Adsorption of Multicomponent Mixtures by Solid Adsorbents

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A procedure based on kinetic principles is presented for the development of models for the adsorption of mixtures of gases in any number of layers by solid adsorbents. Equations of state for two-dimensional gas mixtures which are thermodynamically consistent with the adsorption models are also presented. The constants in the adsorption models for mixtures are obtained from the isotherms for the pure components. Good accuracy for the predicted adsorption of mixtures for the data available was obtained by use of a model for the adsorption of mixtures in bimolecular layers.

The increased use of solid adsorbents in separation processes has led to the need for methods for predicting the equilibria of multicomponent mixtures from a knowledge of the equilibrium adsorptions for pure components. Hill (*9*) followed by Arnold (*1*) proposed extensions of the BET equations (*3*) for the description of multicomponent adsorption. Mason and Cooke (*17*) used Hill's equations for two-layer adsorption to describe the equilibria of multicomponent mixtures.

Lewis et al. (*14, 15*) followed by others (*6, 7, 11*) extended the application of the Polanyi theory to include the correlation of the adsorption equilibria for multicomponent mixtures.

Recently, Myers and Prausnitz (*19*) proposed a method that makes use of Gibbs' equation for pure component, the experimental isotherm for each pure component, and the expression for an ideal adsorbed solution in the presence of perfect gas vapors. Subsequently, Kinay and Myers (*12*) suggested a modification which improved the accuracy of the method of Myers and Prausnitz (*19*) at low pressures. To include the deviations of the adsorbed phase, Henson and Kabel (*8*) proposed a method based on the supposition of a hypothetical liquid phase in equilibrium with the adsorbed phase. And, more recently, Myers (*18*) presented a simplified method to handle ideal adsorbed solutions.

DEVELOPMENT OF THE KINETIC MODELS FOR THE ADSORPTION OF MIXTURES OF GASES IN BIMOLECULAR LAYERS

The development of the models for the adsorption of mixtures of gases is a rather obvious extension of Langmuir's kinetic model for the adsorption of a pure component. The model for the adsorption of mixtures in unimolecular layers was first proposed by Markham and Benton (*16*), and it has been used to describe both physical and chemical adsorption (*2, 4, 10, 15, 22*). The model for unimolecular adsorption is obtained as a special case of the more general model for the adsorption of mixtures in multimolecular layers.

Following Hill (*9*), Myers and Prausnitz (*19*), de Boer (*4*), and others, the following assumptions are made:

1. The adsorbent is inert; that is, all of its thermodynamic properties are the same in the presence as in the absence of adsorbate molecules. As pointed out by Hill (*9*), this approximation may well be inaccurate in the chemisorption of gases by solids.
2. The surface area of the adsorbent is independent of temperature and pressure. This assumption is subject to the same inaccuracies as those encountered in the determination of surface areas (*3*) where relatively large gas molecules and porous adsorbents are involved.

In addition, the kinetic model presented inherits some of the basic assumptions of Langmuir (*13*):

1. Molecules striking either the bare surface or the covered surface are candidates for adsorption.
2. The probability of the evaporation of a molecule from an adsorbed layer is independent of whether or not the neighboring positions in a given layer are empty or filled. This assumption could be highly inaccurate for the adsorption of highly polar compounds.
3. The total number of sites available for adsorption is independent of pressure but dependent upon temperature.
4. The total number of sites available for adsorption is the same for all components. This assumption has the same weakness as the first assumption 2.
5. The adsorption of a given molecule in a given layer is independent of the identity of the molecule adsorbed beneath it in the previous layer.
6. The ratios of adsorption equilibrium constants given by Equation (19) are equal to the same constants for all components.
7. The adsorption process is assumed to be at equilibrium.

Admittedly, these assumptions may not represent a physically realistic model of the adsorption process; they do provide, however, a basis for the logical development of expressions for the prediction of multicomponent adsorption equilibria of light hydrocarbon gas systems from a knowledge of the isotherms of the pure components.

In the interest of simplicity, the development of the model for bimolecular adsorption is presented for a binary mixture consisting of components A and B. Let S_0 denote the bare surface and S_1 the surface covered by a unimolecular layer of A and B; that is, it is postulated that the rates of adsorption and desorption of say A are unaffected by the composition of the first layer. The mechanism may be formulated as follows:

$$\begin{aligned}
A(g) + S_0 &\underset{k'_{1A}}{\overset{k_{1A}}{\rightleftarrows}} AS_0 \\
B(g) + S_0 &\underset{k'_{1B}}{\overset{k_{1B}}{\rightleftarrows}} BS_0 \\
A(g) + S_1 &\underset{k'_{2B}}{\overset{k_{2A}}{\rightleftarrows}} AS_1 \\
B(g) + S_1 &\underset{k'_{2B}}{\overset{k_{2B}}{\rightleftarrows}} BS_1
\end{aligned} \tag{1}$$

