Thermodynamics of Mixed-Gas Adsorption

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A simple technique is described for calculating the adsorption equilibria for components in a gaseous mixture, using only data for the pure-component adsorption equilibria at the same temperature and on the same adsorbent. The proposed technique is based on the concept of an ideal adsorbed solution and, using classical surface thermodynamics, an expression analogous to Raoult's law is obtained. The essential idea of the calculation lies in the recognition that in an ideal solution the partial pressure of an adsorbed component is given by the product of its mole fraction in the adsorbed phase and the pressure which it would exert as a pure adsorbed component at the same temperature and spreading pressure as those of the mixture. Predicted isotherms give excellent agreement with experimental data for methane-ethane and ethylene-carbon dioxide on activated carbon and for carbon monoxide-oxygen and propane-propylene on silica gel. The simplicity of the calculation, which requires no data for the mixture, makes it especially useful for engineering applications.

Adsorption equilibria are required in the design of heterogeneous chemical reactors and in certain types of separation equipment. In many cases the desired equilibria are for a mixed rather than for a pure gas, and it is therefore of considerable practical interest to develop a technique for estimating the adsorption equilibria of a gaseous mixture from the known adsorption isotherms of the pure components. Such a technique is described here. The principal idea on which the proposed technique is based is the proper definition of an ideal adsorbed solution in a manner analogous to that used for liquid-phase solutions. As shown towards the end of this work, the equations developed from the ideal-solution concept predict adsorption isotherms which are in excellent agreement with experimental adsorption data for gaseous mixtures.

A complete review of the current status of mixed-gas adsorption is given in the excellent monograph by Young and Crowell (12). The usual procedure for the interpretation of experimental adsorption equilibria for a gaseous mixture is to compare the experimental data with the prediction of some theoretical model. Most models for physical adsorption contain two or three parameters, and it is usually assumed that the parameters for mixture adsorption can be written as some simple function of the pure-component parameters and the composition of the adsorbed phase. Thus, a determination of the pure-component parameters from experimental data permits the prediction of mixture adsorption equilibria.

Unfortunately, the above procedure has not been very successful; the predictions have not been in quantitative agreement with the experimental data (2) and often not even in qualitative agreement (1).

An alternative procedure for interpreting mixture data is the liquid entropy model of Arnold (1). In this model, it was proposed that Raoult's law should be obeyed but only for adsorption sites having the same heat of adsorption. Using two additional assumptions, Arnold proposed a method for calculating mixture data from pure component adsorption isotherms. The disadvantages of the liquid entropy model are that it is thermodynamically inconsistent and that separate numerical integrations are required for each vapor composition.

When one considers these facts, it is surprising that the valuable concept of an activity coefficient, which has proved to be useful in correlating and interpreting other types of equilibria, has not yet been applied to the case of mixed-gas physical adsorption. It is shown in this work how the concept of an activity coefficient can readily be introduced for the case of mixture adsorption equilibria.

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The thermodynamics of physical adsorption has been thoroughly discussed by Hill (4). The validity of the usual thermodynamic equations for the adsorbed phase rests upon three assumptions:

1. The adsorbent is assumed to be thermodynamically inert; that is the change in a thermodynamic property of the adsorbent, such as internal energy, during an adsorption process at constant temperature is assumed to be negligible compared with the change in the same property for the adsorbing gas.

2. The adsorbent possesses a temperature-invariant area which is the same for all adsorbates. This assumption would not be valid, for example, for a molecular sieve adsorbent, where the area available for adsorption depends on the size of the adsorbate molecule.

3. The Gibbs definition of adsorption applies; this definition corresponds to the usual volumetric technique of obtaining experimental adsorption isotherms. In most practical cases, the volumetric technique gives the same experimental results as other methods (the gravimetric measurement of adsorption, for example).

The above assumptions are implicit in almost all theories of physical adsorption. These details have been emphasized here to indicate the generality of the theory to be discussed below. With this thermodynamic model, the basic thermodynamic equations for the adsorbed phase emerge in a form perfectly analogous to the familiar thermodynamic equations for a real fluid. To write these equations for the adsorbed phase, it is necessary only to substitute spreading pressure π for pressure P and to substitute area A for volume V. For example, the equations for the internal energy U and the Gibbs free energy G of the adsorbed phase are

$$dU = TdS - \pi dA + \Sigma \mu_i dn_i \tag{1}$$

$$dG = -SdT + Ad\pi + \Sigma \mu_i dn_i \tag{2}$$

Thus, the intensive variables for the Gibbs free energy are the temperature, spreading pressure, and composition. This definition of a free energy has the advantage that the free energy may be written as

$$G = \Sigma n_i \mu_i \quad \text{(constant } \pi \text{ and } T) \tag{3}$$

Equation (3) follows directly from Euler's theorem.

