A Gas Adsorption Isotherm Equation Based on Vacancy Solution Theory

SOLOT SUWANAYUEN

and

RONALD P. DANNER

Department of Chemical Engineering
The Pennsylvania State University
University Park, Pa. 16802

A new isotherm equation for pure gas adsorption is developed and tested. In the new method, the adsorption equilibrium is treated as an osmotic equilibrium between two "vacancy" solutions having different compositions. One solution represents the gas phase and the other the adsorbed phase. The vacancy solution is composed of adsorbates and vacancies. The latter is an imaginary entity defined as the vacuum space which acts as the solvent for the system. Thermodynamic equations governing the equilibrium of this system are used to derive the equation of state for the adsorbed phase. The non-ideality of the adsorbed solution is accounted for in terms of an activity coefficient whose composition dependence is described by the Wilson equation. The equation of state, together with the Gibbs adsorption equation, is then used in the derivation of the adsorption isotherm equation. The developed correlation has been evaluated with the adsorption isotherm data of O_2, N_2, and CO on zeolite 10X at 144.3 K, 172.0 K, 227.6 K and 273.2 K, and that of CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, nC_4H_{10}, and CO_2 on Nuxit-AL activated carbon at 293.2 K, 313.2 K, 333.2 K and 363.2 K. For both adsorbents, the correlations are better than those obtained by any other adsorption model which has been extended to gas mixtures. The parameters obtained from the pure component data can be used to predict *a priori* gas-mixture equilibria.

SCOPE

Although multicomponent gas adsorption is a separation process that is widely used in industry, our knowledge of the adsorption equilibria still remains limited. We need equilibrium information to design such processes. However, a careful analysis of single-component adsorption is necessary before dealing with a mixture.

In a study of a single-component adsorption system, experimental data are generally determined at one or more constant temperatures. These data can be correlated by an adsorption isotherm equation whose parameters contain, either implicitly or explicitly, information on the system being investigated. Some available isotherm equations have been derived for a specific type of system, and cannot be applied to other types of systems. For example, the simplified statistical thermodynamic model of Ruthven (1976) is useful only for zeolite adsorbents. The Langmuir equation and the equation which was derived by assuming that an adsorbed phase obeys the two dimensional van der Waals equation of state (de Boer 1953, Young and Crowell 1962, Ross and Olivier 1964) are too simplified to give accurate predictions.

The objective of our work is to develop an adsorption isotherm correlation that is not subjected to such limitations. The desired isotherm equation can most likely be obtained by using a rigorous thermodynamic method, since it is generally independent of the type of adsorption system. The isotherm equation should have a simple mathematical form so that the calculations can be made conveniently, and it should be designed so that the constants determined from the pure gas data can be used directly to predict multicomponent adsorption equilibria. A new isotherm equation which meets the above criteria is developed and evaluated with single-component adsorption data of two different systems, namely the adsorption isotherms of O_2, N_2, and CO on zeolite 10X (Danner and Wenzel 1969, Dorfman 1974, Nolan 1978), and those of CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, nC_4H_{10}, and CO_2 on Nuxit-AL activated carbon (Szepesy and Illés 1963a, b). The extension of this method to gas-mixture equilibria predictions is described by Suwanayuen and Danner (1980).

CONCLUSIONS AND SIGNIFICANCE

The new isotherm equation (19) is of the form

$$p = \left[\frac{n_1^{s,\infty}}{b_1} \frac{\theta}{1-\theta} \right] f(\Lambda_{13}, \Lambda_{31}, \theta)$$

The first term on the right-hand side is the Langmuir equation. The second term represents the nonideality of the system in terms of the activity coefficient, as defined by the Wilson equation parameters (Λ_{13} and Λ_{31}) and the surface coverage. This equation accurately correlates the single-component gas adsorption on two different types of solids over wide ranges of conditions. The maximum fractional coverage is over 0.9 in both systems. The values of the isotherm parameters have been correlated with temperature for the adsorption of O_2, N_2, and CO on zeolite 10X (144.3 K to 273.2 K) and for the adsorption of the hydrocarbons on Nuxit-AL activated carbon (293.2 K to 363.2 K).

The accuracy of the developed correlation surpasses those of the simplified statistical thermodynamic and the virial equations. Accordingly, it is recommended for use in predicting thermodynamic properties, such as spreading pressures and heats of adsorption. The applicability of the

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Address correspondence to R. P. Danner.

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new correlation is general, since the use of the dividing surface in its derivation circumvents the need for the usual assumptions about the solids and the adsorbed phase. For example, we obtain an isotherm equation (18), having the same mathematical form as that of the Fowler isotherm, when the regular solution activity coefficient is employed in its derivation. The derived equation is, however, not subjected to the assumptions on which the Fowler equation is based (i.e., a regular localized monolayer on a homogeneous surface). The new method can be extended to describe multicomponent systems, since the activity coefficient governing the non-ideality of adsorbed mixtures can be readily calculated from binary parameters. These are obtained from single-component adsorption data by using a procedure analogous to a bulk solution.

For the adsorption of the light hydrocarbons on Nuxit-AL activated carbon, we obtained linear correlations for 1) the logarithm of the limiting adsorption amount with respect to the van der Waals size parameter, and 2) for the initial isosteric heat of adsorption with respect to the logarithm of the van der Waals energy parameter.

Among various separation processes, gas adsorption on solids is often the cheapest and therefore most favored alternative. To design an efficient gas adsorber, adsorption data over a wide range of temperature and pressures are required. Therefore, an accurate correlation for interpolating as well as extrapolating single-component data for a variety of conditions is desirable, to keep the requirements for experimental data to a minimum. The goal of this article is to present a single-component adsorption isotherm equation that gives accurate predictions. In the paper by Suwanayuen and Danner (1980), this pure-component isotherm is extended to the more important case of multicomponent adsorption.

Most isotherm equations in the literature contain two to four parameters, and all have some limitations. The Langmuir equation is subjected to a very serious assumption of no lateral interactions. The equation based on the two-dimensional gas model in which the adsorbed phase is governed by the van der Waals equation of state (de Boer 1953, Young and Crowell 1962, Ross and Olivier 1964) is limited by the simplifications required in the derivation of the equation of state. Accordingly, these correlations fail to give accurate predictions for most non-ideal systems. The virial isotherm equation truncated at an appropriate point (Barrer and Lee 1968, Barrer and Davies 1970, Kiselev 1971) has been used successfully for representing pure gas data. Its prediction can always be improved by adding higher order terms. In this case, however, the correlation becomes more empirical, and the values of its parameters exhibit random behavior. The simplified statistical thermodynamic correlation of Ruthven (1976) contains only two parameters, and its accuracy is generally good. The equation, however, was derived for gas adsorption on molecular sieves only, and its mathematical form is very complex.