The quantities k_{1A}, k'_{1A} denote the rate constants for the adsorption of A on the bare surface, and k_{2A} and k'_{2A} are the rate constants for the adsorption of A in the second layer. Let C_{1A} and C_{2A} denote the pound moles of A adsorbed in the first and second layers, respectively, per unit mass of adsorbent. The symbols for component B are defined in an analogous manner. Let C_T represent the total pound moles of sites available for adsorption per unit mass of adsorbent, and let C_{S_0} and C_{S_1} denote the pound moles of vacant sites in the first and second layers per unit mass of adsorbent. The rates of adsorption of A on the bare surface S_0 and on the first layer S_1 are given by

$$(r_A)_{a,1} = k_{1A}\, p_A\, C_{S_0}, \quad \text{and} \quad (r_A)_{a,2} = k_{2A}\, p_A\, C_{S_1} \tag{2}$$

respectively. The rates of desorption of A from the bare surface and from the first layer are given by

$$(r_A)_{d,1} = k'_{1A}\, C_{1A}, \quad \text{and} \quad (r_A)_{d,2} = k'_{2A}\, C_{2A} \tag{3}$$

respectively. The rate expressions for component B are stated in an analogous manner. At equilibrium, the rates of adsorption and desorption for each layer are equal [$(r_A)_{a,1} = (r_A)_{d,1}$, for example], which gives

$$\begin{aligned}
C_{1A} &= K_{1A}\, p_A\, C_{S_0} \\
C_{1B} &= K_{1B}\, p_B\, C_{S_0} \\
C_{2A} &= K_{2A}\, p_A\, C_{S_1} \\
C_{2B} &= K_{2B}\, p_B\, C_{S_1}
\end{aligned} \tag{4}$$

where K_{1i} and K_{2i} ($i = A$ or B) are the adsorption equilibrium constants for the first and second layers, respectively (also, $K_{1A} = k_{1A}/k'_{1A}$).

The concentration of vacant sites is given by

$$C_{S_0} = C_T - C_{1A} - C_{1B} \tag{5}$$

When the first two relationships of Equation (4) are combined with Equation (5) and rearranged, the following result is obtained:

$$C_{S_0} = \frac{C_T}{1 + K_{1A}\, p_A + K_{1B}\, p_B} \tag{6}$$

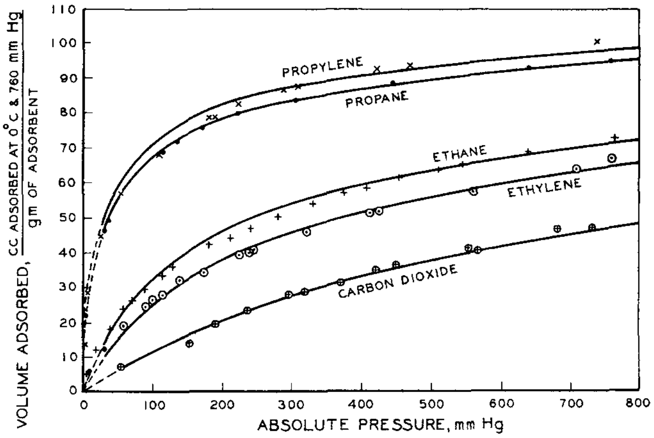

Fig. 1. Comparison of experimental isotherms at 20°C. [determined by Szepesy and Illés (20)] with the isotherms curve fitted by the bimolecular-layer model.

Substitution of this result into the first two expressions of Equation (4) yields

$$C_{1A} = K_{1A}\, p_A \left[\frac{C_T}{1 + K_{1A}\, p_A + K_{1B}\, p_B} \right] \tag{7}$$

and

$$C_{1B} = K_{1B}\, p_B \left[\frac{C_T}{1 + K_{1A}\, p_A + K_{1B}\, p_B} \right] \tag{8}$$

Since

$$C_{S_1} = C_{1A} + C_{1B} \tag{9}$$

Equations (7) and (8) may be added to give an expression for C_{S_1} in terms of p_A and p_B. Use of the expression so obtained to eliminate C_{S_1} from the last two expressions given by Equation (4) yields

$$C_{2A} = K_{2A}\, p_A \left[\frac{C_T(K_{1A}\, p_A + K_{1B}\, p_B)}{1 + K_{1A}\, p_A + K_{1B}\, p_B} \right] \tag{10}$$

$$C_{2B} = K_{2B}\, p_B \left[\frac{C_T(K_{1A}\, p_A + K_{1B}\, p_B)}{1 + K_{1A}\, p_A + K_{1B}\, p_B} \right] \tag{11}$$

Then the total surface concentrations of A and B follow immediately from Equations (7), (8), (10), and (11); namely

$$\begin{aligned}
C_A &= C_{1A} + C_{2A} \\
&= C_T \left[\frac{K_{2A}\, p_A(K_{1A}\, p_A + K_{1B}\, p_B) + K_{1A}\, p_A}{1 + K_{1A}\, p_A + K_{1B}\, p_B} \right]
\end{aligned} \tag{12}$$

$$\begin{aligned}
C_B &= C_{1B} + C_{2B} \\
&= C_T \left[\frac{K_{2B}\, p_B(K_{1A}\, p_A + K_{1B}\, p_B) + K_{1B}\, p_B}{1 + K_{1A}\, p_A + K_{1B}\, p_B} \right]
\end{aligned} \tag{13}$$

For the general case of the adsorption of a multicomponent mixture in two layers, the total surface concentration of any component i is given by

$$C_i = C_{1i} + C_{2i} = C_T \left\{ \frac{K_{2i}\, p_i \left(\sum\limits_{i=1}^{c} K_{1i}\, p_i \right) + K_{1i}\, p_i}{1 + \sum\limits_{i=1}^{c} K_{1i}\, p_i} \right\} \tag{14}$$

For the special case of the adsorption of a pure component A, Equation (14) reduces to

$$\frac{C_A}{C_T} = \frac{C_{1A} + C_{2A}}{C_T} = \frac{K_{2A}\, P\, (K_{1A}\, P) + K_{1A}\, P}{1 + K_{1A}\, P} \qquad (15)$$

This same result may be obtained by use of the BET equations for two-layer adsorption (3).

