \Lambda_{ij}) \right] \quad (4)$$

For a binary mixture, activity coefficients from Eq. (4) contain two constants, Λ_{12} and Λ_{21} , whose values would be found by the optimization procedure. If the statistical test is not satisfied, then a more complicated equation containing more constants should be used. Eq. (4) is only an example.

In adsorption Eq. (4) (or a more complex equation containing more constants) can be used to describe adsorbed-phase activity coefficients, but only at constant ψ . Results from Monte-Carlo calculations⁵ of adsorption on heterogeneous surfaces indicate that the dependence of g^e on ψ and x_1 has the form:

$$g^e = (1 - e^{-c\psi}) g^e(x_1) \quad (5)$$

where g^e is any excess Gibbs free energy function from VLE like Eq. (4) that satisfies the differential equation:

$$\sum_i x_i d \ln \gamma_i = 0 \quad (6)$$

for activity coefficients γ_i . The equilibrium conditions for fugacity are then:

$$P y_i = P_i^\circ \gamma_i x_i \quad (7)$$

where the adsorbed-phase activity coefficients are obtained from:

$$\ln \gamma_i = \left(\frac{\partial (n_i g^e / RT)}{\partial n_i} \right)_{T, \psi, n_j} \quad (8)$$

For example, for the particular case of Eq. (4):

$$\ln \gamma_i = (1 - e^{-c\psi}) \left[1 - \ln \sum_j (x_j \Lambda_{ij}) - \sum_k \left(\frac{x_k \Lambda_{ki}}{\sum_j x_j \Lambda_{kj}} \right) \right] \quad (9)$$

Nonidealities ($g^e \neq 0$) in the adsorbed phase according to Eq. (5) generate corrections to the ideal area change upon mixing⁶ so that

$$\frac{1}{n_i} = \sum_{i=1}^N \left(\frac{x_i}{n_i^{\circ}} \right) + ce^{-\psi} \left(\frac{g^{\circ}}{RT} \right) \quad (10)$$

n_i° and P_i° refer to the standard states for adsorption of single gases at the same value of ψ as the mixture.

The procedure is summarized as follows. Given the single-gas adsorption isotherms $n_i^{\circ}(P_i^{\circ})$, ψ is obtained from:

$$\psi = \int_0^{P_i^{\circ}} \frac{n_i^{\circ}}{P_i^{\circ}} dP_i^{\circ} \quad (11)$$

Inversion of this relation gives $P_i^{\circ}(\psi)$ and therefore $n_i^{\circ}(\psi)$. Both γ_i and G° in the above equations are functions of ψ and x_1 . Eqs. (2), (7), and (10) constitute a set of 4 algebraic equations in 4 unknowns: m_i , n_i , x_1 , and ψ . Given values of T , P , and y_1 , this set of equations is solved for m_i and the result is compared with the experimental value. Values for the three constants c , Δ_{12} , and Δ_{21} are determined by optimization using the sum of squares of deviations Δm_i between the calculated and experimental points as the objective function. If agreement is unsatisfactory, then Eq. (4) is replaced by a more flexible equation containing more constants.

Only a few mixture points (about a dozen) are needed. After obtaining values for the constants of the equation for adsorbed-phase activity coefficients by optimization, the adsorbed-phase composition may be calculated as a function of the independent variables T , P , and y_1 . Because of Eq. (11), the procedure is sensitive to the accuracy of the single-gas adsorption isotherms.

TEST OF THEORY

The ability of the theory to predict accurate values of composition was tested using the experimental data of Talu and Zwiebel⁷, who measured the composition of both the gas and adsorbed phases. First, experimental data for the amount adsorbed (moles) were converted to mass adsorbed. Then the composition of the adsorbed phase was calculated from the simulated gravimetric data and compared with experiment.

Adsorption isotherms of the pure gases CO_2 , H_2S , and C_3H_8 measured⁷ at 30°C on H-mordenite are reproduced in Figs. 1–3. These isotherms are very steep at the origin and the isosteric heats of adsorption fall rapidly with coverage, indicating a high degree of energetic heterogeneity of adsorption sites.

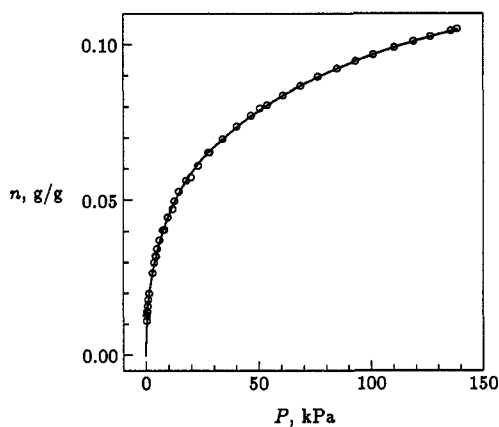


Figure 1. Adsorption of CO_2 on H-mordenite at 303.15 K.

