# Characteristic Adsorption Isotherm for Adsorption of Vapors on Heterogeneous Adsorbents

The dimensionless group $[(mRT/\Delta G)\ln(P/P_o)]$ is a universal function of $\theta$ (fractional filling of micropores) for different vapors adsorbed on a heterogeneous adsorbent. Adsorptive parameters are the saturation capacity ($m$) and the free energy of immersion of the solid in bulk liquid adsorbate ($\Delta G$). The heat of immersion of the adsorbent determines the temperature dependence of $\Delta G$ according to the Gibbs-Helmholtz equation $\Delta H = \partial(\Delta G/T)/\partial(1/T)$.

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## SCOPE

Thermodynamic methods for predicting adsorption from gas mixtures (Sircar and Myers, 1973) are based upon the postulate that adsorbates form ideal adsorbed solutions (IAS). No mixture data are needed to make these predictions, but experimental data for the adsorption of each pure vapor are required. The possibility of predicting adsorption isotherms of pure vapors from that of a reference vapor has received considerable attention (Lewis et al., 1950; Potter and Sussman, 1957; Grant et al., 1962). Let the adsorption isotherm of a pure vapor be $n(P)$, where $n$ is the number of moles of vapor adsorbed per unit mass of adsorbent and $P$ is the pressure. The idea is to identify reduced variables $n^*$ and $P^*$ such that the functions $n^*(P^*)$ for different vapors coalesce into a single curve, called the characteristic curve, that is unique for each adsorbent. The reduced variables should be dimensionless. This characteristic curve, once determined for a reference vapor at a particular temperature, could be used to predict adsorption isotherms of other vapors. Moreover, adsorption at other temperatures could be predicted from the characteristic curve, as proposed originally by Polanyi (Young and Crowell, 1962). Such an idea, if successful, would be extremely useful for the design of adsorbers.

## CONCLUSIONS AND SIGNIFICANCE

Isotherms for adsorption of different vapors on an energetically heterogeneous adsorbent can be coalesced into a single characteristic curve using Eq. 38. Two properties are required to generate the isotherm of an absorbate from that of another reference adsorbate: $\Delta G$ and $m$. $\Delta G$ is the free energy of immersion of the adsorbent in liquefied adsorbate, and $m$ is the adsorptive capacity at saturation. For porous adsorbents, $m$ can be obtained from the value for the reference adsorbate ($m_R$) using Eq. 40. There is, however, no simple relation between the free energies of immersion of the adsorbate and the reference substance. Experimental data on adsorption from binary liquid mixtures of the adsorbate and the reference substance are needed to calculate $\Delta G$ from $\Delta G_R$ using Eq. 41. Since liquid isotherms are easier to measure than gas isotherms, this may be the most convenient method to obtain $\Delta G$. Alternatively, one experimental point for the pure vapor adsorbate is sufficient to generate its entire isotherm using Eq. 38 along with the data for the reference substance.

The ability of Eq. 38 to correlate isotherms of different vapors is tested using data for benzene, cyclohexane, *n*-heptane and 1,2-dichloroethane adsorbed on silica gel. Although these molecules differ significantly in their structure, polarity, and chemical properties, Eq. 38 coalesces their isotherms into a single curve as shown in Figure 4. Earlier attempts to generate characteristic curves of this type have been successful only for adsorbates having similar molecular structure and properties or for members of a homologous series.

Systematic measurements of the free energy of immersion of different adsorbents in a wide variety of adsorbates are needed so that theories for predicting $\Delta G$ can be developed and tested.

## INTRODUCTION

The concept of a characteristic curve does not apply to a nonporous, homogeneous adsorbent, for which the surface is energetically uniform and adsorbed molecules behave like a two-dimensional gas. The two-parameter principle of corresponding states may be applied to the adsorbed film, and it has been shown (Myers and Prausnitz, 1965) that:

$$P^* = \frac{B_{1s}P}{RTm} = \psi(\theta, T_r) \qquad (1)$$

where $\psi$ is a universal function for different adsorbates. Here $m$ is monolayer coverage, $B_{1s}$ is the adsorption second virial coefficient, $\theta$ is the fractional surface coverage, and $T_r$ is the reduced temperature of the adsorbate. $\psi$ is a corresponding states function, but it is not a characteristic curve because it depends upon $T_r$ as well as $\theta$. A characteristic curve is a function of $\theta$ only.