For the special case of the adsorption of mixtures of gases in unimolecular layers, $C_{2i} = 0$, and it is readily shown that Equation (14) reduces to

$$C_i = K_{1i}\, p_i \left[\frac{C_T}{1 + \sum_{i=1}^{c} K_{1i}\, p_i} \right] \qquad (16)$$

For the case of a pure component, this expression [Equation (16)] reduces to Langmuir's isotherm. An expression for the adsorption of mixtures which was of the same general form as Equation (16) was proposed by Markham et al. (16). Actually, their model was more general than the one given by Equation (16) in that the total number of sites available for adsorption was assumed to depend upon the identity of each component i; that is, the model of Markham et al. is given by replacing C_T in Equation (16) by C_{Ti}.

KINETICS MODEL FOR THE ADSORPTION OF GASES IN *n* LAYERS

When the mechanism implied by Equation (1) is extended to include the adsorption of n layers as follows for two components A and B

$$A(g) + S_2 \underset{k'_{3A}}{\overset{k_{3A}}{\rightleftarrows}} AS_2$$

$$B(g) + S_2 \underset{k'_{3B}}{\overset{k_{3B}}{\rightleftarrows}} AS_2$$

$$\vdots \qquad \vdots \qquad \vdots \quad \vdots$$

$$A(g) + S_{n-1} \underset{k'_{nA}}{\overset{k_{nA}}{\rightleftarrows}} AS_{n-1}$$

$$B(g) + S_{n-1} \underset{k'_{nB}}{\overset{k_{nB}}{\rightleftarrows}} BS_{n-1}$$

it is readily shown in a manner analogous to that used to obtain Equation (14) that the concentration of any component i of a multicomponent mixture adsorbed in n layers is given by

$$C_i = \frac{(p_i C_T)(K_{1i} + K_{2i}\,\phi_1 + K_{3i}\,\phi_1\phi_2 + \ldots + K_{ni}\,\phi_1\phi_2 \ldots \phi_{n-1})}{1 + \phi_1} \qquad (17)$$

where

$$\phi_j = \sum_{i=1}^{c} K_{ji}\, p_i, \quad (1 \leqq j \leqq n-1) \qquad (18)$$

For the adsorption of mixtures in n layers, let it be postulated that

$$\nu = \frac{K_{2i}}{K_{1i}} = \frac{K_{3i}}{K_{2i}} = \frac{K_{4i}}{K_{3i}} = \ldots = \frac{K_{ni}}{K_{n-1,i}} = \text{constant} \qquad (19)$$

Thus, it follows that:

$$\nu = \frac{\phi_2}{\phi_1} = \frac{\phi_3}{\phi_2} = \frac{\phi_4}{\phi_3} = \ldots = \frac{\phi_n}{\phi_{n-1}} = \text{constant} \qquad (20)$$

and also

$$\begin{array}{ll} \phi_2 = \nu\phi_1 & K_{2i} = \nu K_{1i} \\ \phi_3 = \nu^2\phi_1 & K_{3i} = \nu^2 K_{1i} \\ \phi_4 = \nu^3\phi_1 & K_{4i} = \nu^3 K_{1i} \\ \vdots & \vdots \\ \phi_n = \nu^{n-1}\phi_1 & K_{ni} = \nu^{n-1} K_{1i} \end{array} \qquad (21)$$

Equation (17) reduces to the following general expression for the total concentration of component i in n adsorbed layers of a multicomponent mixture:

$$C_i = \left[\frac{C_T\, K_{1i}\, p_i}{1 + \phi_1} \right] \left[1 + \nu\phi_1 + \nu^3\phi_1^2 + \nu^6\phi_1^3 + \nu^{10}\phi_1^4 + \ldots + \nu^{\frac{(n-1)n}{2}} \phi_1^{n-1} \right] \qquad (22)$$

For two layers, this expression reduces to

$$C_i = \left[\frac{C_T\, K_{1i}\, p_i}{1 + \phi_1} \right] (1 + \nu\phi_1) \qquad (23)$$

and for the two-layer adsorption of pure component i, the expression further reduces to

$$C_i = \left[\frac{C_T\, K_{1i}\, P}{1 + K_{1i}\, P} \right] (1 + \nu K_{1i} P) \qquad (24)$$

THERMODYNAMIC CONSISTENCY OF ADSORPTION MODELS

A proposed model for the description of vapor-liquid equilibria is said to be thermodynamically consistent if it satisfies the Gibbs-Duhem equation. Similarly, a proposed model for the description of the equilibria between vapors and adsorbed phases is said to be thermodynamically consistent if it satisfies the Gibbs' equation (or Gibbs' formula), which may be stated as follows:

$$\frac{d\pi}{RT} = \sum_{i=1}^{c} C_i^\sigma\, d \log_e \bar{f}_i^V \quad (\text{at constant } T) \qquad (25)$$