For the adsorbed phase, the work term analogous to PdV mechanical work for a three-dimensional fluid is πdA. The spreading pressure is the negative of the familiar surface tension and has units of dynes per centimeter. In physical adsorption, π is positive (even for a multilayer adsorption); therefore the system does work on the sur-

roundings during the conceptual process of increasing the area of the adsorbent.

There is no experimental technique for measuring the spreading pressure directly, similar to the mechanical measurement of the surface tension of a liquid. But it must be emphasized that spreading pressure is as much a fundamental thermodynamic variable as entropy or internal energy. There is also no way to measure the entropy of adsorption directly, but this fact does not alter the usefulness of the entropy concept.

It is therefore important to distinguish the thermodynamic variable spreading pressure from its interpretation by a particular physical model. The thermodynamic variable spreading pressure is defined in Equation (1) as the intensive variable for the work term. This thermodynamic spreading pressure can always be calculated from the experimental adsorption isotherm (as shown later) and is independent of any particular physical model of the adsorbed phase.

As an example, the two-dimensional gas model (3) suggests that the adsorbate molecules exert a mechanical force which might, in principle, be capable of experimental measurement. Thus, in the two-dimensional gas model, an ideal gas law is obeyed at low surface coverages (6):

$$\pi A = n_t RT \qquad (4)$$

On the other hand, the localized model of adsorption assumes that adsorbed molecules are not free to translate parallel to the surface and are attached to sites on the adsorbent surface. In this model, it is difficult to conceive a way of measuring a mechanical force parallel to the surface; yet the same ideal gas law given by Equation (4) can be shown to apply at low surface coverage (6).

ACTIVITY COEFFICIENTS

In Equation (2) the intensive variables are π, T, and composition. The authors now propose that activity coefficients for a mixed adsorbed fluid be defined in the same way as that used in the usual thermodynamic treatment of a fluid mixture. Thus, the molar Gibbs free energy change upon mixing at constant T and π is given by

$$g^m(T, \pi, x_1, \ldots) = RT \, \Sigma x_i \ln \gamma_i x_i \qquad (5)$$

The superscript m signifies the change due to mixing at constant T and π; that is for any extensive molar thermodynamic property w

$$w^m(T, \pi, x_1, \ldots) = w(T, \pi, x_1, \ldots) - \Sigma x_i \, w_i{}^\circ(T, \pi) \qquad (6)$$

where $w_i{}^\circ$ is the molar value of the variable for pure i at spreading pressure π and temperature T, and w is the molar value of the variable for the mixture of composition $x_1, \ldots, x_n$.

With the activity coefficients defined in Equation (5), the other thermodynamic functions for the change upon mixing at constant π and T are obtained in the same way as that used in the usual thermodynamic treatment of a fluid mixture. Thus

$$h^m(T, \pi, x_1, \ldots) = -T^2 \left[\frac{\partial (g^m/T)}{\partial T} \right]_{\pi, x_i} =$$
$$- RT^2 \, \Sigma x_i \left(\frac{\partial \ln \gamma_i}{\partial T} \right)_{\pi, x_i} \qquad (7)$$

$$a^m(T, \pi, x_1, \ldots) = \left(\frac{\partial g^m}{\partial \pi} \right)_{T, x_i} = RT \, \Sigma x_i \left(\frac{\partial \ln \gamma_i}{\partial \pi} \right)_{T, x_i} \qquad (8)$$

Equations (3), (5), and (6) may be combined to yield

$$\mu_i(T, \pi, x_1, \ldots) = g_i{}^\circ(T, \pi) + RT \ln \gamma_i x_i \qquad (9)$$

In Equation (9), $g_i{}^\circ$ is the molar Gibbs free energy of component i, when i is adsorbed in the absence of the other components, at the temperature T and at the spreading pressure π. Since there are only 2 deg. of freedom for the adsorption of a pure component, the pressure P in the gas phase is uniquely determined by specification of T and π, and

$$g_i{}^\circ(T, \pi) = g_i{}^\circ(T) + RT \ln P_i{}^\circ(\pi) \qquad (10)$$

In Equation (10), the standard state free energy $g_i{}^\circ(T)$ is defined as the molar Gibbs free energy of component i at the perfect gas state and at a pressure of 1 atm.

In Equation (10) and the derivation to follow, it is assumed that the gas phase obeys the perfect gas law, both for the adsorption of the pure components and for the adsorption of the mixed gas. The pressures of interest in most experimental studies of adsorption are usually less than 1 atm.; therefore, this is usually an excellent approximation.

