A Simplified Method for the Prediction of Multicomponent Adsorption Equilibria from Single Gas Isotherms

A. J. KIDNAY
National Bureau of Standards, Boulder, Colorado

A. L. MYERS
University of Pennsylvania, Philadelphia, Pennsylvania

The ideal adsorbed solution theory of Myers and Prausnitz (7) provides an accurate and thermodynamically consistent method for predicting multicomponent adsorption equilibria. The major difficulty in the application of this theory lies in the calculation of the spreading pressure curves for the pure adsorbates. The purpose of this article is to show that in many cases of practical interest, the spreading pressure calculations may be greatly simplified or altogether eliminated with little or no loss in the accuracy of the calculations. The problem of adsorption azeotropy is also briefly discussed.

In many cases the multicomponent equilibrium adsorption data necessary for the design of large-scale adsorption operations can be predicted by using ideal adsorbed solution theory (7). The application of this theory, however, requires the calculation of the spreading pressures from the pure gas isotherms, and this calculation is attended with some mathematical as well as practical difficulties.

The purpose of this paper is threefold: to show that a simple transformation alleviates the mathematical difficulties in the calculation of the spreading pressure; to show that in many cases of practical interest, the spreading pressure calculations can be avoided altogether; and to discuss the problem of adsorption azeotropy.

THE IDEAL ADSORBED SOLUTION

The concept of an ideal adsorbed solution has been discussed previously (7). The thermodynamic equations which define an ideal adsorbed solution are analogous to those for liquid solutions at low vapor pressures, as shown in Table 1.

The ideal adsorbed solution satisfies the Gibbs adsorption isotherm, and therefore predictions of multicomponent adsorption equilibria are thermodynamically consistent. A detailed comparison with experimental data of the ideal adsorbed solution theory has shown that the method provides excellent predictions of multicomponent adsorption equilibria. However, it is significant that all of these comparisons with experimental data (7) were for adsorbed solutions at less than monolayer coverage.

TABLE 1. COMPARISON OF LIQUID AND ADSORBED SOLUTIONS

	Liquid solution	Adsorbed solution
Intensive variables held constant during conceptual mixing process	P, T	π, T
Density of solution	$\frac{1}{\rho} = \frac{x_1}{\rho_1^\circ} + \frac{x_2}{\rho_2^\circ}$	$\frac{1}{n_t} = \frac{x_1}{n_1^\circ} + \frac{x_2}{n_2^\circ}$
Raoult's law	$Py_i = P_i^\circ x_i$	$Py_i = P_i^\circ x_i$
Physical meaning of P_i°	Saturation vapor pressure of pure liquid i at T	Vapor pressure of adsorbate i at T, π

The intensive variable for the adsorbed phase is the spreading pressure π. Although this variable plays a key role in the thermodynamic description of the adsorbed phase (3), numerical values of spreading pressure are seldom tabulated with other experimentally measured quantities such as the amount adsorbed. One reason for this omission is that the calculation of spreading pressure is attended with certain mathematical difficulties which are described below.

CALCULATION OF SPREADING PRESSURE FOR PURE GAS ISOTHERMS

If the adsorption isotherm of a pure gas $n(P)$ is known, the spreading pressure of the adsorbed phase at the total pressure P° is given by

$$\frac{\pi A}{RT} = \int_0^{P^\circ} \frac{n}{P}\, dP \tag{1}$$

The objective in this instance is the determination of vapor pressures of different adsorbates on the same adsorbent for the variable π. The area A is constant for different adsorbates on the same adsorbent, and it is sufficient to determine vapor pressures as a function of the variable $\pi A/RT$. Therefore the numerical value of A is not needed.