If the gas phase behaves as a perfect gas mixture, this expression reduces to

$$\frac{d\pi}{RT} = \sum_{i=1}^{c} C_i^\sigma \frac{dp_i}{p_i} \quad (\text{at constant } T) \qquad (26)$$

For the adsorption of a pure component i, Equations (25) and (26) reduce to

$$\frac{d\pi}{RT} = C_i^\sigma\, d \log_e f^V \qquad (27)$$

and

$$\frac{d\pi}{RT} = C_i^\sigma\, d \log_e P \qquad (28)$$

respectively. The concentration C_i^σ has the units of pound moles of component i adsorbed per unit area. Then, if a is the surface area per unit mass of adsorbent, it follows that

$$C_i^\sigma = C_i/a, \quad \text{and} \quad C_T^\sigma = C_T/a$$

The formula for C_i^σ as given by the kinetic model for two-layer adsorption is obtained from Equation (14) by dividing both sides by a.

The following expression for the spreading pressure π for two-layer or bimolecular-layer adsorption satisfies the Gibbs' equation

$$\frac{\pi}{RT} = C_T^{\sigma}\{\log_e(1+\phi_1) + \nu[\phi_1 - \log_e(1+\phi_1)]\} \tag{29}$$

The total differential of π at constant T is given by the formula

$$d\pi = \sum_{i=1}^{c} \frac{\partial \pi}{\partial p_i}\, dp_i \text{ (at constant } T) \tag{30}$$

Then, for each i, the partial derivatives are found by use of Equation (29):

$$\begin{aligned} \frac{1}{RT}\frac{\partial \pi}{\partial p_i} &= C_T^{\sigma}\left[\frac{K_{1i}}{1+\phi_1} + \nu\left(K_{1i} - \frac{K_{1i}}{1+\phi_1}\right)\right] \\ &= C_T^{\sigma} K_{1i}\left[\frac{1+\nu\phi_1}{1+\phi_1}\right] \end{aligned} \tag{31}$$

Thus, the total differential $d\pi$ is given by

$$\frac{d\pi}{RT} = \sum_{i=1}^{c}\left[C_T^{\sigma} K_{1i}\, p_i \left(\frac{1+\nu\phi_1}{1+\phi_1}\right)\right]\frac{dp_i}{p_i} \tag{32}$$

In view of the formula for C_i as given by the kinetic model [Equation (23)], it follows that Equation (32) reduces to Gibbs' equation [Equation (26)].

The preceding analysis serves not only to establish the thermodynamical consistency of the kinetic model, but it also establishes Equation (29) as the equation of state of the adsorbed phase for either pure components or mixtures whose isotherms obey the relationship indicated by Equation (23).

The equation of state for the case of the adsorption of n layers of a multicomponent mixture which is thermodynamically consistent with Equation (22) is given by

$$\frac{\pi}{RT} = C_T^{\sigma} \sum_{j=1}^{n} \chi_j \tag{33}$$

where

$$\begin{aligned} \chi_1 &= \log_e(1+\phi_1) \\ \chi_2 &= -\nu\chi_1 + \nu\phi_1 \\ \chi_3 &= -\nu^2\chi_2 + \frac{\nu^3\phi_1^2}{2} \\ \chi_4 &= -\nu^3\chi_3 + \frac{\nu^6\phi_1^3}{3} \\ \chi_5 &= -\nu^4\chi_4 + \frac{\nu^{10}\phi_1^4}{4} \\ &\vdots \\ \chi_n &= -\nu^{n-1}\chi_{n-1} + \frac{\nu^{\frac{(n-1)n}{2}}\phi_1^{n-1}}{n-1} \end{aligned}$$

Although Equation (33) is applied with about equal ease for any arbitrary number of layers, only the first two terms $(1 + \nu\phi_1)$ of the series in this expression (which corresponds to adsorption in bimolecular layers) were needed to represent the available experimental results with good accuracy.

USE OF THE BIMOLECULAR-LAYER MODEL FOR THE PREDICTION OF THE ADSORPTION EQUILIBRIA OF MIXTURES OF GASES BY SOLID ADSORBENTS

The procedure described for the use of the two-layer (or bimolecular-layer) adsorption model in the correlation of adsorption data is precisely analogous to that employed for a model based on three or more layers.

TABLE 1. CONSTANTS FOR THE BIMOLECULAR-LAYER-ADSORPTION MODEL: BASED ON THE DATA OF SZEPESY AND ILLES (*20*) FOR THE ADSORPTION OF PURE COMPONENTS ON CARBON AT 20°C. AND AT PRESSURES BELOW 1,000 MM. HG. (Use pressure units in pounds per square inch absolute to obtain pound mole adsorbed per 100 lb. of adsorbent.)

Component	K_{1i}
Ethylene	0.2043
Ethane	0.3125
Propylene	2.5819
Propane	2.1261
Carbon dioxide	0.0818

$C_T = 0.3816$
$\nu = 0.0043$

Carbon nuxit—AL, particle size: 1.5 mm.
Diameter: 3 to 4 mm. long.