A heterogeneous surface has a distribution $f_E(E)$ of energies such that adsorption on the portion of the surface with energy $E$ is $\theta = \theta(P, T, E)$. Here $E$ is a positive quantity corresponding to the decrease in energy for the transfer of one mole of adsorbate from the gas to the adsorbed phase. $\theta(P, T, E)$ is the local adsorption isotherm; the total adsorption is given by integration over the entire surface:

$$\theta(P, T) = \int_{E_{\min}}^{E_{\max}} \theta(P, T, E) f_E(E)\, dE \qquad (2)$$

$f_E(E)$ is the energy density function, normalized so that:

$$\int_{E_{\min}}^{E_{\max}} f_E(E)\, dE = 1 \qquad (3)$$

This model of a heterogeneous surface is based upon the assumption that patches of energy $E$ may be treated independently of patches of different energy (Zolandz and Myers, 1979). Thus the patches are large enough so that interactions across boundaries can be neglected but small enough to justify the concept of an energy distribution. The integrations in Eqs. 2 and 3 extend from the lowest ($E_{\min}$) to the highest ($E_{\max}$) values of energy of adsorption.

The detailed shape of the local adsorption isotherm in Eq. 2 becomes less important as the surface heterogeneity increases. To illustrate this fact, consider the two local isotherms drawn in Figure 1. One is the Langmuir equation:

$$\theta = \frac{Cx}{1 + Cx} \qquad (4)$$

and the other is the step function:

$$\theta = 0 \text{ for } \{x < 1/C\}$$
$$\theta = 1 \text{ for } \{x \geqq 1/C\} \qquad (5)$$

where $x = P/P_o$ = reduced vapor pressure and $C = C_o \exp(E/RT)$.

We choose this particular pair of equations because they portray two limits: abrupt condensation due to cooperative effects for the step isotherm, and no cooperative effects at all for the Langmuir isotherm. Thus a comparison of the two exaggerates the influence of the local isotherms, which coincide only at $\theta = 1/2$. Figure 1 is drawn for the case $C = e^5$.

Let the energy distribution be uniform over the interval $E_{\min} \leqq E \leqq E_{\max}$, so that $f_E = 1/(E_{\max} - E_{\min})$ = constant. Substitution of Eqs. 4 and 5 into Eq. 2 yields the isotherms for the heterogeneous surface. For the local step isotherm:

$$\theta = 1 + \frac{RT \ln x}{\sigma} \qquad (6)$$

where

$$\sigma = E_{\max} - E_{\min}$$

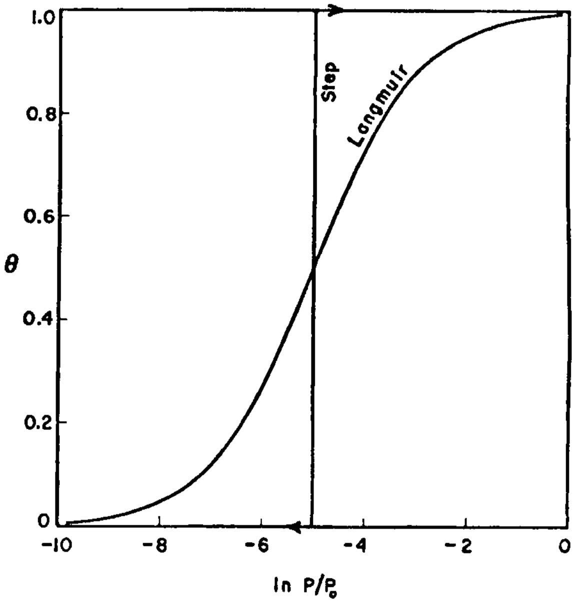

Figure 1. Langmuir local isotherm ($C = e^5$) and step local isotherm.