The experimental values for the integrand (n/P) become very large as the pressure approaches zero, as shown in Figure 1 for the adsorption of ethane on activated carbon. Consequently, a large amount of low coverage data is necessary if the graphical integration is to be accomplished with any degree of accuracy. For this reason, many investigators fit the low coverage portion of the adsorption isotherm with an empirical equation and integrate analytically. This procedure was used by Hill, Emmett, and Joyner (3) and by Myers and Prausnitz (7). But the

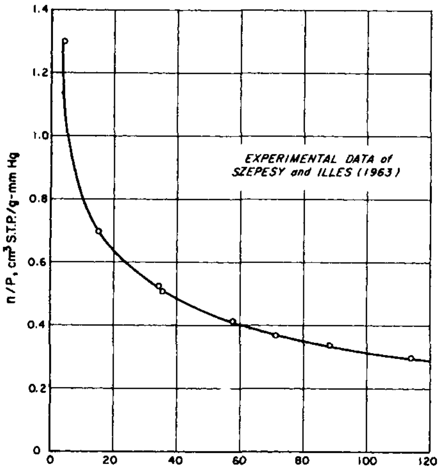

Fig. 1. Graphical integration of *n/P* to obtain spreading pressure of ethane adsorbed on activated carbon at 20°C.

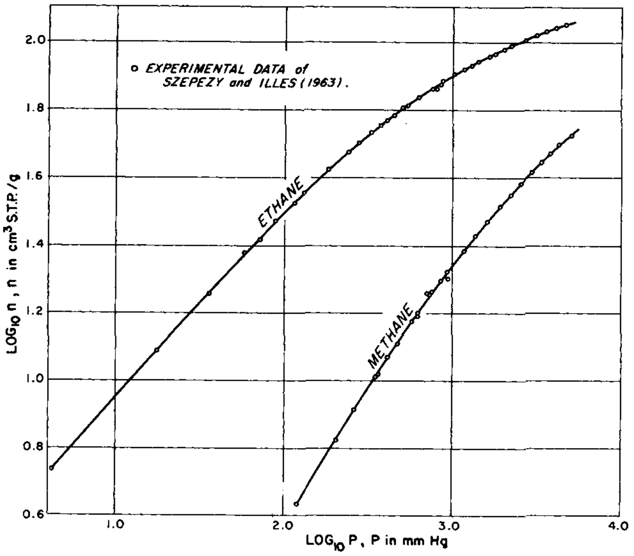

Fig. 3. Adsorption isotherms of methane and ethane on activated carbon at 20°C.

integral of Equation (1) is sensitive to the analytic function chosen for the extrapolation to zero pressure, and therefore the spreading pressures calculated in this way are subject to uncertainty.

The difficulties described above may often be alleviated by changing the variable of integration. By changing the independent variable from P to n, Equation (1) becomes

$$\frac{\pi A}{RT} = \int_0^{n^\circ} \frac{d \log P}{d \log n}\, dn \qquad (2)$$

Thus the spreading pressure becomes a function of the total amount adsorbed n°. Figure 2 shows a plot of the integrand of the integral in Equation (2) vs. n for pure ethane and pure methane adsorbed on activated carbon at 20°C. The slopes $d \log P/d \log n$ were obtained from the experimental data of Szepesy and Illés (9), shown in Figure 3.

It is known (4) that the slope $d \log P/d \log n$ intersects the ordinate at unity for zero surface coverage. Referring to Figure 2 for ethane, we see that the slope must be extrapolated from point A to point E, because experimental data were not obtained for this low coverage portion of the adsorption isotherm. For ethane the estimated extrapolation is the curve ADE. The curves ABE and ACE represent extremes for the extrapolation. At the lowest surface coverage measured experimentally (n = 5.45 cc. STP/g.) the absolute uncertainty in $\pi A/RT$ due to the extrapolation is ± 10%. At higher surface coverage, say, at n = 50 cc. STP/g., this uncertainty is only ± 1%. Since the curves ABE and ACE represent extremes in the extrapolation, the error in $\pi A/RT$ due to the extrapolation is smaller than the values quoted above.

In summary, the integral of Equation (1) is difficult to evaluate because the integrand becomes very large at low pressures, but this difficulty may be overcome by using the integral of Equation (2) to calculate spreading pressures in the low coverage region.