Since the same constants appear in Equation (23) as appear in Equation (24), it follows that the isotherms for the pure components may be employed to determine the constants appearing in the expressions for mixtures. However, at high pressures, the partial pressure and total pressure in Equations (23) and (24), respectively, must be replaced by their corresponding fugacities to give

$$[C_i]_{\substack{\text{pure}\\\text{component}}} = C_T K_{1i} f_i^V \left[\frac{1 + \nu K_{1i} f_i^V}{1 + K_{1i} f_i^V}\right] \tag{34}$$

$$[C_i]_{\text{mixture}} = C_T K_{1i} \bar{f}_i^V \left[\frac{1 + \nu \sum_{i=1}^{c} K_{1i} \bar{f}_i^V}{1 + \sum_{i=1}^{c} K_{1i} \bar{f}_i^V}\right] \tag{35}$$

where f_i^V is the fugacity of pure component i evaluated at the total pressure and temperature of the adsorption, and $\bar{f}_i^V$ is the fugacity of component i in the vapor phase of the multicomponent mixture that is in equilibrium with the adsorbed phase.

The curve fitting of all the isotherms was done simultaneously, and the quantities C_T and ν were common for all components while the K_{1i}'s were determined from the isotherms of the respective pure components. Once the above step has been completed, the individual K_{1i}'s can be used in Equation (35) to predict the equilibrium adsorptions for gas mixtures.

In this work, the coefficients were found by fitting pressures in pounds per square inch absolute vs. surface concentrations given in pound moles of a component adsorbed per one hundred pounds of adsorbent material. This choice of units gives values of C_T at room temperature that range from 0.2 to 0.5 for the adsorption of the light hydrocarbons on most silica gels and activated carbon adsorbents. For the systems considered, the variation of the coefficients C_T, ν, and the K_{1i}'s with temperature could be curve fitted by use of exponential functions of the reciprocal of the absolute temperature.

The constants in Equation (34) were determined for each component by use of data that covered a range of pressures of the same order of magnitude as the respective partial pressures of these components in the mixtures of interest. The use of the proposed expressions [Equation (34) and (35)] for the prediction of the adsorption of mixtures of gases from the isotherms of the pure components is demonstrated by use of the data of Szepesy and Illés (*20, 21*) and the data of Mason and Cooke (*17*).

The pure component isotherms given by Szepesy and

TABLE 2. STANDARD DEVIATIONS FOR THE PREDICTED ISOTHERMS FOR THE PURE COMPONENTS AND FOR THE PREDICTED ADSORPTION EQUILIBRIA FOR FIVE OF THE BINARY PAIRS INVESTIGATED BY SZEPESY AND ILLES (*20*)

Component	Standard deviation
Ethylene	0.058
Ethane	0.077
Propylene	0.052
Propane	0.032
Carbon dioxide	0.074
Binary pairs	0.086

Illés were curve fitted for a range of pressures extending from 30 to 1,000 mm. with the aid of regression analysis (see Figure 1). The function minimized was the square of the fractional deviations of the predicted values from the experimental values.

The constants in Equation (34) which were determined for the pure components on the basis of the data of Szepesy and Illés (*20*) are shown in Table 1. The coefficients for the pure components given in Table 1 were then used in Equation (35) for the prediction of the adsorption equilibrium for multicomponent mixtures. Comparisons of the predicted experimental values for the adsorption of several binary mixtures studied by Szepesy and Illés (*21*) are given in Figure 2 and elsewhere.* Table 2 gives the standard deviations for each of the predicted isotherms from the experimental pure component values as well as the standard deviations of the predicted equilibria for five gas mixtures from the corresponding observed equilibria.

The relatively small value ν for the data of Szepesy and Illés implied that only one layer was present to any appreciable extent. For Szepesy and Illés data, $\nu = 0.005$ and $\phi_1 \cong 2$. The terms in the numerator of Equation (22) represent the contributions of the second, third, and higher-order layers relative to the first layer; that is

first layer: 1.0
second layer: $\nu\phi_1 = (0.005)(2) = 0.01$
third layer: $\nu^3\phi_1^2 = (0.005)^3(2)^2 = 0.0000005$

which clearly indicates that in this case the predicted influence of the second layer is only 1% and that a direct curve fit to a one-layer model would have produced equivalent results.

The use of the constants for the pure components in the prediction of the equilibrium adsorptions of multicomponent mixtures is demonstrated by the following illustrative example.

Illustrative Example

Calculate the predicted equilibrium adsorptions on the adsorbent used by Szepesy and Illés (*20, 21*) for the case where the gas phase contains 11.5% ethane and 88.5% ethylene at the equilibrium temperature and pressure of 20°C. and 759.5 mm., respectively.

Solution. From Table 1:

$$C_T = 0.3816; \quad \nu = 0.0048$$
$$K_{C_2H_6} = K_{11} = 0.3125$$
$$K_{C_2H_4} = K_{12} = 0.2043$$

TABLE 3. CONSTANTS FOR THE BIMOLECULAR-LAYER MODEL: BASED ON THE DATA OF MASON AND COOKE (*17*) FOR THE ADSORPTION OF PURE COMPONENTS ON SILICA GEL AT 100°F. AND HIGH PRESSURES

(Use pressure units in pounds per square inch absolute to obtain pound mole adsorbed per 100 lb. of adsorbent.)