In deriving an adsorption correlation, the theory used should circumvent the limitations described above. A statistical thermodynamic method (the most rigorous treatment) gives rise to very complicated mathematical equations that can be applied only to specific types of systems. On the other hand, a treatment analogous to the solution theory used in vapor-liquid equilibria is a very general approach. Based on thermodynamics, it can be applied without directly addressing the molecular details; only macroscopic or measurable properties of a solution system are involved. In general, the equation should contain three to four parameters to predict the isotherm accurately. Including a larger number of parameters makes it very difficult to obtain reasonable functional behavior. In addition, a method based on the thermodynamic theory of solutions has the advantage that it can be extended to multicomponent systems by using already available methods. For these reasons, a solution theory model is developed.

ISOTHERM DERIVATION

A number of developments reported in the literature can be applied to the derivation of an isotherm equation. Dubinin (1977) treated single-component adsorption on molecular sieves as an equilibrium between two "vacancy solutions" having different compositions. The vacancy is defined as a vacuum entity having the same size as the adsorbate and occupying the remaining adsorption spaces. An equation of state was then derived, using the criterion for an osmotic equilibrium. Adsorption interactions were accounted for in terms of the osmotic coefficient. Finally, an adsorption isotherm equation was derived for the molecular sieve system.

Lucassen-Reynders (1972, 1973, 1976) used an unusual dividing surface to represent a surfactant monolayer adsorbed at the surface of its bulk solution, and derived the equation of state for the monolayer. The activity coefficient is used to account for non-ideality in the adsorbed phase. His method has the advantage that it can be extended to predict the surface pressure of a mixed surfactant system from pure-component adsorption data. This approach is sufficiently general that it can be applied to other kinds of surface phases, such as found in the adsorption of gases on solids.

In our work, parts of the two concepts described above are used for developing the desired isotherm correlation. First, the equilibrium of the vacancy solutions was adopted as the model for the gas adsorption system. The derivation was then carried out, using the method of Lucassen-Reynders. Before presenting any details, we first define the model representing the adsorption equilibrium.

- Both gas and adsorbed phases are considered to be solutions of adsorbates in a hypothetical solvent called "vacancy." A vacancy is a vacuum entity occupying adsorption spaces that can be filled by adsorbate molecules. Unlike the results of Dubinin, its size is not defined, since it is not required in the present treatment.
- The properties of the adsorbed phase are defined as excess properties in relation to a dividing surface (defined later).
- The entire system including the solid is in thermal equilibrium, but only the gas and the adsorbed solutions are in osmotic or phase equilibrium with each other.
- The equilibrium of the system is maintained by a pressure usually called surface, spreading, or osmotic

pressure which arises from a potential force field at the surface.

According to this model, gas adsorption equilibrium can be considered as an equilibrium between a bulk surfactant solution and its surface phase. Solvent for this system is the vacancy, and the solutes or surfactants are the adsorbates. A pure gas adsorption equilibrium thus becomes an equilibrium between binary vacancy solutions. The expression for the chemical potential of a component in the surface phase was given by Lucassen-Reynders (1972, 1973, 1976):

$$\mu_i^s = \mu_i^{0s} + RT \ln\gamma_i^s x_i^s + \pi\bar{a}_i \tag{1}$$

The last term of the right hand side is the contribution of the surface potential. For the bulk solution, this term vanishes, and the equation for the chemical potential is

$$\mu_i^g = \mu_i^{0g} + RT \ln\gamma_i^g x_i^g \tag{2}$$

Since the system is in equilibrium, both chemical potentials must be equal. Therefore

$$\mu_i^g = \mu_i^s \tag{3}$$

By applying Equations (1), (2), and (3) to the case of a pure solvent (which we call component 3 to allow for easy expansion to at least binary adsorption systems), the relationship between its standard state chemical potentials can be obtained. Since in this situation

$$x_3^g = x_3^s = 1$$

$$\gamma_3^g = \gamma_3^s = 1$$

and $\pi = 0$, the result is

$$\mu_3^{0g} = \mu_3^{0s} \tag{4}$$

Now, by reasoning that in all cases, the bulk vacancy solution is extremely dilute ($x_3 \simeq 1$ and $\gamma_3 \simeq 1$), the contribution of the logarithmic term in Equation (2) to the chemical potential of the vacancy (μ_3) is negligible. The equation of state for the adsorbed phase is obtained by substituting Equations (1), (2) and (4) into Equation (3). After rearranging terms, one obtains

$$\pi = \frac{-RT}{\bar{a}_3} \ln\gamma_3^s x_3^s \tag{5}$$

The next step is to choose a composition dependent equation for the activity coefficient to describe the nonideality in the adsorbed binary vacancy solution. In this work, two different equations are used. The first is an equation to describe non-ideality of a regular solution. The expression for a binary solution was adopted because we are dealing with single-component adsorption, equivalent to a system of binary vacancy solutions. For an adsorbed binary solution of an adsorbate (component 1) and the vacancy (component 3), the activity coefficient of the vacancy is

$$\ln\gamma_3^s = \frac{W_{13}}{RT}(x_1^s)^2 \tag{6}$$

This equation, the two-suffix Margules equation, contains only one parameter. It was chosen because of its simple form.

The second equation employed was the Wilson equation. Wilson (1964) considered the case where the components in a mixture differ not only in molecular size, but also in their intermolecular forces. His development provides a direct method of using binary information to predict multicomponent equilibria. These considerations, together with the proven success of the Wilson equation for vapor-liquid-equilibria when there are no immiscible liquid phases, suggests that it might be useful in the case of adsorption equilibria also.

This equation appeared to be applicable to systems with adsorbates of different sizes and varying adsorbate-adsorbent interactions. Further, it does not introduce undue mathematical complexity. In this case, the activity coefficient of the vacancy in the surface phase is

$$\ln\gamma_3^s = -\ln(x_3^s + \Lambda_{31}x_1^s) - x_1^s\left[\frac{\Lambda_{13}}{x_1^s + \Lambda_{13}x_3^s} - \frac{\Lambda_{31}}{x_3^s + \Lambda_{31}x_1^s}\right] \tag{7}$$

Now, to define the dividing surface that represents the adsorbed phase: Until this point, all the properties mentioned, except those of the bulk solution, depend on the surface definition, since they are functions of the surface excess mole fractions. A simple and meaningful definition is chosen. The dividing surface is located such that the partial molar area of both components (adsorbate and vacancy) are equal to a constant, taken to be the reciprocal of the limiting excess adsorption concentration (Lucassen-Reynders 1976). That is

$$\bar{a}_1 = \bar{a}_3 \equiv \frac{1}{\Gamma_1^\infty} \tag{8}$$

Since, by definition, the excess adsorption concentration is

$$\Gamma_i \equiv \frac{n_i^s}{A} \tag{9}$$

one obtains

$$\bar{a}_1 = \bar{a}_3 = \frac{A}{n_1^{s,\infty}} \equiv a_1^\infty \tag{10}$$

In other words, the partial molar area of each component in the surface phase is defined as equal to the limiting molar area of the adsorbate.