Figure 4 shows the spreading pressures of pure ethane and pure methane, calculated as described above. Once the spreading pressures of the pure adsorbates have been determined, the mixture adsorption equilibria can be calculated with the ideal adsorbed solution theory. Such a calculation for the methane-ethane system has been carried out (7), and the predictions were found to be in excellent agreement with the experimental data.

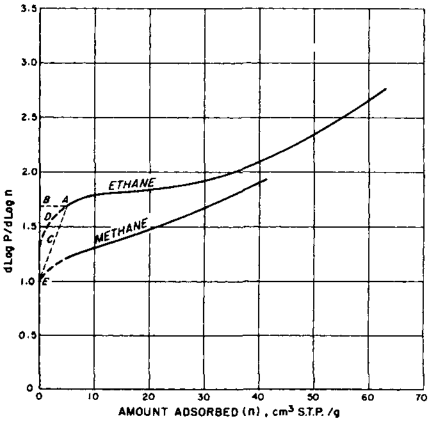

Fig. 2. Graphical integration of *d* log *P/d* log *n* to obtain spreading pressure.

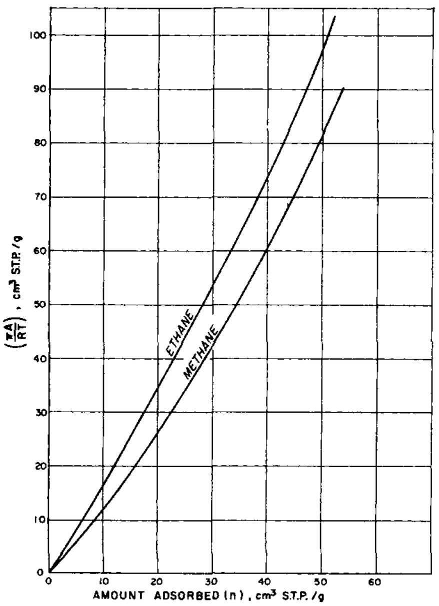

Fig. 4. Spreading pressure for methane and ethane adsorbed on activated carbon at 20°C.

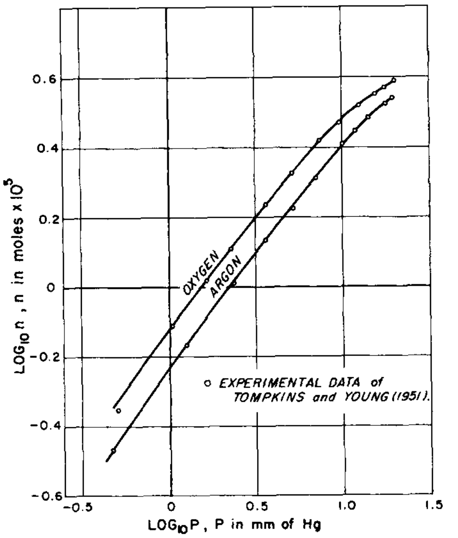

Fig. 5. Adsorption isotherms of oxygen and argon on cesium iodide at 77.49°K.

THE PREDICTION OF MULTICOMPONENT ADSORPTION EQUILIBRIA—A SIMPLIFIED METHOD

Although ideal adsorbed solution theory (7) provides a thermodynamically consistent means for predicting multicomponent equilibria, the necessary calculations of spreading pressures are tedious and time-consuming. However, under certain conditions to be described, a simplified technique for the prediction of multicomponent equilibria can be used which eliminates the necessity for calculating the spreading pressures, and which yields predictions which are entirely adequate for engineering design applications.

Equation (2) indicates that the spreading pressure is given by the integral of the slope of the adsorption isotherm on a logarithmic plot of P vs. n. If the slopes at all values of n are the same for different adsorbates, then the spreading pressure curves for different adsorbates, when plotted vs. n, will coincide. It is found experimentally that such a coincidence often occurs, particularly below monolayer surface coverage.