For the local Langmuir equation,

$$\theta = \frac{RT}{\sigma} \ln \left[ \frac{1 + C_1 x \exp(\sigma/RT)}{1 + C_1 x} \right] \qquad (7)$$

where

$$C_1 \equiv C_o \exp(E_{\min}/RT)$$

Equations 6 and 7 are plotted in Figure 2 for the case $(\sigma/RT) = 10$, with the same average energy of adsorption as for Figure 1:

$$C_o \exp(\bar{E}/RT) = e^5$$

For a uniform distribution

$$\bar{E} = E_{\min} + (\sigma/2)$$

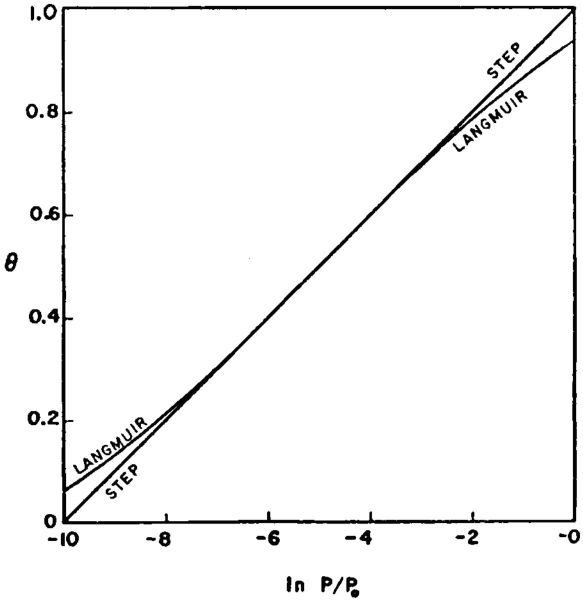

Figure 2. Adsorption isotherms for heterogeneous surface with a uniform distribution ($\sigma/RT = 10$) for Langmuir local isotherm and step local isotherm.

and, for the particular values of $\bar{E}$, $C_o$, and $\sigma$ chosen above:

$$C_l = C_o \exp(E_{\min}/RT) = C_o \exp(\bar{E}/RT) \exp(-\sigma/2RT) = 1$$

Figure 2 shows that the shape of the local adsorption isotherm is obliterated by the energy distribution in the region $0.2 < \theta < 0.8$. In this region, the overall isotherm for the heterogeneous surface is a property of the energy distribution (here, a uniform distribution). Actual surfaces may not be as heterogeneous as this one, but their local isotherms will be more alike than those in Figures 1 and 2. Thus the concept of a surface sufficiently heterogeneous for the adsorption to depend only on the energy distribution function should be a useful idealization.

## GENERALIZED ISOTHERM FOR HETEROGENEOUS SURFACES

The adsorptive properties of a heterogeneous surface will be examined without specifying the form of the energy distribution. Let the energy distribution $f_E(E)$ extend over the interval:

$$E_{\min} \leqq E \leqq E_{\max}$$

The energy function is normalized according to Eq. 3 but is otherwise arbitrary. Since the model is a surface with sufficient heterogeneity to mask the influence of the local isotherm, we choose the step isotherm for its simple mathematical form. From Eqs. 5 and 6:

$$\begin{aligned} \theta = 0;& \text{ for } \{x < 1/C \text{ or } E_{\min} \leqq E < -RT \ln(C_o x)\} \\ \theta = 1;& \text{ for } \{x \geqq 1/C \text{ or } E_{\max} \geqq E \geqq -RT \ln(C_o x)\} \end{aligned} \tag{8}$$

Substitution of Eq. 8 into Eq. 2 gives:

$$\theta(P,T) = \int_E^{E_{\max}} f_E(E)dE = 1 - \int_{E_{\min}}^{E} f_E(E)dE \tag{9}$$

The limit of integration is:

$$E = -RT \ln(C_o x) \tag{10}$$

The boundary condition is $\theta = 1$ at $P = P_o$, where the sites of lowest energy become occupied:

$$E_{\min} = -RT \ln C_o \tag{11}$$

Subtracting Eq. 11 from Eq. 10, we get:

$$E = E_{\min} - RT \ln x \tag{12}$$

A new energy variable $z$ is defined:

$$z = E - E_{\min} = -RT \ln x \tag{13}$$

With the aid of Eq. 13, the adsorption isotherm, Eq. 9, may now be written:

$$\theta(P,T) = 1 - \int_0^z f_z(z)dz \tag{14}$$

The normalization requirement for the density function is:

$$\int_0^1 f_z(z)dz = 1 \tag{15}$$

The cumulative distribution function for the energy is:

$$F(z) = \int_0^z f_z(z)dz \tag{16}$$

Substituting Eqs. 13 and 16 into Eq. 14, the adsorption isotherm assumes the form:

$$-RT \ln x = F^{-1}(1 - \theta) \tag{17}$$

where $F^{-1}$ is the inverse function of $F$. Note that $(-RT \ln x)$ is not a characteristic function because $F^{-1}$ has units of energy and its value is therefore different for each adsorbate. $(-RT \ln x)$ is the well-known Polanyi potential (Young and Crowell, 1962). According to Polanyi's theory, the potential for a particular adsorbate is independent of temperature if plotted vs. the volume of adsorbate ($nv_o$), where $v_o$ is the molar volume of saturated liquid adsorbate. This agrees with Eq. 17 if the pore volume is independent of temperature, as is customarily assumed. The advantage of Eq. 17 is that it relates the potential to the energy distribution. The classical derivation of the Polanyi theory (Aveyard and Haydon, 1973) rests upon the existence of equipotential surfaces, but their distribution is left undefined.