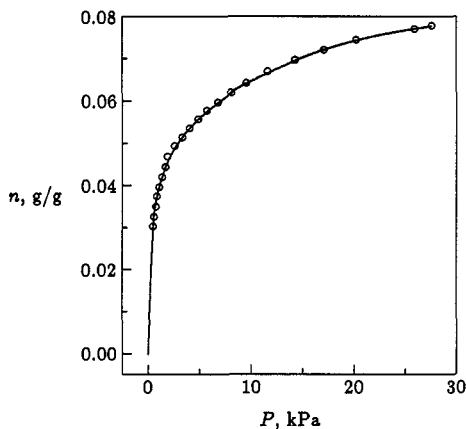


Figure 2. Adsorption of H_2S on H-mordenite at 303.15 K.

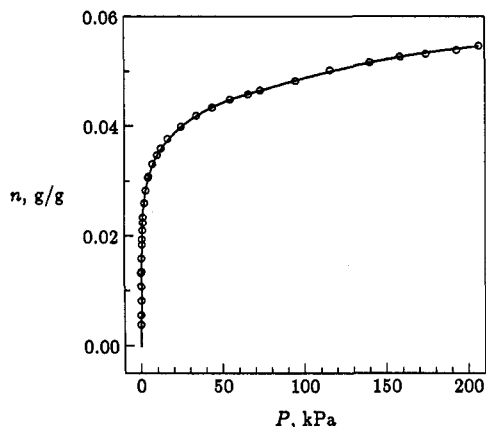


Figure 3. Adsorption of C_3H_8 on H-mordenite at 303.15 K.

Fig. 4 shows the simulated gravimetric data for mixtures of CO_2 and C_3H_8 adsorbed at constant temperature and pressure. Four additional experimental points at the same temperature but other pressures⁷ were used to derive values of constants in the thermodynamic equations for the excess Gibbs free energy, Eq. (5). Of course, experimental data for the composition of the adsorbed phase were not used in the optimization. The composition of the adsorbed phase (x_1) was calculated from the thermodynamic equations with their derived constants and compared with experiment in Fig. 5. The $\text{CO}_2 + \text{C}_3\text{H}_8$ system is quite nonideal as indicated by its azeotrope at $x_1 = y_1 = 0.54$. Calculated values of x_1 are almost in quantitative agreement with experiment.

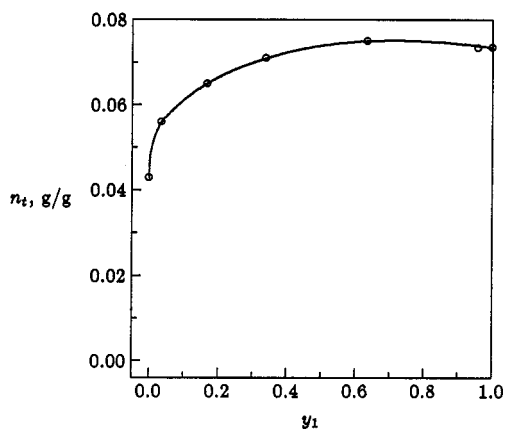


Figure 4. Experimental data (o) for total mass of gas adsorbed from mixtures of CO_2 (1) and C_3H_8 (2) on H-mordenite at 303.15 K and 41.13 kPa.

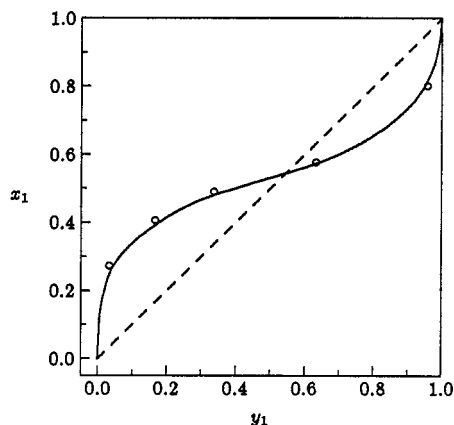


Figure 5. Composition of adsorbed phase (x_1) versus composition of gas phase (y_1) for mixtures of CO_2 (1) and C_3H_8 (2) adsorbed on H-mordenite at 303.15 K and 41.13 kPa. Solid line: theory. o: experiment.

Simulated gravimetric data for mixtures of H_2S and CO_2 are reproduced in Fig. 6; six additional experimental points for m_t at other pressures were used⁷. The calculated composition of the adsorbed phase in Fig. 7 agrees very well with experiment. These data exhibit small deviations from Raoult's law in the adsorbed phase. Therefore the phase diagram on Fig. 7 could have been predicted with fair accuracy from the single-gas isotherms in Figs. 1 and 2 by the theory of ideal adsorbed solutions⁸, without using the mixture data in Fig. 6.

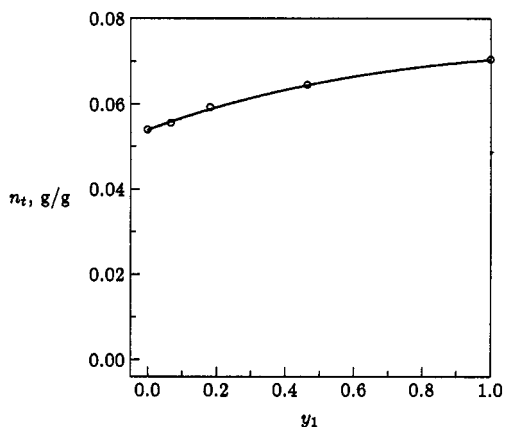


Figure 6. Experimental data (o) for total mass of gas adsorbed from mixtures of H_2S (1) and CO_2 (2) on H-mordenite at 303.15 K and 15.67 kPa.