In order to relate the surface excess mole fractions, x_i^s, with a measurable quantity (i.e., a fractional coverage, θ), one has to make use of another thermodynamic relationship

$$\sum_i \bar{a}_i n_i^s = A \tag{11}$$

or

$$\sum_i \bar{a}_i \Gamma_i = 1 \tag{12}$$

By substituting Equation (10) into (12), one gets (for a binary mixture)

$$\Gamma_1 + \Gamma_3 = \frac{1}{a_1^\infty} = \Gamma_1^\infty \tag{13}$$

Since

$$x_i^s \equiv \frac{\Gamma_i}{\Sigma\Gamma_i} \tag{14}$$

then

$$x_1^s = \frac{\Gamma_1}{\Gamma_1^\infty} = \frac{n_1^s}{n_1^{s,\infty}} = \theta \tag{15}$$

$$x_3^s = \frac{\Gamma_3}{\Gamma_1^\infty} = \frac{n_3^s}{n_1^{s,\infty}} = 1 - \theta \tag{16}$$

At this point, it is possible to derive the adsorption isotherm equation from the equation of state (Equation 5) and the Gibbs adsorption equation. The Gibbs adsorption equation for gas adsorption on a solid is

$$RT\, d(\ln p) = \frac{A}{n_1^s}\, d\pi \tag{17}$$

By substituting for π from Equation (5) and integrating, two isotherm equations are obtained, corresponding to the expressions for the activity coefficient in Equation (6) or (7).

$$p = \left[\frac{n_1^{s,\infty}}{b_1} \frac{\theta}{1-\theta} \right] \exp \left[\frac{-2W_{13}}{RT} \theta \right] \tag{18}$$

$$p = \left[\frac{n_1^{s,\infty}}{b_1} \frac{\theta}{1-\theta} \right] \left[\Lambda_{13} \cdot \frac{1-(1-\Lambda_{31})\theta}{\Lambda_{13}+(1-\Lambda_{13})\theta} \right]$$
$$\exp \left[-\frac{\Lambda_{31}(1-\Lambda_{31})\theta}{1-(1-\Lambda_{31})\theta} - \frac{(1-\Lambda_{13})\theta}{\Lambda_{13}+(1-\Lambda_{13})\theta} \right] \tag{19}$$

The integration constant, b_1, is defined such that agreement with Henry's Law is assured as the pressure approaches zero.

$$b_1 = \lim_{p \to 0} \left(\frac{n_1^s}{p} \right) \tag{20}$$

The first bracket of each isotherm equation is exactly the same as the Langmuir equation. The remaining terms can be considered as correction factors to this adsorption isotherm correlation. These terms originate from the activity coefficient, which accounts for the non-ideality or the solute-solvent interaction in the vacancy solution. If the solution is ideal (i.e. the activity coefficient is unity), the correction terms vanish. The vacancy is actually an abstract entity assumed to be the solvent in the model representing the gas-solid system. Therefore, the non-ideality accounted for by the activity coefficient is due to various effects at the gas-solid interface. These interactions, which are generally functions of the adsorption coverage, include those between a molecule in the bulk phase and molecules already adsorbed, and those between an adsorbate molecule and the adsorbent. If the solid is homogeneous, the adsorbate-adsorbent interaction is independent of the coverage. For heterogeneous adsorbents, highly active adsorption sites are filled up before less active ones. Therefore, the adsorbate-adsorbent interaction weakens as the adsorption amount increases.

The effects of the interactions described above are implicitly embedded in the values of the activity coefficient. They are not accounted for separately. The non-ideality in the adsorbed solution is therefore assumed to be similar to that in a bulk solution—such that the composition dependence of both solutions can be described by the same expression.

The isotherm equation derived by using the regular solution activity coefficient (Equation 18) has exactly the same form as that of the Fowler equation. The latter was derived subject to the assumption of a regular localized monolayer, i.e. immobile monolayer with lateral interactions on a homogeneous surface (Young and Crowell 1962, Steele 1974). In this model, the non-ideality is due only to the lateral interactions among adsorbed molecules. Since the imperfection in the adsorbed phase of both models (vacancy solution and Fowler's) is described by the same theory (the lattice theory), it is not surprising that the same isotherm equation was obtained. The fundamental difference between the two approaches is in the assumptions made to develop the equation of state for the adsorbed phase. The assumption for Fowler's model is impractical, since all solids are heterogeneous and the immobility of adsorbed molecules is truly valid for chemisorption only. In our approach, no assumption has been made concerning either the heterogeneity of the solid nor the mobility of the adsorbed phase. The variation of the non-ideality with respect to concentration, caused by various kinds of interactions, is simply assumed to obey the regular solution equation. Therefore, the present method of developing the isotherm equation is a more general one.

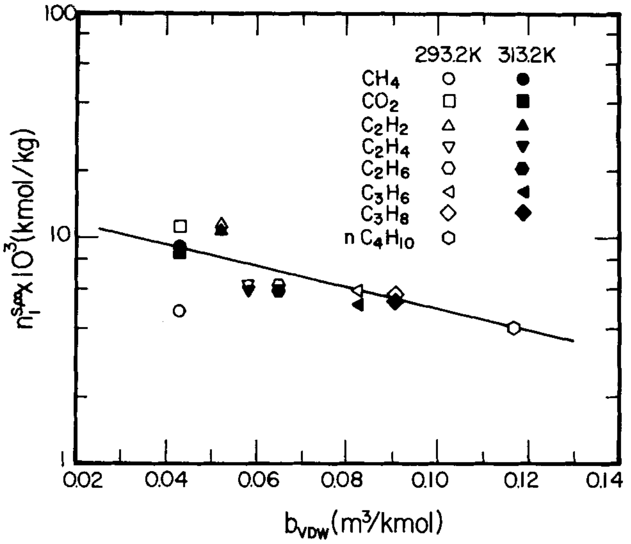

Figure 1. Relationship between the limiting adsorption amount, $n_1^{s,\infty}$, and the van der Waals size parameter, b_{VDW}, obtained for the adsorption of light hydrocarbons and CO_2 on Nuxit-AL activated carbon.

Table 1. Parameters of the Vacancy Solution Model for the Pure-Component Adsorption of Hydrocarbons and Carbon Dioxide on Nuxit-AL Activated Carbon