Component	K_{1i}	Range of curve fits, lb./sq.in.abs.
Methane	0.0018	0 to 1,400
Ethane	0.0072	0 to 400
Propane	0.023	0 to 20
i-butane	0.068	0 to 20
n-butane	0.076	0 to 20
i-pentane*	0.21	
n-pentane	0.28	0 to 10
n-hexane	0.85	
	$C_T = 0.4098$	
	$\nu = 0.1252$	

* Estimated by extrapolation, see Figure 3.

Because of the relatively low pressures at which these adsorptions occur, pressures instead of fugacities may be used in the predictions:

$P = 759.5$ mm. or 14.687 lb./sq.in.abs.
$p_{C_2H_6} = p_1 = (0.115)(14.687) = 1.689$ lb./sq.in.abs.
$p_{C_2H_4} = p_2 = (0.885)(14.687) = 12.998$ lb./sq.in.abs.

The surface concentrations may now be computed by use of Equation (35) as follows:

$$C_{C_2H_6} = C_1 = \frac{(0.3816)(0.3125)(1.689)\left[1 + 0.0048\left[\sum_{i=1}^{c} K_{1i}\,p_i\right]\right]}{1 + [(0.3125)(1.689) + (0.2043)(12.998)]}$$

$= 0.04888$ g.-moles of C_2H_6/100 g. of carbon.

$$C_{C_2H_4} = C_2 = \frac{(0.3816)(0.2043)(12.998)\left[1 + 0.0048\left[\sum_{i=1}^{c} K_{1i}\,p_i\right]\right]}{1 + [(0.3125)(1.689) + (0.2043)(12.998)]}$$

$= 0.2460$ g.-moles of C_2H_4/100 g. of carbon.

Thus

volume of C_2H_6 adsorbed (at 0°C. and 760 mm.)/g. of carbon $= 10.95$ cc./g.,
volume of C_2H_4 adsorbed (at 0°C. and 760 mm.)/g. of carbon $= 55.10$ cc./g.

The corresponding experimental observations were 10.62 cc./g. (for ethane) and 55.02 cc./g. (for ethylene) as given by Szepesy and Illés (*21*), and the respective deviations of the experimental and predicted adsorptions were 3 and 0%.

CORRELATION OF THE DATA OF MASON AND COOKE (*17*)

The pure component data of Mason and Cooke (*17*) were used to determine the constants in Equation (34). In order to estimate the equilibrium adsorption constants for *i*-pentane and *n*-hexane, the graph shown in Figure 3

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* Tables 5 through 10 have been deposited as document 00982 with the ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 W. 34th St., New York 10001 and may be obtained for $2.00 for microfiche or $5.00 for photocopies.

Table 4. Comparison of the Experimental and Predicted Adsorption Equilibria for Mixture A on Silica Gel at 100°F. and 1,400 lb./sq.in.abs. Based on the Data of Mason and Cooke (*17*)

Component	y	Fugacity factor, $\bar{f}^v/Py$	Experimental, lb. mole/ 1,000 lb.	Calculated Mason and Cooke	Calculated This method	Percent deviations Mason and Cooke	Percent deviations This method
Methane	0.9184	0.870	—	—	2.605	—	—
Ethane	0.0400	0.580	—	—	0.304	—	—
Propane	0.0240	0.395	0.335	0.322	0.394	−4	18
i-butane	0.0068	0.325	0.274	0.192	0.273	−30	−1
n-butane	0.0056	0.300	0.235	0.235	0.232	0	−1
i-pentane	0.0020	0.250	0.187	0.144	0.191	−23	2
n-pentane	0.0012	0.230	0.136	0.125	0.140	−8	3
n-hexane	0.0020	0.160	0.516	0.480	0.494	−7	−4

was prepared, and the *K*'s for these components were approximated by extrapolation as indicated. The complete set of coefficients for the pure components is given in Table 3. Comparison of the adsorptions predicted by use of Equation (35) and those observed by Mason and Cooke (*17*) for mixture *A* is given in Table 4. The corresponding comparison for mixture *B* is not significantly different, and it is given in Table 10.*

It should be remarked that the relatively large value of ν given in Table 3 reflects the fact that the model predicts a significant amount of adsorption in the second layer. For these data, $\nu = 0.125$ and $\phi_1 \cong 2$. The ratios of the amounts adsorbed in each different layer relative to the first layer follows:

first layer: 1.0
second layer: $\nu\phi_1 = (0.125)(2) = 0.25$
third layer: $\nu^3\phi_1^2 = (0.125)^3(2)^2 \cong 0.008$
fourth layer: $\nu^6\phi_1^3 = (0.125)^6(2)^3 \cong 0.00003$
fifth layer: $\nu^{10}\phi_1^4 = (0.125)^{10}(2)^4 \cong 0.000000015$

The above results indicate that the second layer contributed approximately one fifth of the total amount adsorbed and is therefore quite important. The third layer would have contributed less than 1%, and the effect of higher-order layers is negligible. Curve fitting of the data to models based on one layer, two, three, four, and five layers indicated a significant improvement in the curve fits when going from one layer to two layers, only very small changes in the values of the coefficients when going from two to three layers, and negligible changes between the predictions of models assuming more than two layers.

The multicomponent equilibrium values predicted by the one-layer model for the high pressure data were inaccurate. For the case of models of two or more layers, the predicted values were accurate, and there were negligible variations among the multicomponent equilibrium values.