Substituting Equation (10) into Equation (9) one gets

$$\mu_i(T, \pi, x_1 \ldots) = g_i{}^\circ(T) + RT \ln P_i{}^\circ(\pi) \, RT \ln \gamma_i x_i \qquad (11)$$

Equation (11) gives the chemical potential for the adsorbed phase. The chemical potential for the gas phase, with the same reference state, is

$$\mu_i(T, P, y_i) = g_i{}^\circ(T) + RT \ln P y_i \qquad (12)$$

When one uses the equilibrium criterion that the chemical potential in the adsorbed phase is equal to the chemical potential in the gas phase, Equations (11) and (12) yield the equation of equilibrium for mixed-gas adsorption:

$$P y_i = P_i{}^\circ(\pi) \gamma_i x_i \quad \text{(constant } T) \qquad (13)$$

At high pressures, Equation (13) can be derived in a similar way, with the result

$$P y_i \phi_i = f_i{}^\circ(\pi) \gamma_i x_i \quad \text{(constant } T) \qquad (14)$$

THERMODYNAMIC CONSISTENCY

The Gibbs adsorption isotherm (4) is

$$-A d\pi + \Sigma n_i d\mu_i = 0 \quad \text{(constant } T) \qquad (15)$$

At constant spreading pressure, Equation (15) becomes

$$\Sigma x_i d\mu_i = 0 \quad \text{(constant } T \text{ and } \pi) \qquad (16)$$

Substituting Equation (11) into Equation (16) one gets

$$\Sigma x_i \, d \ln \gamma_i = 0 \quad \text{(constant } T \text{ and } \pi) \qquad (17)$$

Equation (17) is the Gibbs-Duhem equation for an adsorbed phase at constant temperature and spreading pressure. In the case of the usual binary equilibria, such as vapor-liquid equilibria, it is actually impossible to vary the composition while holding the temperature and pressure constant because there are only 2 degrees of freedom. But in the case of adsorption, the area of the adsorbent becomes an additional thermodynamic variable. A similar situation arises for the equilibria of small liquid drops, where a specification of droplet size is necessary to define the thermodynamic system. The pertinent additional intensive variable for the equilibria of liquid droplets is surface tension; similarly, the spreading pressure becomes an additional intensive variable for adsorption equilibria. The phase rule for adsorption is

(degrees of freedom) = (number components) −

(number phases) + 3 $\qquad (18)$

The absorbent is not counted as a component in Equation (18) since it is assumed to be thermodynamically inert. Thus, for binary adsorption equilibria there are 3 degrees of freedom. Unlike the case for vapor-liquid equilibria, Equation (17) for adsorption does not encounter the impossibility of holding two intensive variables constant and varying the composition.

CALCULATION OF ACTIVITY COEFFICIENTS

The calculation of an activity coefficient, from Equation (13), requires the following experimental data: the total pressure of the gas-phase mixture, the composition x_i of the adsorbed phase, the composition y_i of the gas phase, the spreading pressure π for the adsorbed mixture, and the pure-component adsorption isotherms for each adsorbate.

For a pure component, integration of Equation (15) gives

$$\pi(P_i^{\circ}) = \frac{RT}{A} \int_{t=0}^{P_i^{\circ}} n_i^{\circ}(t)\, d \ln t \qquad (19)$$

$$\text{(constant } T)$$

where n_i° (P_i°) is the adsorption isotherm for pure component i. Since n_i° is directly proportional to P_i° at low surface coverage, the integral of Equation (19) is well defined at the lower limit. The integral may be evaluated graphically by plotting n_i°/P_i° vs. P_i° and determining the area beneath the curve. Thus, Equation (19) can be used to calculate $\pi(P_i^{\circ})$ from the experimental adsorption isotherm for pure i.

But the spreading pressure π for the experimental mixture point must be known in order to calculate the activity coefficient from Equation (13). For the case of adsorption of a binary mixture, Equation (15) yields

$$\frac{A}{RT} d\pi = n_1 d \ln Py_1 + n_2 d \ln Py_2 \qquad (20)$$

$$\text{(constant } T)$$

With the pressure P of the mixture held constant, Equation (21) becomes

$$\frac{A}{RT} d\pi = n_1 d \ln y_1 + n_2 d \ln y_2 \qquad (21)$$

$$\text{(constant } T \text{ and } P)$$

Thus, to calculate the spreading pressure π for the experimental mixture point of interest, experimental data are needed at constant temperature and pressure for the entire range of vapor compositions. Such data permit the integration of Equation (21) for the spreading pressure at a given vapor composition. Such a calculation completes the information necessary for the calculation of an activity coefficient.

It is apparent from the above discussion that very accurate experimental data would be required for the accurate calculation of an activity coefficient by means of Equation (13).

THE IDEAL ADSORBED SOLUTION

In the case of an ideal solution, such that the activity coefficient is equal to unity for all values of T, π, and x_i, Equation (13) simplifies to

$$Py_i = P_i^{\circ}(\pi) x_i \quad \text{(constant } T) \qquad (22)$$

The analogy with Raoult's law for vapor-liquid equilibria is clear, but there is the subtle difference in the meaning of P_i°. In the case of vapor-liquid equilibria, P_i° is the vapor pressure of the pure saturated liquid i at the temperature of the solution; here $P_i^{\circ}(\pi)$ is the equilibrium gas-phase pressure corresponding to the solution temperature and to the solution spreading pressure π for the adsorption of pure component i. Thus $P_i^{\circ}(\pi)$ can be thought of as the pure adsorbate vapor pressure for component i at the temperature T and spreading pressure π of the mixture.