If the spreading pressures of different adsorbates are nearly equal for a given amount adsorbed, the prediction of multicomponent adsorption equilibria can be greatly simplified. The equality of spreading pressures of different adsorbates at constant amount adsorbed means that the term $P_i^\circ(\pi)$ can be replaced by $P_i^\circ(n_i^\circ)$. The equations describing an ideal adsorbed solution become, for a binary mixture

$$Py_1 = P_1^\circ x_1 \tag{3}$$

$$P(1-y_1) = P_2^\circ(1-x_1) \tag{4}$$

$$P_1^\circ = P_1^\circ(n_1^\circ) \tag{5}$$

$$P_2^\circ = P_2^\circ(n_2^\circ) \tag{6}$$

$$n_t = n_1^\circ = n_2^\circ \tag{7}$$

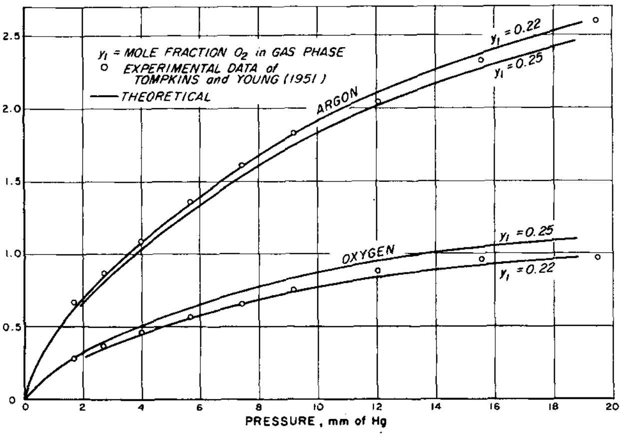

Fig. 6. Adsorption of oxygen and argon on cesium iodide at 77.49°K.

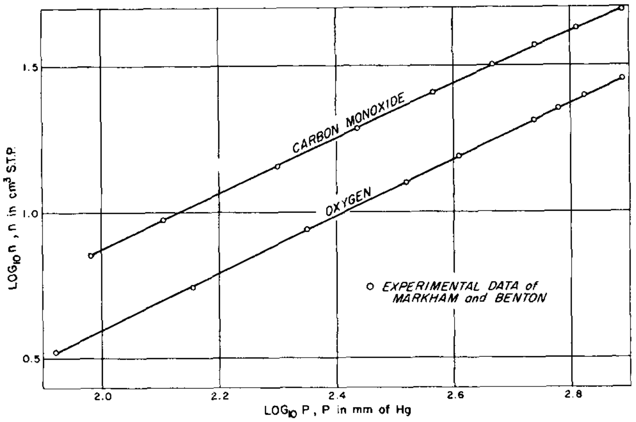

Fig. 7. Adsorption isotherm of oxygen and carbon monoxide on silica gel at 0°C.

Equations (3) and (4) equate the fugacities in the gas and in the adsorbed phase for each component. The pure component adsorbate vapor pressures are both functions of the amount adsorbed n_i°, and the functional dependence is given by the pure component adsorption isotherms, Equations (5) and (6). Equality of spreading pressures for the pure components and for the mixture is insured by means of Equations (7). Equations (3) through (7) constitute six independent equations in eight unknowns. For binary adsorption at constant temperature there are two degrees of freedom, so that selection of any two of the unknowns permits a solution of Equations (3) through (7) for the remaining unknowns. Of course, once the total amount adsorbed and mole fraction of the adsorbed phase are known, the individual adsorption of each component is given by

$$n_1 = x_1 n_t \tag{8}$$

$$n_2 = (1-x_1)\, n_t \tag{9}$$

Equations (3) through (9) were written for the case of binary adsorption for simplicity, but the extension to any number of adsorbates is obvious. In the case of gas phase nonidealities, the partial pressures of Equations (3) and (4) should be replaced by the respective fugacities.

Although the usual experimental independent variables are P and y, the most convenient independent variables for prediction of mixture adsorption are P and n_t. The procedure is as follows:

1. Select the value of P arbitrarily. A value of n_t lying between $n_1^\circ(P)$ and $n_2^\circ(P)$ is then selected.
2. From the pure component isotherms obtain $P_1^\circ(n_t)$ and $P_2^\circ(n_t)$.
3. Calculate x_1 from the relation $P = P_1^\circ x_1 + P_2^\circ(1 - x_1)$.
4. Calculate y_1 from Equation (3) or (4).
5. The individual amounts adsorbed are given by Equations (8) and (9).