Adsorbate	$n_1^{s,\infty} \times 10^3$ (kmol/kg)	Temp. (K)	b_1 (kmol/kg · kPa)	Λ_{13}	Λ_{31}
CH_4	8.92	293.2	1.279×10^{-5}	1.611	2.142
		313.2	8.152×10^{-6}	0.304	3.287
		333.2	5.324×10^{-6}	0.285	3.508
		363.2	2.920×10^{-6}	0.189	3.854
C_2H_2	8.12	293.2	1.823×10^{-4}	0.282	3.543
		313.2	8.962×10^{-5}	0.282	3.550
		333.2	4.521×10^{-5}	0.290	3.443
		363.2	1.701×10^{-5}	0.111	4.160
CO_2	8.92	293.2	4.852×10^{-5}	0.368	2.721
		313.2	2.659×10^{-5}	0.215	3.443
		333.2	1.502×10^{-5}	0.356	2.812
		363.2	7.734×10^{-6}	0.338	2.960
C_2H_4	7.63	293.2	2.808×10^{-4}	0.928	3.033
		313.2	1.134×10^{-4}	0.982	2.728
		333.2	6.439×10^{-5}	0.670	3.022
		363.2	2.557×10^{-5}	0.217	3.909
C_2H_6	7.05	293.2	4.632×10^{-4}	0.977	3.044
		313.2	1.555×10^{-4}	1.120	2.485
		333.2	8.557×10^{-5}	0.851	2.734
		363.2	2.132×10^{-5}	0.0565	4.718
C_3H_6	5.89	293.2	4.140×10^{-3}	2.351	2.259
		313.2	1.590×10^{-3}	3.221	2.135
		333.2	5.599×10^{-4}	1.832	2.169
		363.2	1.840×10^{-4}	2.276	1.956
C_3H_8	5.40	293.2	6.255×10^{-3}	1.963	2.670
		313.2	1.631×10^{-3}	2.268	2.172
		333.2	6.663×10^{-4}	2.226	2.034
		363.2	2.076×10^{-4}	2.013	1.988
nC_4H_{10}	4.10	293.2	1.777×10^{-2}	1.501	2.234
		313.2	4.598×10^{-3}	2.923	1.145
		333.2	1.820×10^{-3}	3.526	0.979
		363.2	4.688×10^{-4}	4.336	0.653

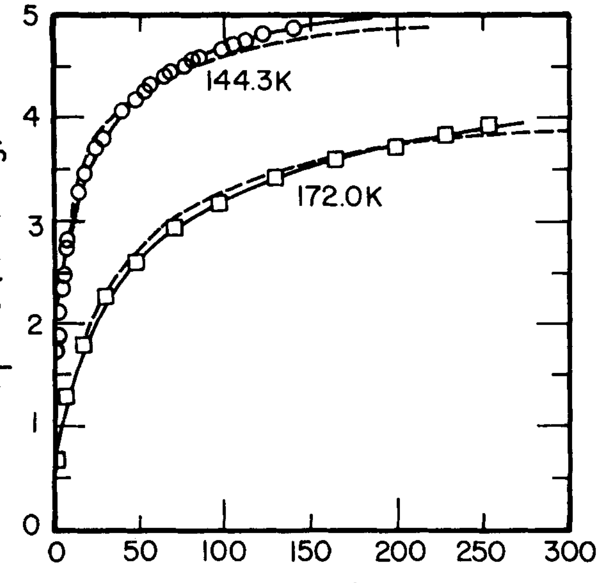

Figure 2. Adsorption isotherms of nitrogen on zeolite 10X at 144.3 K and 172.0 K. Points are experimental data of Danner and Wenzel (1969) and Nolan (1978). Solid line—vacancy solution model; dashed line—simplified statistical thermodynamic model.

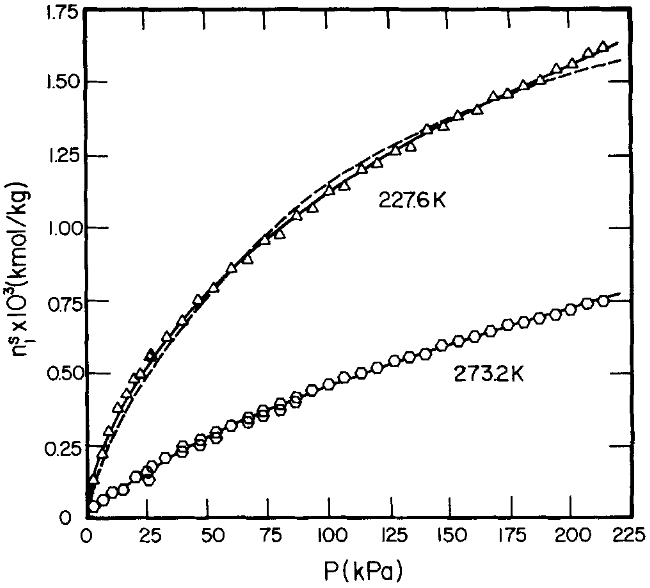

Figure 3. Adsorption isotherms of nitrogen on zeolite 10X at 227.6 K and 273.2 K. Points are experimental data of Nolan (1978). Solid line—vacancy solution model; dashed line—simplified statistical thermodynamic model.

The Fowler isotherm correlation is a well-known three-parameter equation. In general, it can only be applied satisfactorily to adsorption equilibria which deviate only slightly from the Langmuir isotherm. Accordingly, it is not investigated further. Only the new four-parameter isotherm equation (Equation 19) is evaluated with available adsorption data.

ISOTHERM EVALUATION

The new isotherm correlation (Equation 19) was examined with pure gas adsorption data for two different systems: O_2, N_2, and CO on zeolite 10X at 144.3 K, 172.0 K, 227.6 K and 273.2 K (Danner and Wenzel 1969, Dorfman 1974, Nolan 1978) and CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, nC_4H_{10}, and CO_2 on activated carbon type Nuxit-AL (Szepesy and Illés 1963a, b). Both adsorbents are microporous solids. The zeolite has a very uniform pore structure, while the pore size distribution of the activated carbon is random.

The evaluation was carried out in two steps. First, the isotherm parameters were obtained by fitting the isotherm equation to the experimental data. In the second step, the temperature dependence of the values of these parameters was investigated.

A least-squares fitting procedure utilizing the Marquardt-Levenberg optimization algorithm is used to obtain the isotherm parameters from the pure gas adsorption data. The optimization program is a subroutine in the International Mathematical and Statistical Library (IMSL).

The new isotherm equation contains four independent parameters, $n_1^{s,\infty}$, b_1, Λ_{13}, and Λ_{31}, obtained empirically by fitting the experimental data. Plots of experimental adsorption isotherms at various temperatures given in the works of Dubinin (1977) and Fomkin et al. (1975) indicate that the limiting adsorption amount $n_1^{s,\infty}$ varies negligibly with respect to temperature. Consequently, if the $n_1^{s,\infty}$ value is known at one temperature, it should be approximately the same at all temperatures, and only three parameters need to be determined. Since the most reliable limiting value from an isotherm is obtained at the lowest temperature, the limiting value $n_1^{s,\infty}$ was determined from the lowest experimental temperature available. Only the three remaining parameters were determined for the other adsorption isotherms. Another reason for not fitting all four parameters to the data at high temperature is that the isotherms usually have very small curvatures, unless the adsorption pressure is quite high.

In the case of the O_2, N_2, and CO data at 144.3 K, the $n_1^{s,\infty}$ values differed slightly, depending on whether the value was regressed from the data of Danner and Wenzel (1969) or Dorfman (1974). The value used for $n_1^{s,\infty}$ subsequently affected the values of b_1, Λ_{13}, and Λ_{31} at the other temperatures. The isotherms predicted by either set of parameters are essentially identical, however, for each temperature.

An interesting correlation was obtained from the investigation of the adsorption data of the light hydrocarbons on Nuxit-AL carbon. A linear correlation between the logarithms of the calculated values of $n_1^{s,\infty}$ with respect to the van der Waals size parameters (b_{VDW}) of the adsorbates was obtained from the analysis (Figure 1). This type of correlation may be used for generalizing the model to adsorbates of similar kinds. The correlated values for $n_1^{s,\infty}$ (line shown on Figure 1), instead of the experimental ones, were employed throughout the rest of the fitting scheme. The vacancy solution parameters for these systems are listed in Table 1.