Equation (17) indicates that the adsorption ideal solution $(\gamma_i = 1)$ is thermodynamically consistent. Furthermore, Equations (7) and (8) reduce to

$$h^m = 0 \qquad (23)$$

$$a^m = 0 \qquad (24)$$

Therefore, for an ideal adsorbed solution, there is no enthalpy change and no area change upon mixing at constant temperature and spreading pressure. Equation (24) can be combined with Equation (6) to yield

$$a = a_1^{\circ} x_1 + a_2^{\circ} x_2 \quad \text{(constant } T \text{ and } \pi) \qquad (25)$$

or

$$\frac{1}{n_t} = \frac{x_1}{n_1^{\circ}} + \frac{x_2}{n_2^{\circ}} \quad \text{(constant } T \text{ and } \pi) \qquad (26)$$

where n_1° is the amount of component 1 adsorbed at spreading pressure π and temperature T in the absence of component 2. (The above and subsequent equations are written for the special case of binary adsorption, but they may readily be extended to the multicomponent case.)

A relative volatility $\alpha_{1,2}$ may be defined by

$$\alpha_{1,2} = \frac{y_1/x_1}{y_2/x_2} = \frac{P_1^{\circ}}{P_2^{\circ}} \qquad (27)$$

In adsorption work, a selectivity coefficient has been defined (2):

$$s_{1,2} = \frac{x_1/y_1}{x_2/y_2} = \frac{P_2^{\circ}}{P_1^{\circ}} = \frac{1}{\alpha_{1,2}} \qquad (28)$$

The selectivity coefficient $s_{1,2}$ for component 1 is greater than unity if component 1 is the more strongly adsorbed; the relative volatility $\alpha_{1,2}$ of component 1, however, is greater than unity if component 1 is the less strongly adsorbed of the two gases.

Equation (22) yields, for a binary mixture

$$P = P_1^{\circ} x_1 + P_2^{\circ} x_2 \qquad (29)$$

Thus, all of the relationships for the ideal adsorbed solution are of the same form as the well-known equations for ideal vapor-liquid equilibria.

A SPECIAL CASE, VERY LOW SURFACE COVERAGE

At very low surface coverage a statistical mechanical treatment of adsorption (6) gives

$$n_i^{\circ} = K_i P_i^{\circ} \qquad (30)$$

and

$$n_i = K_i P y_i \qquad (31)$$

Thus, at very low surface coverage, the amount of pure component adsorbed is directly proportional to the pressure, and the amount of component i adsorbed in the adsorption of mixtures is directly proportional to the partial pressure in the gas phase. In Equations (30) and (31), K_i is the Henry's law constant, a function only of temperature. Substituting Equation (30) into (19) one obtains

$$\frac{\pi A}{RT} = K_i P_i^{\circ} = n_1^{\circ} = n_2^{\circ} \qquad (32)$$

At constant T and π, Equation (32) yields

$$K_1 P_1^{\circ} = K_2 P_2^{\circ} \qquad (33)$$

and

$$\frac{P_1^{\circ}}{P_2^{\circ}} = \frac{K_2}{K_1} = \frac{n_2/Py_2}{n_1/Py_1} = \frac{y_1/x_1}{y_2/x_2} \qquad (34)$$

Furthermore

$$\frac{1}{n_t} = \frac{x_1}{n_t} + \frac{x_2}{n_t} = \frac{x_1}{n_1^{\circ}} + \frac{x_2}{n_2^{\circ}} \qquad (35)$$
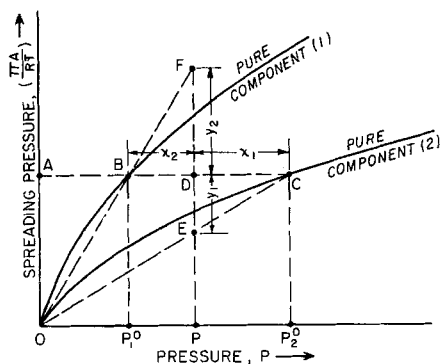
Fig. 1. Calculation of mixture adsorption
equilibria from pure component spreading
pressures.

When Equations (34) and (35) are compared with Equations (26) and (27), it is evident that the equations for the ideal adsorbed solution are rigorous for the special case of low surface coverages.