This simplified method is thermodynamically consistent, provided that the spreading pressures of the different adsorbates are equal at a given amount adsorbed. An equivalent criterion, which can be tested without actually

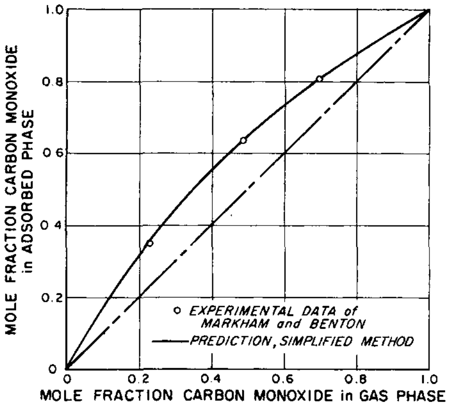

Fig. 8. Prediction of equilibrium gas and adsorbed phase compositions for carbon monoxide-oxygen mixtures on silica gel at 0°C., 1 atm. pressure.

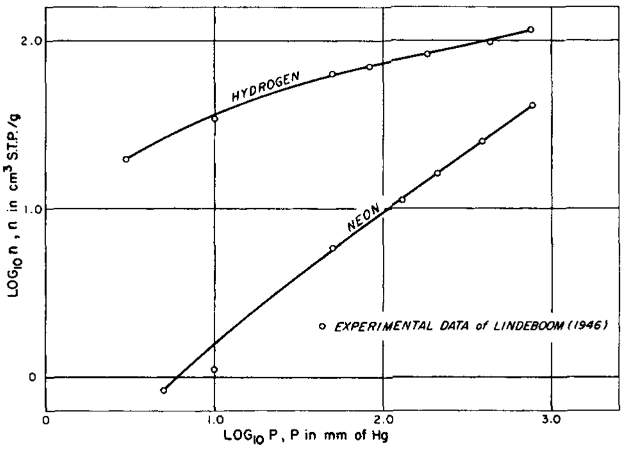

Fig. 9. Adsorption isotherms of hydrogen and neon on activated carbon at —192°C.

calculating spreading pressures, is that logarithmic plots of the pure component isotherms must be capable of superposition by means of lateral translation parallel to the pressure axis. This criterion should be applied before using the simplified method for predicting mixture adsorption equilibria.

One point should be emphasized: equivalency of the curves of spreading pressure vs. amount adsorbed does not guarantee that the simplified method will accurately predict the multicomponent adsorption data. It simply shows that the method is thermodynamically consistent. If the activity coefficients in the adsorbed phase differ from unity, neither the simplified method nor the ideal adsorbed solution theory (*7*) will give accurate predictions of the mixture data. However, previous work indicates that the activity coefficients are often close to unity for less than monolayer coverage (*7*).

Basmadjian (*1*) has proposed an empirical method for the prediction of multicomponent equilibria; under certain rather severe restrictions his method can be shown to be equivalent to the simplified theory described above. These restrictions are not really necessary. For the use of the simplified method it is only necessary that the slopes of the adsorption isotherms (on a logarithmic plot) be equal as described above.

COMPARISON WITH EXPERIMENTAL DATA—SIMPLIFIED METHOD

The experimental adsorption isotherms of pure oxygen and pure argon on cesium iodide (*10*) are shown in Figure 5. The criterion of superposition of isotherms by lateral translation is nearly satisfied. The predictions of mixture adsorption with the simplified method are compared with the experimental data of Tompkins and Young (*10*) in Figure 6. Two gas phase compositions are given for each adsorbate, because the experimental gas phase composition varied from 22 to 25% oxygen. As shown by Figure 6, the predictions are in very good agreement with the experimental data.