In the correlation of the data, the values for both the fugacities of pure components and the fugacities for the components in mixtures were taken from work of Edmister (*5*).

CONCLUSIONS

The procedure proposed for the development of adsorption models from kinetic considerations is seen to be relatively easy to apply. From the demonstrated use of this procedure in the development of the models for the adsorption of mixtures in bimolecular layers as well as *n* layers, it is evident that the procedure may be extended to include the development of more generalized models wherein the number of molecules of any component adsorbed per site, say *A*, may vary from layer to layer. For example

$$\begin{aligned} a_0A(g) + S_0 &\leftrightarrows A_{a_0}S_0 \\ a_1A(g) + S_1 &\leftrightarrows A_{a_1}S_1 \\ &\vdots \\ a_nA(g) + S_n &\leftrightarrows A_{a_n}S_n \end{aligned}$$

The models proposed for the adsorption of mixtures provide a quick and simple procedure for the prediction of adsorption equilibria for mixtures on the basis of parameters determined from the respective isotherms of the pure components of the mixture. Equilibrium adsorptions were predicted with good accuracy by the bimolecular model at both low and high pressures when applied to systems of light hydrocarbon gases.

A two-dimensional equation of state which is thermodynamically consistent with the model for the adsorption of gas mixtures in any number of layers is presented. Since the two-dimensional equation of state and corresponding adsorption model for the same number of adsorbed layers form a thermodynamically consistent set, it is anticipated

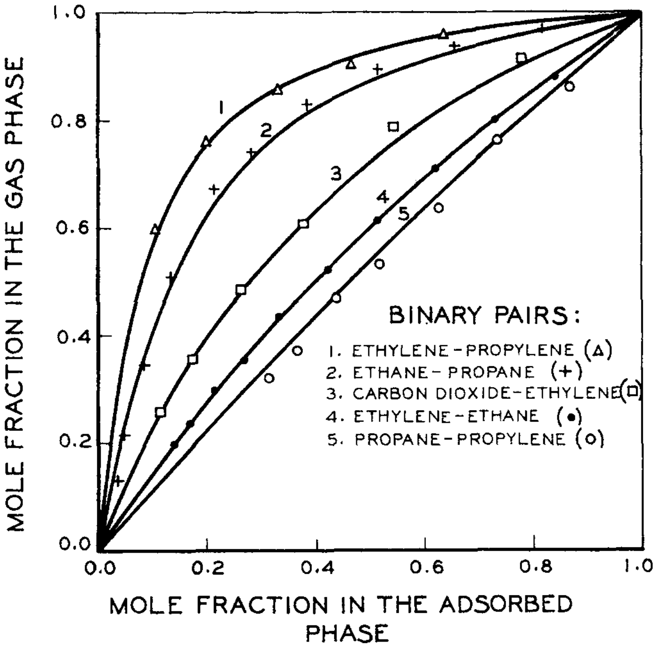

Fig. 2. Comparison of experimental (*21*) and predicted adsorption equilibria for binary gas mixtures at 20°C. and at pressures approximately equal to atmospheric.

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* See footnote on p. 722.

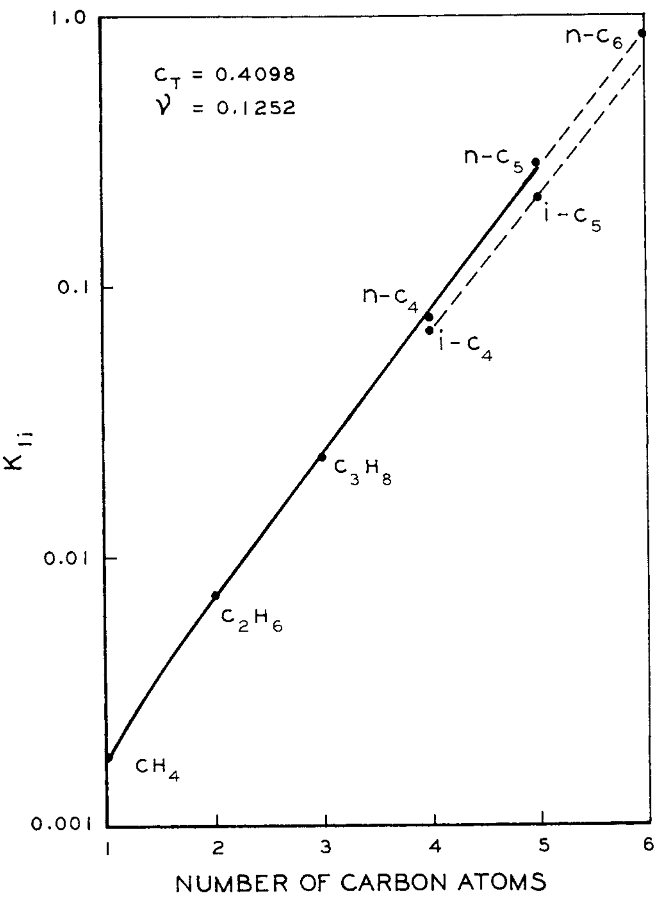

Fig. 3. Constants for the bimolecular-layer model for pure components: based on the high pressure data of Mason and Cooke (17).

that they may be used for the prediction of thermodynamic properties of the adsorbed phase.