CALCULATION OF ADSORBED SOLUTION EQUILIBRIA

The calculation of the isothermal mixture adsorption equilibria proceeds as follows:

1. Equation (19) is applied to the experimental data for pure-component adsorption $n_i^o = F_i(P_i^o)$, yielding two relationships:

$$\pi_1^o = \psi_1(P_1^o) \tag{36}$$

$$\pi_2^o = \psi_2(P_2^o) \tag{37}$$

2. Equation (22) is written for both components:

$$Py_1 = P_1^o x_1 \tag{38}$$

$$Py_2 = P_2^o x_2 \tag{39}$$

3. Since the mixing process indicated by Equation (17) is carried out at constant π

$$\pi_1^o = \pi_2^o \tag{40}$$

4. Also

$$x_1 + x_2 = 1 \tag{41}$$

$$y_1 + y_2 = 1 \tag{42}$$

5. There are nine unknowns: π_1^o, π_2^o, P_1^o, P_2^o, P, x_1, x_2, y_1 and y_2. Equations (36) through (42) are seven independent equations. By specifying two independent quantities, such as P and y_1, it is possible to calculate all of the other variables.

6. The total amount adsorbed n_t can be calculated by means of Equation (26) since the experimental data for pure-component adsorption give the values of n_1^o and n_2^o corresponding to the known values of P_1^o and P_2^o.
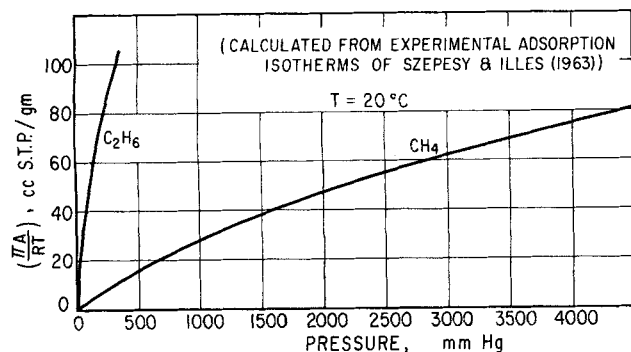
For the special case when the pure-component adsorption isotherms can be fitted empirically by an analytic equation of the form

$$n_i^o = F_i(P_i^o) \tag{43}$$

the procedure described above yields an analytic relationship between P, y_1, and x_1:

$$\int_{t=0}^{\frac{Py_1}{x_1}} F_1(t) \, d \ln t = \int_{t=0}^{\frac{Py_2}{x_2}} F_2(t) \, d \ln t \tag{44}$$

In general, a graphical procedure may be employed as shown in Figure 1. Points A and D are selected arbitrarily, except that point D must lie on the horizontal line AC between the points B and C. The selection of point D specifies the pressure of the mixture. It is easy to verify the following lever-rule relations from Equations (27) and (29):

$$y_1 = \frac{\text{length of line DE}}{\text{length of line FE}} \tag{45}$$
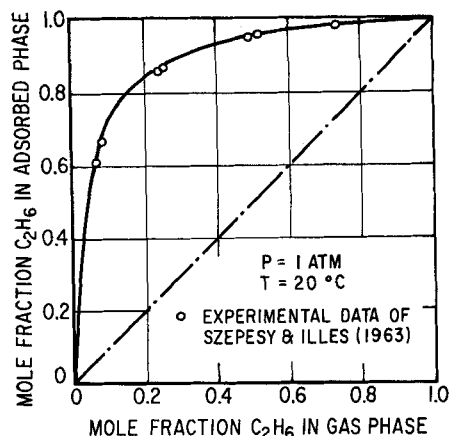
$$x_1 = \frac{\text{length of line DC}}{\text{length of line BC}} \tag{46}$$

Fig. 3. Prediction of equilibrium gas- and
adsorbed-phase compositions by ideal solution
theory, methane-ethane mixtures.

Fig. 2. Spreading pressure for methane and ethane on activated
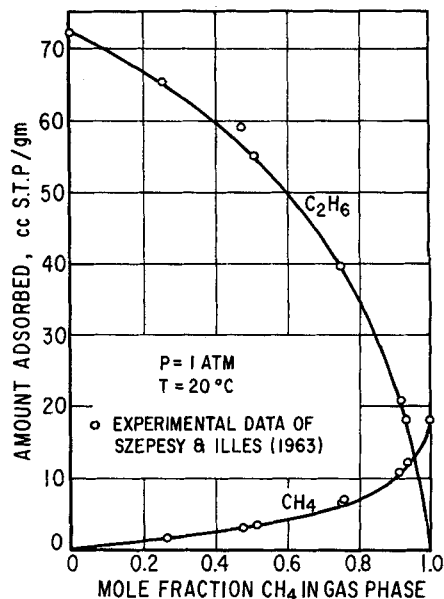carbon.

Fig. 4. Prediction of moles adsorbed by ideal
solution theory, methane-ethane mixtures.
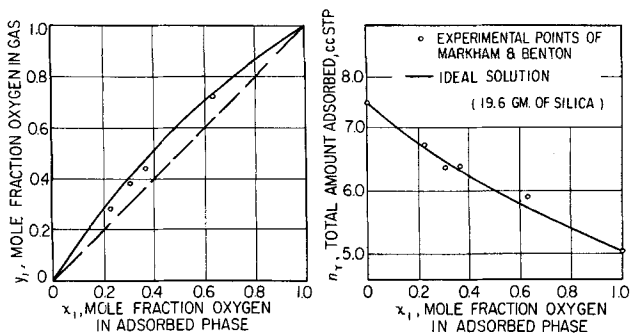
Fig. 5. Prediction of adsorption of carbon monoxide-oxygen mixtures on silica at 100°C., total pressure = 1 atm.