Another set of data which satisfies the superposition criterion is that of Markham and Benton (*6*), as shown in Figure 7. The predictions of the gas and adsorbed phase composition with the simplified method are compared with the experimental values in Figure 8. The agreement between theory and experiment is nearly perfect.

In the systems tested above, the slopes of the experimental adsorption isotherms at all values of n are very nearly equal. Often, however, it is necessary to predict mixture adsorption for systems where the slopes of the isotherms are only roughly the same, or are decidedly different. Two such systems are the methane-ethane system of Szepesy and Illés (*9*), shown in Figure 3, and the hydrogen-neon system of Lindeboom (*5*), Figure 9. Although in systems of this type the simplified method is not thermodynamically consistent, Figures 10 and 11 show that the values calculated with the simplified method are still in qualitative agreement with the experimental data.

It should be noted that for the systems tested above, the total surface coverage did not exceed a monolayer.

ADSORPTION AZEOTROPY

An adsorption azeotrope occurs when the relative volatility is equal to unity. Since the mole fraction of either component is identical in the vapor and in the adsorbed phases, no separation is achieved. In some cases, however, the azeotrope can be avoided by operating at a different total pressure.

The only system of practical interest for which azeotropy has been observed experimentally is that of the multilayer adsorption of argon and nitrogen on silica gel at 89.5°K. (*2*). Since the pure component isotherms can-

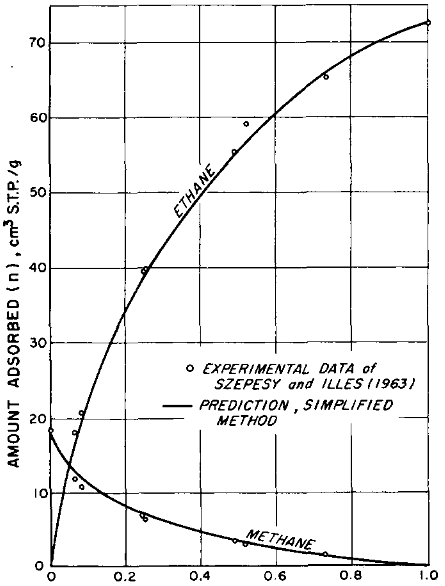

Fig. 10. Prediction of amount adsorbed for methane-ethane mixtures on activated carbon at 20°C., 1 atm. pressure.

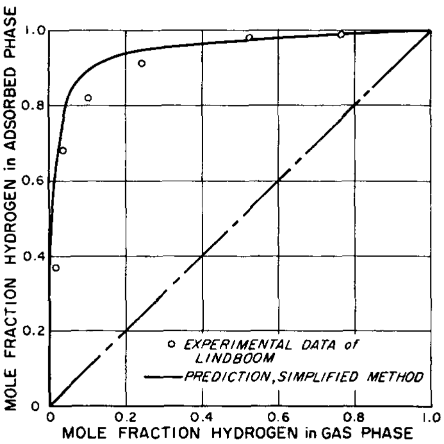

Fig. 11. Prediction of equilibrium gas and adsorbed phase compositions for neon-hydrogen mixtures on activated carbon at —192°C., 50 mm. Hg pressure.

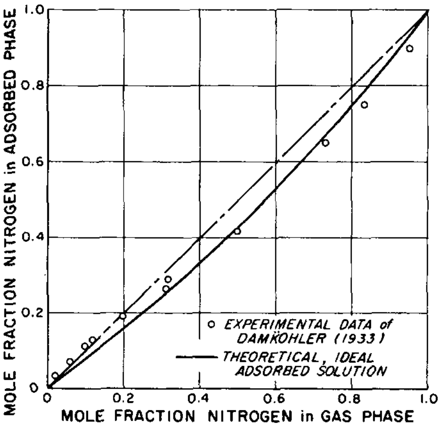

Fig. 13. Prediction of equilibrium gas and absorbed phase compositions for argon-nitrogen mixtures on silica gel at 89.5°K., 600 mm. Hg pressure.

not be superimposed by lateral translation, the spreading pressure curves (Figure 12) were used to predict the mixture adsorption equilibria.