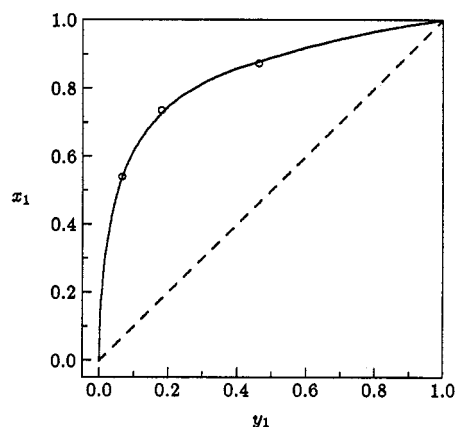


Figure 7. Composition of adsorbed phase (x_1) versus composition of gas phase (y_1) for mixtures of H_2S (1) and CO_2 (2) adsorbed on H-mordenite at 303.15 K and 15.67 kPa. Solid line: theory. o: experiment.

Finally, Fig. 8 shows "gravimetric" data for adsorption of mixtures of H_2S and C_3H_8 . Four values of total amount adsorbed at other pressures⁷ were used to carry out the optimization. Again, experimental and calculated values of adsorbed-phase composition in Fig. 9 are in very good agreement even though this system is highly nonideal.

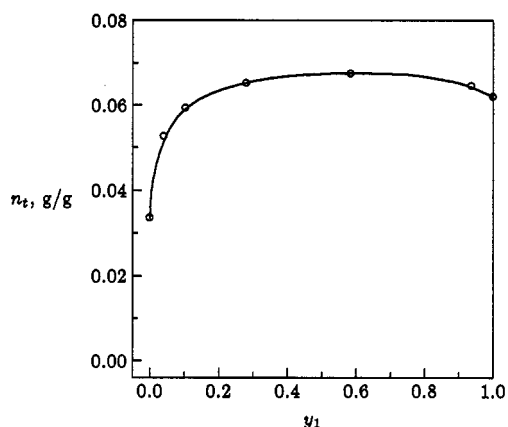


Figure 8. Experimental data (o) for total mass of gas adsorbed from mixtures of H_2S (1) and C_3H_8 (2) on H-mordenite at 303.15 K and 8.13 kPa.

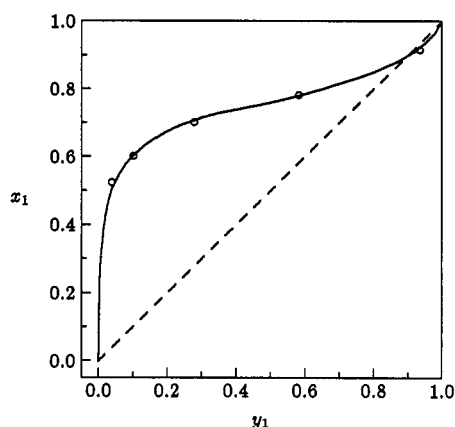


Figure 9. Composition of adsorbed phase (x_1) versus composition of gas phase (y_1) for mixtures of H_2S (1) and C_3H_8 (2) adsorbed on H-mordenite at 303.15 K and 8.13 kPa. Solid line: theory. o: experiment.

DISCUSSION OF RESULTS

Our results show that the total amount adsorbed is a sensitive indicator of nonideality in the adsorbed phase. Binary mixtures $\text{CO}_2 + \text{C}_3\text{H}_8$ and $\text{H}_2\text{S} + \text{C}_3\text{H}_8$ exhibit very large negative deviations from Raoult's law, with activity coefficients at infinite dilution $\gamma^\infty < 0.1$. In fact, these two systems are some of the most nonideal ones yet reported in the literature of adsorption. The physical explanation of these nonidealities are twofold. First, all three adsorbates (CO_2 , H_2S , C_3H_8) exhibit a high degree of energetic heterogeneity of adsorption energies, as indicated by the rapid decrease of their isosteric heat of adsorption with surface coverage. This accounts for some of the nonideality. Second, the C_3H_8 molecules are too large to penetrate the side pockets of the main channels in H-mordenite, but the smaller CO_2 and H_2S molecules can easily enter the side pockets. Therefore, within these pockets, neither small molecule has to compete with C_3H_8 for surface area. This effect of partial exclusion generates apparent negative deviations from Raoult's law. These large negative deviations nearly disappear if the combined effects of exclusion and energetic heterogeneity of adsorption sites are taken into account. However, the objective of this research was to establish that adsorbed-phase nonidealities, regardless of their magnitude or physical basis, can be handled by a thermodynamic approach.

It is concluded that gravimetric measurements are a sensitive and convenient method for measuring equilibrium adsorption of gas mixtures.

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