Fig. 7. Adsorption of propane-propylene mixtures on silica gel at 25°C., total pressure = 1 atm.

PREDICTION OF MIXED-GAS ADSORPTION EQUILIBRIA USING THE IDEAL-SOLUTION CONCEPT

The original intention of this work was to calculate activity coefficients from the available experimental adsorption equilibria and then to interpret the resulting activity coefficients by a suitable theory. Surprisingly, the calculated activity coefficients were found to be equal to unity within the experimental error. It was therefore possible to predict mixed-gas adsorption equilibria from the pure-component adsorption isotherms. These predictions were found to be in quantitative agreement with the experimental data.

For example, consider the experimental pure-component adsorption isotherms for methane and ethane on activated carbon at 20°C. (9, 10). With these experimental pure-component adsorption isotherms used, the spreading pressure (actually, $\pi A/RT$) was calculated by graphical integration of Equation (19); the result is given in Figure 2 for both pure gases. With the procedure described in the previous section, the mixed-gas adsorption equilibria were calculated for a total pressure of 1 atm. The (y-x) diagram is given in Figure 3. The solid line is the prediction based on ideal solution theory, and the circles are the experimental points (11). Even though ethane shows strong preferential adsorption, the ideal solution prediction is in quantitative agreement with the experimental results. Figure 4 shows the prediction of the amount of each component adsorbed as a function of the mole fraction of methane in the gas phase. The agreement with experimental data is excellent.

Markham and Benton (8) measured the adsorption equilibria of carbon monoxide-oxygen mixtures on silica at 100°C., at a total pressure of 1 atm. Figure 5 compares the ideal solution prediction with the experimental data. These experimenters also measured the same adsorption equilibria at 0°C. The comparison of the ideal solution prediction (solid line) with the experimental data for 0°C. (8) is given in Figure 6.

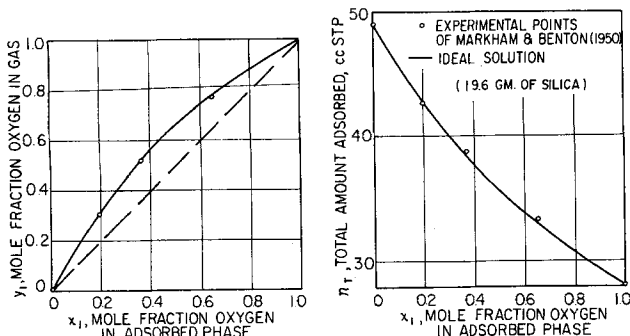Lewis et al. (7) measured the adsorption equilibria of
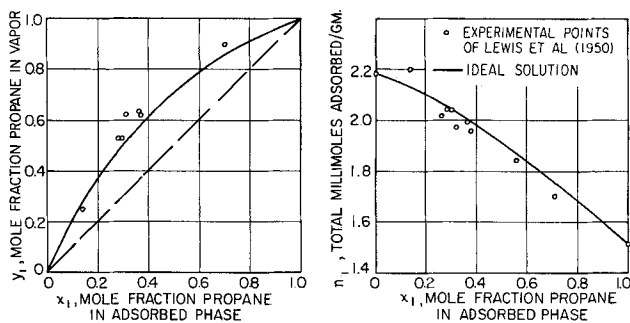
propane-propylene mixtures on silica gel at 25°C. for a total pressure of 1 atm. The comparison of the prediction of ideal solution theory with the experimental data is given in Figure 7.

Finally, Bering and Serpenskii (2) studied the entire equilibrium surface for the adsorption of carbon dioxide-ethylene mixtures on activated carbon at 25.4°C. These authors fitted the Langmuir equation (6) to the pure-component isotherms and then calculated the mixture adsorption equilibria using the Langmuir model for mixtures. The Langmuir model explained the qualitative features of the mixture adsorption equilibria, but the predictions were not quantitative. These authors also noted that the Langmuir equation for mixture adsorption was not thermodynamically consistent. One difficulty, however, not mentioned by these authors was that the Langmuir equation provided a rather poor fit of the pure-component adsorption isotherms. The prediction of the adsorption ideal solution theory is given in Figure 8 for the amount adsorbed; the calculations were made for total pressures of 50, 150, and 250 mm. Hg. The (y-x) diagram predicted by ideal solution theory (solid line) is given in Figure 9 for the total pressures 50 and 200 mm. Hg. Finally, the selectivity coefficient for ethylene, calculated by Equation (28), is given in Figure 10. Bering and Serpenskii concluded that the selectivity depended on the total pressure, but from their data they could not detect any variation with the gas-phase composition. The adsorption ideal solution theory, however, predicts a small composition dependence for the selectivity coefficient of ethylene. The solid lines on Figure 10 indicate that the maximum value of the selectivity coefficient occurs when the gas-phase