For liquid mixtures, Raoult's law predicts that at constant temperature an azeotrope can never exist unless the saturation pressures of the two components are identical, in which case all compositions are azeotropes. For ideal adsorbed solution theory, the prediction is analogous: at constant P and T an azeotrope cannot exist unless the adsorbate vapor pressures are identical, in which case all compositions are azeotropes. Referring to Figure 12, we see that the theory predicts that at a pressure of about 140 mm. Hg all compositions will be azeotropic, but at higher and lower pressures argon and nitrogen, respectively, are selectively adsorbed at all compositions. Thus at a total pressure of 600 mm. Hg, as shown in Figure 13, the apparent experimental azeotrope is not predicted by ideal adsorbed solution theory.

It is known that in the case of liquid solutions even small deviations from ideality can produce azeotropy if the two pure component saturation pressures are close to one another. By analogy the apparent experimental azeotrope shown in Figure 13 suggests that the adsorbed phase activity coefficients are not unity. The liquid phase activity coefficients of argon and nitrogen at 85°K. are 1.2 at infinite dilution (*8*); therefore small deviations from ideality might be expected for adsorbed argon-nitrogen mixtures.

It is concluded that a method of measuring (and hopefully of predicting) activity coefficients of adsorbed mixtures is needed. Unfortunately, the problem is not easily solved, because the measurement of activity coefficients requires knowledge of the spreading pressure of the mixture, and the large amount of experimental data needed for such a calculation is not available.

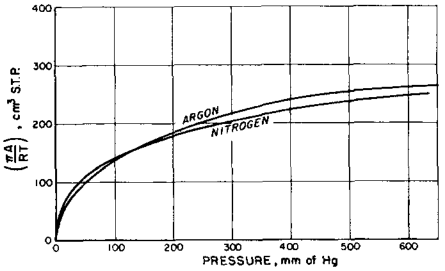

Fig. 12. Spreading pressure for argon and nitrogen adsorbed on silica gel at 89.5°K.

From an engineering point of view, however, the small value of the selectivity predicted for argon in Figure 13 would have led to the conclusion that a process designed for the separation of argon-nitrogen mixtures, by using silica gel at 89.5°K. and 600 mm. Hg, would not be very practical.

CONCLUSIONS

1. The simplified method of predicting multicomponent adsorption equilibria permits rapid and accurate calculations of the entire equilibrium surface, provided that logarithmic plots of the adsorption isotherms have nearly equal slopes.
2. For data in which the isotherms cannot be superimposed, the ideal adsorbed solution theory (*7*) provides nearly quantitative predictions of monolayer, multicomponent adsorption isotherms.

ACKNOWLEDGMENT

The authors thank Dr. R. J. Corruccini and Dr. J. M. Prausnitz for their many helpful suggestions. A. L. Myers is grateful to the National Science Foundation for financial support.

NOTATION

A = specific surface area of the adsorbent
n = moles in the adsorbed phase per unit mass of adsorbent
n_t = total number of moles in the adsorbed phase per unit mass of adsorbent
P = total system pressure
$P_i^\circ(\pi)$ = equilibrium pressure for pure i corresponding the spreading pressure π
$P_i^\circ(n_i^\circ)$ = equilibrium pressure for pure i corresponding to the amount adsorbed n_i°
R = gas constant
T = absolute temperature
x_i = mole fraction of component i in the adsorbed phase
y_i = mole fraction of component i in the gas phase
ρ = liquid density, moles per unit volume
π = spreading pressure