The predicted curves are compared with the experimental points for the two systems examined in Figures 2-5. Only a portion of the data tested are presented here; the rest gave analogous results. The accuracy of the new isotherm equation is quite good. Predictions by the simplified statistical thermodynamic correlation, only applicable to the molecular sieve systems, are also shown in Figures 2 and 3. The correlation parameters were obtained by the same least-squares technique used for the present correlation, rather than by the graphical procedure described by Ruthven. The results are not as good as those of the new correlation. For an activated carbon system, predicted curves obtained from the vacancy solution isotherm equation were also compared with those calculated from the virial isotherm equation truncated after the third term. Since in the case of the new isotherm the values of $n_1^{s,\infty}$ were fixed by the correlation shown in Figure 1,

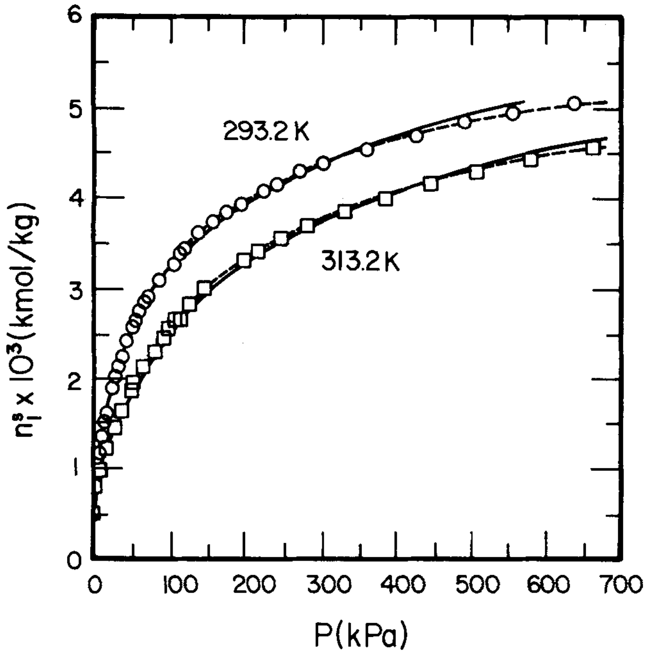

Figure 4. Adsorption isotherms of C_2H_6 on Nuxit-AL activated carbon. Points—experimental data of Szepesy and Illés (1963a,b); solid line—vacancy solution model; dotted line—virial isotherm equation.

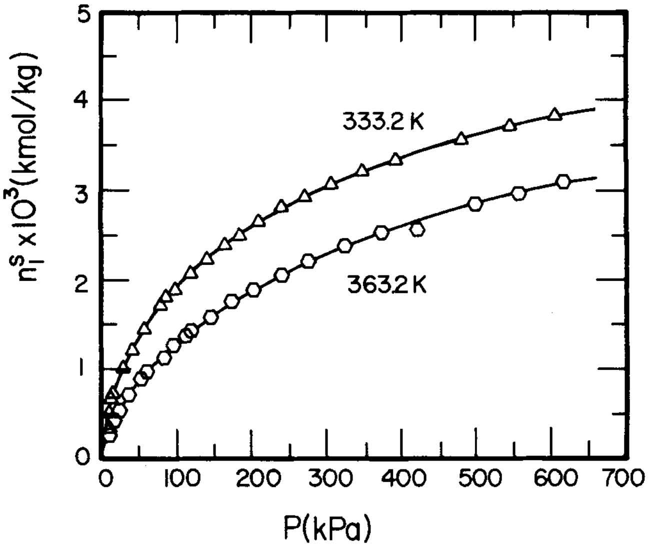

Figure 5. Adsorption isotherms of C_2H_6 on Nuxit-AL activated carbon. Experimental data of Szepesy and Illés (1963a,b). Curves for the vacancy solution model and the virial isotherm equation coincide.

the new equation also has only three parameters to be calculated from the data. The predicted results by both three-parameter correlations are quite similar, as shown in Figures 4 and 5.

Temperature dependencies of the three estimated parameters were then investigated. The plot of the Henry's Law constant (b_1) against $1/T$ (Figures 6 and 7) is linear, as expected. This constant contains information about the adsorbate-adsorbent interaction at infinite dilution. From the relationship between b_1 and T

$$b_1 = b_0 \exp \frac{-q^\theta{}_{st}}{RT} \tag{21}$$

an isosteric heat of adsorption, $q^\theta{}_{st}$, at infinite dilution can be calculated. Since the parameter b_0 is, in general, characteristic only of the sorbate-sorbent system, the logarithmic plot of Equation (21) is a straight line, with a slope of $q^\theta{}_{st}$. Further investigation indicated that $q^\theta{}_{st}$ of the hydrocarbons-activated carbon system could be correlated with the van der Waals interaction parameters,

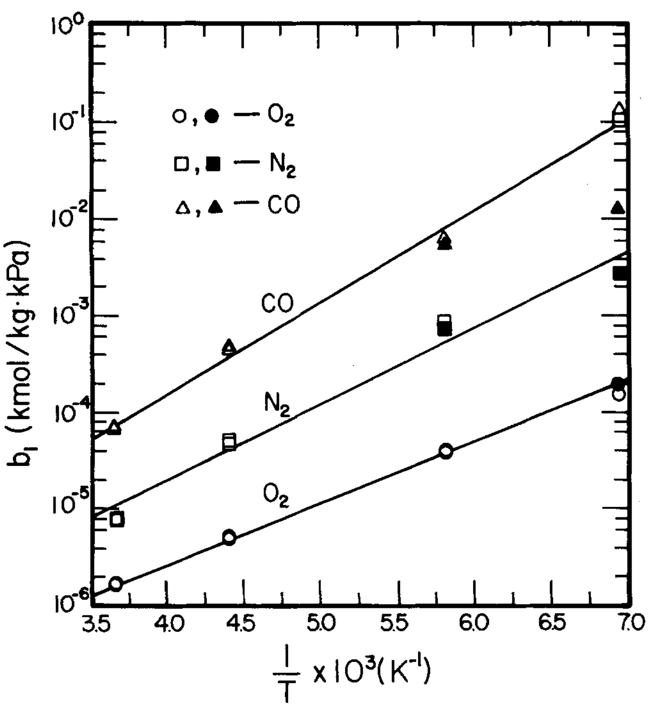

Figure 6. Effect of temperature on Henry's law constant, b_1, for the adsorption of O_2, N_2 and CO on zeolite 10X. Solid symbols—$n_1^{s,\infty}$ obtained from data of Dorfman at 144.3 K. Open symbols—$n_1^{s,\infty}$ obtained from data of Danner and Wenzel at 144.3 K.