Fig. 6. Prediction of adsorption of carbon monoxide-oxygen mixtures on silica at 0°C., total pressure = 1 atm.
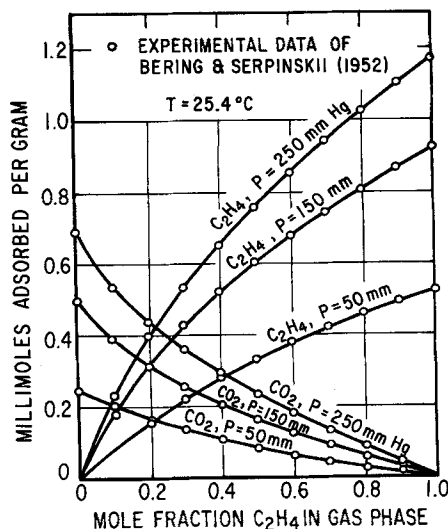

Fig. 8. Prediction of moles adsorbed by ideal solution theory, ethylene-carbon dioxide mixtures.
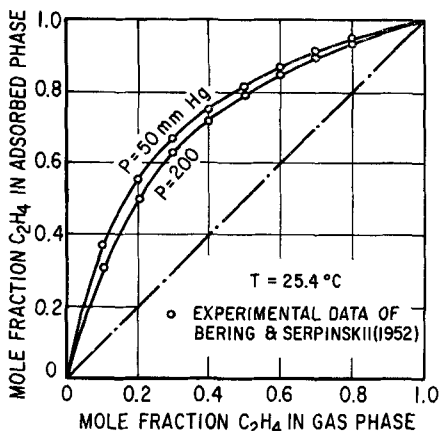
Fig. 9. Prediction of equilibrium gas- and adsorbed-phase compositions by ideal solution theory, ethylene-carbon dioxide mixtures

composition approaches pure carbon dioxide, and the minimum occurs when the gas phase has a large excess of ethylene.

CONCLUSIONS

The predictions of the adsorption ideal solution theory are in quantitative agreement with the experimental data for a wide variety of gas mixtures and for different heterogeneous adsorbents. No mixture parameters were used to make these predictions; the predictions are based entirely on the pure-component adsorption isotherms.

Although there are no ternary (or higher) adsorption equilibria available in the literature, the ideal solution theory for adsorption can be directly applied to multicomponent systems.

Predictions based on the ideal solution concept require that the pure-component adsorption isotherms be measured accurately at low surface coverage, because the integration for spreading pressure is sensitive to this portion of the pure-component adsorption isotherm.

On the basis of physicochemical considerations it is very surprising that mixture adsorption equilibria should be so closely approximated by the concept of an ideal solution. The only way to explain this result is to compare the predictions of a realistic statistical mechanical model with those of an ideal solution. Unfortunately, no such model exists at the present time; the adsorbents which have been studied are highly heterogeneous, but the existing models are for a homogeneous surface. Two pertinent comments can be made:

1. The adsorption equilibria for mixtures are considerably affected by surface heterogeneity, just as in the case
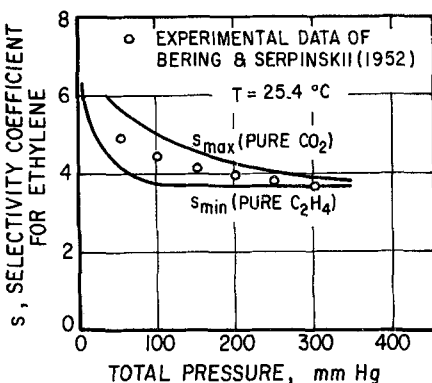
of pure-component adsorption isotherms. Therefore, mixed-gas adsorption equilibria on a homogeneous surface (which have not yet been studied experimentally) may actually exhibit more nonideal behavior than those on a heterogeneous surface.

2. The mixtures studied so far exhibit significant but not excessive deviation from ideal behavior in the case of vapor-liquid equilibria. Further experimental study may reveal mixtures containing highly dissimilar components which may show appreciable nonideality on heterogeneous surfaces. For engineering purposes, however, it is very fortunate that the ideal solution equations appear to do such an excellent job of predicting mixed-gas adsorption equilibria, since these equations are very simple to use and require no mixture data.