Superscript

$^\circ$ = pure component

Subscript

i = component i

LITERATURE CITED

1. Basmadjian, D., *Can. J. Chem.*, **38**, 149 (1960).
2. Damköhler, G., *Z. Phys. Chem.*, **B23**, 69 (1933).
3. Hill, T. L., P. H. Emmett, and L. G. Joyner, *J. Am. Chem. Soc.*, **73**, 5102 (1951).
4. Hill, T. L., in "Advances in Catalysis," Vol. 4, Academic Press, New York (1956).
5. Lindeboom, J., *Rec. Trav. Chim.*, **65**, 877 (1946).
6. Markham, E. C., and A. F. Benton, *J. Am. Chem. Soc.*, **53**, 497 (1931).
7. Myers, A. L., and J. M. Prausnitz, *A.I.Ch.E. J.*, **11**, 121 (1965).
8. Rowlinson, J. S., "Liquids and Liquid Mixtures," p. 137, Butterworths, London (1959).
9. Szepesy, L., and V. Illés, *Acta Chim. Hung.*, **35**, 37 (1963).
10. Tompkins, F. C., and D. M. Young, *Trans. Faraday Soc.*, **47**, 88 (1951).

Manuscript received December 9, 1965; revision received April 11, 1966; paper accepted April 13, 1966.

Model Calculations for Capillary Condensation

JAMES C. MELROSE

Mobil Oil Corporation, Dallas, Texas

Capillary phenomena arising from vapor phase condensation in porous media are discussed in the light of an exact interface curvature theory and a self-consistent thermodynamic theory. The system studied consists of liquid condensed in the form of pendular rings at the contact points between identical spherical particles. The geometrical parameters—the curvature, the confined volume, and the surface area of the liquid-vapor interface—must be expressed in terms of incomplete elliptic integrals. In addition several corrections are introduced for the classical Kelvin relation for lowering of vapor pressure. One of these is based on the density dependence of the isothermal thermodynamic susceptibility. Since the susceptibility vanishes at large negative pressures, an upper limit to the curvature is established. The balance equation for the extensive free energy is considered from the point of view of hydrostatic principles.

The interaction of condensible vapors with porous solids is important in a wide variety of physical contexts. Most frequently the theoretical discussion of such phenomena starts with the concepts and methods of equilibrium thermodynamics. The principal difficulties which arise are those associated with the thermodynamic and geometrical descriptions of the various interfaces. Such descriptions fall within the province of the classical theory of capillarity as expounded by Gibbs (*1*). It is important to note that this thermodynamic approach can be made to conform rigorously with the principles of hydrostatics, as first demonstrated by Buff (*2*).

This paper attempts to clarify some of the difficulties encountered in applying these concepts to porous solids. I will discuss, in as much detail as possible, a relatively simple case of vapor-liquid equilibrium in a capillary system. This is, on the one hand, in contrast to the type of study in which the necessity of treating highly complex and ill-defined physical systems justifies the use of rather inexact methods (*3* to *6*). On the other hand, the model system to be discussed will not be so devoid of geometrical complexity as to obscure several significant features of the phenomena of interest. The restriction to simple geometrical interface shapes is characteristic of a number of treatments that meet adequate standards of thermodynamic rigor (*7* to *9*).

This approach makes it possible to assess quantitatively the validity of various thermodynamic and geometrical approximations. Also, the discussion will illuminate several important concepts in the theory of capillarity and interrelate these concepts within a unified thermodynamic context.

THERMODYNAMIC THEORY

Description of Model System

The system to be examined in detail consists of three homogeneous phases: solid, liquid, and vapor, which are denoted, respectively, by the subscripts S, L, and G. The set of components from which these phases are constituted is restricted to two mutually insoluble components. The component present as the solid phase is denoted by the superscript 1, and the component which forms both of the fluid phases is denoted by the superscript 2. The interfaces between the phases are denoted by subscripts indicating the components involved:

solid-liquid: 12
solid-vapor: 1, 2
liquid-vapor: 2

Further, component 1, the solid, is in the form of two identical spherical particles in contact. These particles, of radius R, are taken to be incompressible, as well as insoluble in the fluid phases. In all thermodynamic states which will be considered, the surface state of strain for the solid phase remains unchanged. To within the limits required by a thermodynamic treatment, the state of strain in the solid surface is also homogeneous and isotropic, in a two-dimensional sense. Such restrictions suffice to define the so-called *inert adsorbent* model of the solid phase.

The external boundaries of the system are assumed to be in contact only with the vapor phase. Hence, the liquid phase, if it exists, is in the form of condensate at the