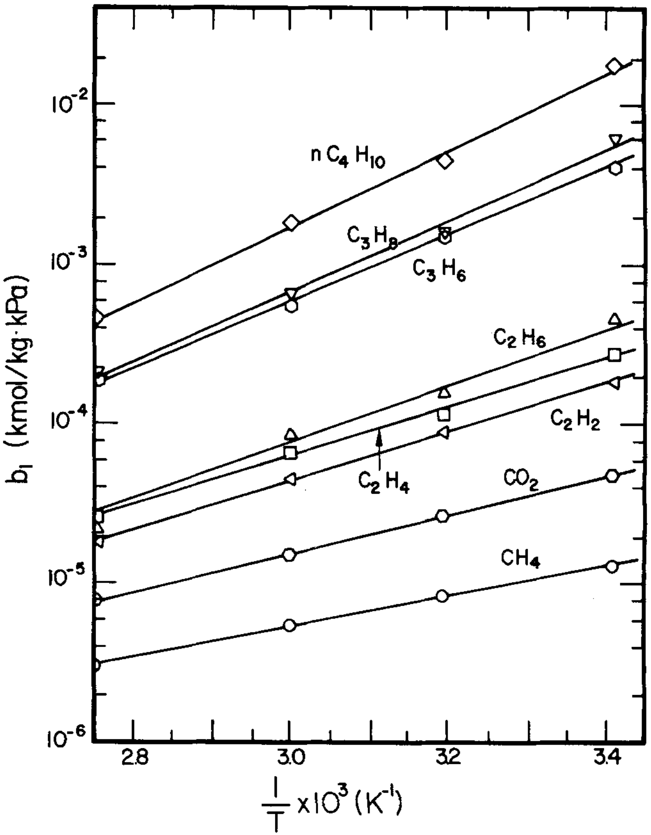

Figure 7. Effect of temperature on Henry's law constant, b_1, for the adsorption of light hydrocarbons and CO_2 on Nuxit-AL activated carbon.

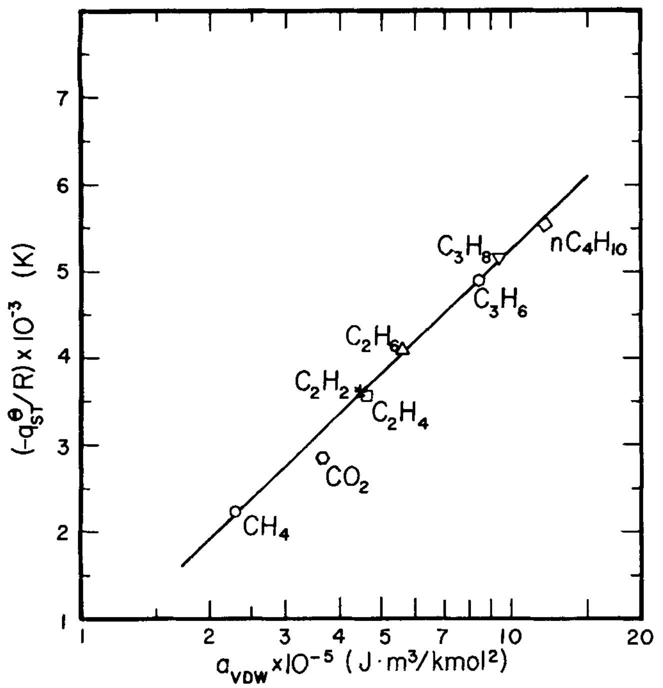

Figure 8. Relationship between the isosteric heat of adsorption at infinite dilution, q^{θ}_{st} and the van der Waals energy parameter, a_{VDW}, obtained for the adsorption of light hydrocarbons and CO_2 on Nuxit-AL activated carbon.

a_{VDW} (Figure 8). Note that the point for CO_2 also falls close to the line.

When the two parameters of the Wilson equation (Λ_{13} and Λ_{31}) were plotted with respect to temperature, the curves shown in Figures 9 through 12 are obtained. For hydrocarbon adsorption, the trends of these curves are approximate functions of the sizes of the adsorbates. For example, the trend of Λ_{13} changes gradually from decreasing with increasing temperature for CH_4 to increasing for nC_4H_{10}. At present, there is still no adequate method of correlating these parameters with temperature. Nevertheless, an empirical equation may be employed to interpolate their values within the experimental range. By this procedure we can predict the adsorption volumes at other temperatures.

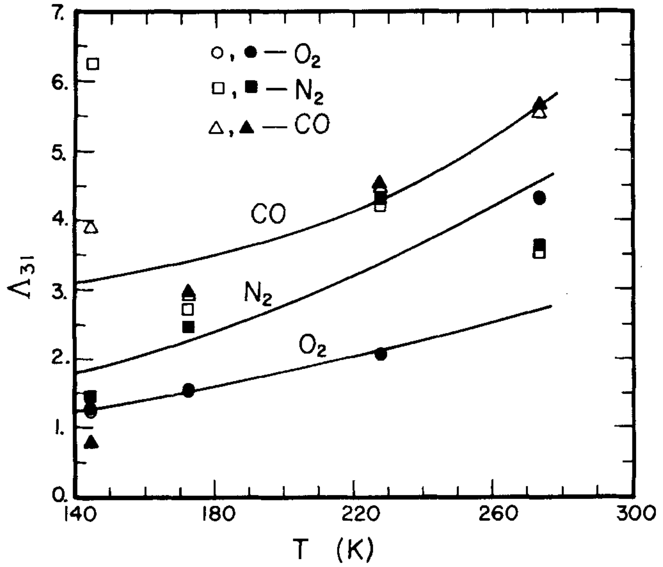

Figure 10. Effect of temperature on the Wilson parameter Λ_{31} for the adsorption of O_2, N_2, and CO on zeolite 10X. Solid symbols—$n_1^{s,\infty}$ obtained from data of Dorfman at 144.3 K. Open symbols—$n_1^{s,\infty}$ obtained from data of Danner and Wenzel at 144.3 K.

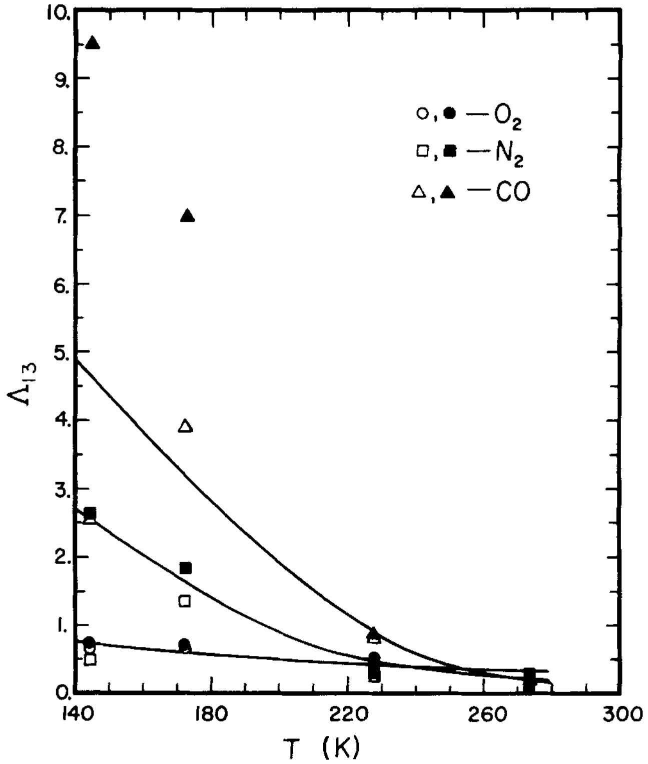

Figure 9. Effect of temperature on the Wilson parameter Λ_{13} for the adsorption of O_2, N_2 and CO on zeolite 10X. Solid symbols—$n_1^{s,\infty}$ obtained from data of Dorfman at 144.3 K. Open symbols—$n_1^{s,\infty}$ obtained from data of Danner and Wenzel at 144.3 K.