ACKNOWLEDGMENT

The support of this project by the National Science Foundation is gratefully acknowledged. The authors also appreciate the encouragement and assistance provided by C. A. Gruver, B. J. Claybourn, W. C. Skinner, L. G. Sharp, and C. L. Humphries of Mobil Oil Company and C. E. Cooke, Jr., of Esso Production Research Company.

NOTATION

$A(g)$ = component A in the gas phase
AS_0 = component A adsorbed on the bare surface
AS_1 = component A adsorbed in the second layer
a = surface area of the adsorbent per unit mass
C_i = concentration of component i in the adsorbed phase, lb. moles of component i adsorbed/unit mass of adsorbent
C_{S_0} = concentration of vacant sites, lb. moles of vacant sites/unit mass of adsorbent
C_{S_1} = concentration sites on the first adsorbed layer which are vacant, moles/unit mass of adsorbent
C_i^σ = lb. moles of component i adsorbed/unit mass of adsorption area
C_T = total number of sites available for adsorption, moles of sites/unit mass of adsorbent. $C_T^\sigma = C_T/a$ and has the units of lb. moles of sites/unit adsorption surface area
C_{1A} = concentration of A in the first adsorbed layer, lb. moles A adsorbed/unit mass of adsorbent. $C^\sigma_{1A} = C_{1A}/a$ and has the units of lb. moles of A/unit of adsorption area
C_{2A} = concentration of A in the second adsorbed layer, lb. moles of A adsorbed/unit mass of adsorbent. $C^\sigma_{2A} = C_{2A}/a$
f_i^V = fugacity of vapor composed of pure component
$\bar{f}_i^V$ = fugacity of component i in a mixture of vapors, lb./sq.in.abs.
k_{1A}, k'_{1A} = rate constants for the adsorption of A on the bare surface; $K_{1A} = k_{1A}/k'_{1A}$
k_{2A}, k'_{2A} = rate constants for the adsorption of A on the first layer; $K_{2A} = k_{2A}/k'_{2A}$
p_i = partial pressure of component i
P = total pressure
$(r_A)_a$, $(r_A)_d$ = rate of adsorption and desorption of A, respectively, moles of A adsorbed (desorbed)/unit time/unit mass of adsorbent
R = conventional gas constant in consistent units
S_0 = vacant sites on the bare surface
S_1 = vacant sites on the first adsorbed layer; $S_1 = AS_0 + BS_0$
T = temperature
ν = constant; defined for a multimolecular-layer adsorption by Equation (19)
π = spreading pressure for the adsorbed phase, force/unit length
ϕ_j = $\sum_{i=1}^{c} K_{ji}\, p_i,\ (1 \leqq j \leqq n)$
χ_j = functions $(1 \leqq j \leqq n)$ of ϕ_1 and ν; defined below Equation (33)

LITERATURE CITED

1. Arnold, James R., *J. Am. Chem. Soc.*, 71 104 (1949).
2. Broughton, D. B., *Ind. Eng. Chem.*, **40**, 1506 (1948).
3. Brunauer, S., P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1939).
4. de Boer, J. H., "The Dynamical Character of Adsorption," Oxford Univ. Press, New York (1953).
5. Edmister, Wayne C., "Applied Hydrocarbon Thermodynamics," pp. 218-285, Gulf Publishing Company, Houston, Tex. (1961).
6. Etherington, L. D., R. E. D. Haney, W. A. Herbst, and H. W. Scheeline, *AIChE J.*, **2**, 65 (1956).
7. Grant, R. J., and M. Manes, *Ind. Eng. Chem. Fundamentals*, 5, 497 (1966).
8. Henson, T. L., and R. J. Kabel, *AIChE J.*, **12**, 606 (1966).
9. Hill, T. L., *J. Chem. Phys.*, **14**, 265 (1946).
10. Hougen, O. A., and K. M. Watson, "Chemical Process Principles," Part III, Wiley, New York (1948).
11. Kapfer, W. H., Monroe Malow, John Happel, and C. J. Marsel, *AIChE J.*, **2**, 456 (1956).
12. Kidnay, A. J., and A. L. Myers, *ibid.*, **12**, 981 (1966).
13. Langmuir, I., *J. Am. Chem. Soc.*, **40**, 1361 (1918).
14. Lewis, W. K., E. R. Gilliland, B. Chertow, and W. P. Dadogan, *Ind. Eng. Chem.*, **42**, 1320 (1950).
15. *Ibid.*, 1326.
16. Markham, E. C., and Arthur Benton, *J. Am. Chem. Soc.*, **53**, 497 (1931).
17. Mason, J. P., and C. E. Cooke, Jr., *AIChE J.*, **12**, 1097 (1966).
18. Myers, A. L., *Ind. Eng. Chem.*, **60**, No. 5, 45 (1968).
19. ———, and J. M. Prausnitz, *AIChE J.*, **11**, 121 (1965).
20. Szepesy, L., and V. Illés, *Acta Chem. Hung.*, **35**, 37 (1963).
21. *Ibid.*, 245.
22. Walas, S. M., "Reaction Kinetics for Chemical Engineers," McGraw-Hill, New York (1959).

Manuscript received June 25, 1968; revision received January 21, 1969; paper accepted January 27, 1969.