ACKNOWLEDGMENT

NOTATION

A = specific area of adsorbent
a = specific area per mole of adsorbate
$f_i^o(\pi)$ = equilibrium fugacity for pure i corresponding to spreading pressure π
F_i = adsorption isotherm function for pure component i
G = Gibbs free energy of adsorbed phase
g = molar Gibbs free energy of adsorbed phase
h = molar enthalpy
K_i = Henry's law constant for adsorption of pure i
n_i = number of moles of component i in adsorbed phase per unit mass of adsorbent
n_t = total number of moles in adsorbed phase per unit mass of adsorbent
$P_i^o(\pi)$ = equilibrium pressure for pure i corresponding to spreading pressure π
P = total pressure
R = gas constant
S = entropy of adsorbed phase
$s_{1,2}$ = selectivity coefficient for component 1 relative to component 2
T = absolute temperature
t = dummy variable
U = internal energy of adsorbed phase
w = any extensive molar property
x_i = mole fraction of component i in adsorbed phase
y_i = mole fraction of component i in gas phase

Greek Letters

$\alpha_{1,2}$ = volatility of component 1 relative to component 2
γ_i = activity coefficient of component i in adsorbed phase
μ_i = chemical potential of component i
π = spreading pressure
ϕ_i = vapor-phase fugacity coefficient of component i
ψ = function

Superscripts

m = change of property upon mixing at constant T and π
o = standard state

Subscripts

i = component i

Fig. 10. Prediction of ideal solution theory: selectivity coefficient varies with vapor composition and total pressure.

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Lateral Transport in a Fluidized-Packed Bed: Part I. Solids Mixing

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A theory was developed to relate the average velocity of a fluidized particle to the fluidizing gas velocity and the minimum fluidization velocity. The development of this relationship was based on a model for particle movement caused by gas bubbles rising through the fluidized bed. The diffusivity for lateral solids mixing in a fluidized-packed bed can then be determined from the average particle velocity and the diameter of the fixed packing by the random walk theory.

The advantages of a fluidized bed over a packed bed as a reactor lie in the movement of the fluidized particles. The moving particles of the fluidized bed transport essentially all of the heat (*1, 12, 13, 14*), whereas heat transfer in the packed bed is essentially by the gas eddies (*7*). Because the volumetric heat capacity of solid particles is much greater than that of gas, the heat content and hence heat transport by fluidized particles is greater. The fluidized particles also disturb surface gas films to increase mass transfer (*14*). The fluidized-packed bed provides a means of utilizing the advantages of fluidized particles in packed-bed reactors. Chemical reactors employing inert solids fluidized in the interstices of a static packed bed of larger bodies undergoing an exothermic gaseous reaction have been demonstrated to provide good reaction control (*5, 6*).

Particle movement in a fluidized-packed bed is in the form of streams of aggregates flowing vertically which are laterally deflected by the fixed packing. The mean distance $\overline{\Delta X}$ that a particle is deflected by a sphere in the x direction (the direction of diffusion) is D_p/π, and the time θ between contacts of the fluidized particle at velocity u with the fixed packing arranged rhombohedrally is $0.909 \, D_p/u$ (*4*). The lateral solids mixing diffusion coefficient D can be related to $\overline{\Delta X}$ and θ by Einstein's (*3*) random walk diffusion equation to yield

$$D = 1/2 \, (\overline{\Delta X^2}/\theta) = 1/2 \frac{u}{0.909 \, D_p} \left(\frac{D_p}{\pi} \right) \quad (1)$$
$$= 0.0558 \, D_p u$$

The random walk theory indicates the mechanism of lateral particle movement and relates the rate of lateral solids mixing to the size of the fixed packing but does not indicate the effect of the physical properties of the fluidized particles and fluidizing gas on the solids mixing. A model is presented which reveals the effect of gas and

solids properties on the mixing by relating the average particle velocity to the fluidizing gas velocity and minimum fluidization velocity. Experimental data are then correlated in terms of the model.

MODEL FOR RELATING AVERAGE PARTICLE VELOCITY TO THE FLUIDIZING GAS VELOCITY

The analysis of Rowe (*8*) and co-workers has shown that the particles are transported by the drag forces in the wake of bubbles rising through the fluidized bed. This concept was used as the basis of a model for particle movement. The model adopted here is defined by these assumptions:

1. Gas flow in excess of the minimum velocity required for fluidization forms bubbles; that is the volumetric rate of bubble formation is $(W - W_{mf})$.

2. The ratio of the volume of particles moved by the bubbles to the volume of the bubbles is a constant F' for a given particle-gas system; that is the volumetric rate of particles in motion is equal to $F' \, (W - W_{mf})$ for particles of a particular size. This assumption is equivalent to asserting that F' is independent of bubble size as well as frequency.

From the above assumptions the volumetric rate of particles per unit area dragged by gas flow through the bubble (average particle velocity) can be expressed as

$$u = F' \left[\frac{W - W_{mf}}{S \, \epsilon_p} \right] = F' \, (V - V_{mf}) \quad (2)$$

The volume F' of particles moved will depend upon the force exerted on the particles (drag force) and the weight of each particle. Rowe and Henwood (*10*) have shown that the drag coefficient for a particle in an array of surrounding particles is 68.5 times the drag coefficient for an isolated particle. On this basis, Rowe (*9*) has shown that