An example of the effects of using temperature-smoothed parameters is given for the case of the zeolite systems. Here the b_1, Λ_{13}, and Λ_{31} values scattered, primarily as a result of which 144.3 K data set is used to calculate the $n_1^{s,\infty}$ values as discussed above. Smoothed curves were constructed for these parameters as shown in Figures 6, 9, and 10. These averaged parameters (listed in Table 2) had very little effect on the accuracy of the isotherm predictions. These averaged values were subsequently used to predict mixture adsorption equilibria as described by Suwanayuen and Danner (1980).

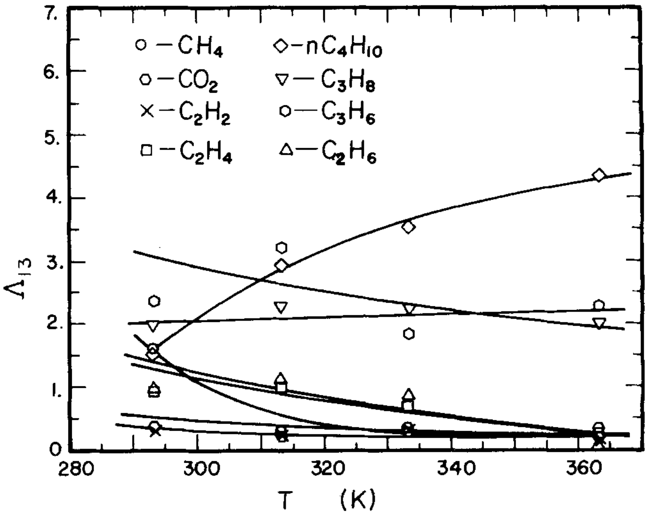

Figure 11. Effect of temperature on the Wilson parameter Λ_{13} for the adsorption of light hydrocarbons and CO_2 on Nuxit-AL activated carbon.

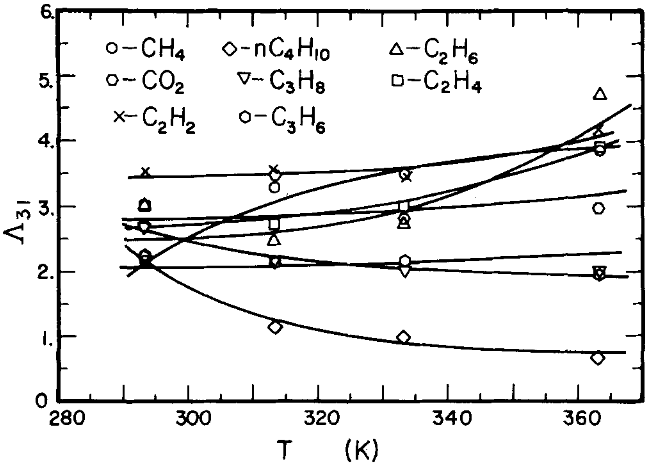

Figure 12. Effect of temperature on the Wilson parameter Λ_{31} for the adsorption of light hydrocarbon and CO_2 on Nuxit-AL activated carbon.

Table 2. Parameters of the Vacancy Solution Model Obtained from the Temperature Curves for the Adsorption of Oxygen, Nitrogen, and Carbon Monoxide on Zeolite 10X

Adsorbate	$n_1^{s,\infty} \times 10^3$ (kmol/kg)	Temp. (K)	b_1 (kmol/kg · kPa)	Λ_{13}	Λ_{31}
O_2	6.62	144.3	1.874×10^{-4}	0.740	1.260
		172.0	3.681×10^{-5}	0.600	1.520
		227.6	4.652×10^{-6}	0.410	2.130
		273.2	1.580×10^{-6}	0.340	2.700
N_2	5.80	144.3	3.949×10^{-3}	2.530	1.840
		172.0	5.087×10^{-4}	1.640	2.250
		227.6	3.949×10^{-5}	0.450	3.360
		273.2	1.071×10^{-5}	0.200	4.550
CO	6.92	144.3	8.868×10^{-2}	4.650	3.120
		172.0	7.730×10^{-3}	3.190	3.410
		227.6	4.016×10^{-4}	0.910	4.270
		273.2	7.429×10^{-5}	0.180	5.630

The vacancy solution isotherm correlation has been applied successfully to the two adsorption systems investigated. For the zeolite 10X system, the equation predicted very accurate adsorption data between the temperature of 144.3 K and 273.2 K. The maximum fractional coverage of the data for this system is approximately 0.91. Between the temperature range of 293.2 K to 363.2 K and coverages up to 0.97, the data for the activated carbon system are represented well by the developed isotherm.

Besides its accuracy, there are several other advantages of the new correlation. First, the isotherm equation can be applied to adsorption systems of gases on all types of solids. This is so because the representation of the adsorbed phase by the dividing surface allows application of the vacancy solution theory, developed originally for the molecular sieve system (Dubinin 1977) to other solid systems. Secondly, the present model is subjected to neither an assumption about the behavior of the adsorbed phase (mobility versus immobility) nor an assumption concerning the characteristics of the solid (homogeneity versus heterogeneity). Nevertheless, these factors are accounted for by the activity coefficient, and the composition dependence of the activity coefficient may be affected by them. Finally, this vacancy solution development can be directly extended to predict gas-mixture adsorption equilibria based only on the pure-component parameters as shown by Suwanayuen and Danner (1980).

ACKNOWLEDGMENT

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NOTATION

$\bar{a}_i$ = partial molar surface area of i (m^2/kmol)
a_1^∞ = molar surface area of 1 at maximum adsorption (m^2/kmol)
a_{VDW} = van der Waals interaction parameter (J·m^3/$kmol^2$)
A = surface area of adsorbent (m^2/kg)
b_0 = temperature independent constant for each adsorbate-adsorbent system (kmol/kg·kPa)
b_1 = Henry's law constant (kmol/kg·kPa)
b_{VDW} = van der Waals size parameter (m^3/kmol)
n_i^s = number of moles of i on surface (kmol/kg)
$n_i^{s,\infty}$ = maximum number of moles of i on surface (kmol/kg)
p = pressure of the gas phase (kPa)
$q^\theta{}_{st}$ = infinite dilution isosteric heat of adsorption (J/mol)
R = universal gas constant = 8.314 J/(mol·K)
T = temperature of the system (K)
W_{13} = regular solution parameter for surface interaction between 1 and 3 (J/mol)
x_i^g = mole fraction of i in gas phase vacancy solution
x_i^s = mole fraction of i in adsorbed phase vacancy solution

Greek Letters

γ_i^g = activity coefficient of i in gas phase vacancy solution
γ_i^s = activity coefficient of i in adsorbed phase vacancy solution
Γ_i = excess surface concentration (kmol/m^2)
Γ_1^∞ = maximum excess surface concentration (kmol/m^2)
θ = fractional coverage
Λ_{13}, Λ_{31} = Wilson's parameters for surface interaction between 1 and 3
μ_i = chemical potential of i in gas phase (J/mol)
μ^0 = standard state chemical potential of i in bulk vacancy solution (J/mol)
μ_i^s = chemical potential of i in adsorbed phase vacancy solution (J/mol)
μ_i^{0s} = standard state chemical potential of i in surface—taken to be that of pure i in equilibrium with pure i in adjoining gas phase at its standard state (J/mol)
π = surface pressure (N/m)

Superscripts

s = surface phase value
0 = standard state value
∞ = value at maximum adsorption limit
θ = value at infinite dilution

Subscripts

i = component i
1 = adsorbate
3 = vacancy

LITERATURE CITED

Barrer, R. M. and J. A. Davies, "Sorption in Decationated Zeolite I. Gases in Hydrogen-chabazite," *Proc. Roy. Soc. Lond.*, **A320**, 289 (1970).

Barrer, R. M. and J. A. Lee, "Hydrocarbons in Zeolite L II. Entropy, Physical State and Isotherm Model," *Surface Sci.*, **12**, 354 (1968).

Danner, R. P. and L. A. Wenzel, "Adsorption of Carbon Monoxide-Nitrogen, Carbon Monoxide-Oxygen and Oxygen-Nitrogen Mixtures on Synthetic Zeolites," *AIChE J.*, **15**, 515 (1969).

de Boer, J. H., *The Dynamical Character of Adsorption*, Oxford Univ. Press, London (1953).

Dorfman, L. R., "Ternary Adsorption Equilibria of Oxygen-Nitrogen-Carbon Monoxide on Molecular Sieves," M.S. thesis, The Pennsylvania State University, University Park (1974).

Dubinin, M. M., "New Results in Investigations of Equilibria and Kinetics of Adsorption of Gases on Zeolites," presented at the Fourth International Conference on Molecular Sieves, Univ. Chicago (April 18-22, 1977).

Fomkin, A. A., V. V. Serpinski and B. P. Bering, "Investigation of the Adsorption of Xenon on NaX Zeolite within a Broad Range of Pressures and Temperatures," *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **24**, 1147 (1975).

Kiselev, A. V., "Vapor Adsorption on Zeolites Considered as Crystalline Specific Adsorbents," Molecular Sieve Zeolite-II, *Adv. Chem. Ser.*, **102**, ACS, Washington, D.C. (1971).

Lucassen-Reynders, E. H., "A Surface Equation of State for Mixed Surfactant Monolayers," *J. Colloid Interface Sci.*, **41**, 156 (1972).

Lucassen-Reynders, E. H., "Interactions in Mixed Monolayers I. Assessment of Interaction between Surfactants," *J. Colloid Interface Sci.*, **42**, 554 (1973).

Lucassen-Reynders, E. H., "Adsorption of Surfactant Monolayers at Gas/Liquid and Liquid/Liquid Interfaces," *Prog. Surf. Membrane Sci.*, **10**, 253 (1976).

Myers, A. L. and J. M. Prausnitz, "Thermodynamics of Mixed-Gas Adsorption," *AIChE J.*, **11**, 121 (1965).

Nolan, J. T., "Effect of Temperature on the Adsorption of Binary Gas Mixtures," M.S. thesis, The Pennsylvania State University, University Park (1978).

Ross, S. and J. P. Olivier, *On Physical Adsorption*, Wiley, New York (1964).

Ruthven, D. M., "Sorption of Oxygen, Nitrogen, Carbon Monoxide, Methane, and Binary Mixtures of These Gases in 5A Molecular Sieve," *AIChE J.*, **22**, 753 (1976).

Steele, W. A., *The Interaction of Gases with Solid Surfaces*, Pergamon Press, Oxford (1974).

Suwanayuen, S. and R. P. Danner, "Vacancy Solution Theory of Adsorption from Gas Mixtures," *AIChE J.*, **26**, 76 (1980).

Szepesy, L. and V. Illés, "Adsorption of Gases and Gas Mixtures, I. Measurement of the Adsorption Isotherms of Gases on Active Carbon up to Pressures of 1000 torr," *Acta Chim. Hung.*, **35**, 37 (1963*a*).

Szepesy, L. and V. Illés, "Adsorption of Gases and Gas Mixtures, II. Measurement of the Adsorption Isotherms of Gases on Active Carbon under Pressures of 1 to 7 atm.," *Acta. Chim. Hung.*, **35**, 53 (1963*b*).

Wilson, G. M., *J. Am. Chem. Soc.*, **86**, 127 (1964).

Young, D. M. and A. D. Crowell, *Physical Adsorption of Gases*, Butterworths, London (1962).

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Vacancy Solution Theory of Adsorption From Gas Mixtures

SOLOT SUWANAYUEN
and
RONALD P. DANNER

Department of Chemical Engineering
The Pennsylvania State University
University Park, Pa. 16802

A new correlation that improves predictions of gas mixture adsorption equilibria from single-component adsorption isotherm data is developed, based on the vacancy solution theory. In this theory, the adsorbed phase and the gas phase are treated as two vacancy solutions. The vacancy is an imaginary solvent occupying spaces that will be filled by adsorbates. The composition relationship between the two phases is derived from thermodynamic equilibrium criteria. The non-ideality of the adsorbed solution is accounted for by an activity coefficient, whose composition dependence is described by the Wilson equation. For an adsorption system, the binary parameters, adsorbate and vacancy, can be obtained from regression of the pure gas adsorption data with the vacancy solution isotherm equation. These parameters are then used to predict multicomponent adsorption equilibrium, assuming that the adsorbate-adsorbate interactions are negligible. The new correlation has been tested on two different kinds of binary adsorption systems. The new method is more general, simpler to apply, and more accurate than other available models. The predictions can be further improved by taking into account the adsorbate-adsorbate interactions.

SCOPE

Numerous industrial purification and bulk separation processes involve gas mixture adsorption. To design such processes, multicomponent equilibrium data are needed. Since it is very tedious to collect the mixture data, a reliable way to estimate the mixture equilibrium from single-component adsorption isotherm data is preferred. While a number of correlations have been developed for this purpose, all have some limitations. Consider the ideal adsorbed solution model of Myers and Prausnitz (1965) or the simplified statistical thermodynamic model of Ruthven (1976). The former is subjected to the assumption that the adsorbed mixture behaves ideally, and it can not predict non-ideal behavior such as adsorption azeotropes. The latter method can predict the non-ideality caused by size differences of the adsorbed molecules, but has been specifically developed for adsorption on zeolites and cannot be applied to other substrates.

Address correspondence to R. P. Danner.

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