The idea of calculating the adsorption isotherm for a heterogeneous surface by neglecting adsorbate interactions was suggested by Drain (1954). Cerofolini (1972) derived the energy distribution of the Dubinin-Radushkevich equation using a local step isotherm. Harris (1968) derived Eq. 14 and showed that if the local isotherm is a Langmuir equation, then the step isotherm overestimates the dispersion of the energy distribution. However, the Langmuir equation is unrealistic in the opposite direction. Harris (1968) called the use of the step isotherm the condensation approximation. Later, Harris (1969) published calculations which showed that the step isotherm, when used to calculate the energy distribution for a Hill-deBoer local isotherm (Young and Crowell, 1962), provides a good approximation to the actual energy distribution. This may be due to the fact that the S-shaped Hill-deBoer isotherm is similar to a step isotherm, at least for high-energy sites.

The accuracy of the approximation of substituting the step isotherm for the actual local adsorption increases with the dimensionless dispersion $\sigma^* = \sqrt{(\overline{E^2}) - (\bar{E})^2}/RT$ of the energy distribution. Detailed information on this parameter is not yet available, but a value of the order of unity or greater would be expected for surfaces characterized as heterogeneous.

Equation 17 predicts that the logarithm of the reduced pressure, which is in general a function of $\theta$ and $T$, may be written as a product:

$$\ln x = J(T) \times \psi(\theta) \tag{18}$$

since $F(z)$ is independent of temperature. The theoretical significance of $\psi(\theta)$ is that the cumulative distribution $F$ for the energy $z$ is given by:

$$F(z) = 1 - \psi^{-1}(z) \tag{19}$$

Several important adsorption isotherms have the form of Eq. 18: the equation of Dubinin-Radushkevich (DR) (1947) and that of Frenkel-Halsey-Hill (FHH) (Young and Crowell, 1962). The DR isotherm applies to microporous solids having type I isotherms and the FHH isotherm is a model for multilayer adsorption on nonporous adsorbents. The DR and FHH isotherms are given in Table 1. Other well-known isotherms (Langmuir, BET, Hill-deBoer) do not satisfy Eq. 17 but they were derived specifically for nonheterogeneous surfaces.

The next step is to investigate the consequences of Eq. 18 without making any assumptions about the $J$ and $\psi$ functions. Formulas for adsorption of pure vapors, derived in the next section, will be used for this purpose. Their derivation is based on thermodynamics and can be skipped without missing any steps in the physical argument.

TABLE 1. CHARACTERISTIC CURVE FOR PARTICULAR THEORIES OF ADSORPTION

| Theory | Adsorption Isotherm | Characteristic Curve, $P(\theta)$ |
|---|---|---|
| Dubinin-Radushkevich | $\ln x = \frac{1}{C}\sqrt{-\ln \theta}$ | $\frac{2}{\sqrt{\pi}}\sqrt{-\ln \theta}$ |
| Halsey-Frenkel-Hill | $\ln x = \frac{C}{\theta^r}$ | $\theta^{-r} \Big/ \int_0^\infty \theta^{-r} d\theta$ |

## THERMODYNAMICS OF ADSORPTION: EXCESS PROPERTIES

For a pure vapor in equilibrium with a solid adsorbent, there are two degrees of freedom $(P, T)$. The adsorption isotherm $n(P)$ is measured over the range $0 \leqq P \leqq P_o$. $n = 0$ at zero pressure, but the amount adsorbed at saturation depends upon the nature of the adsorbent. Type I adsorbents like zeolites, silica gel, and activated carbon have a well-defined saturation capacity $(m)$ corresponding to pore filling. For type II adsorbents such as graphitized carbon, metals, and metal oxides, the loading $(n)$ tends to infinity as $P \rightarrow P_o$.

Conventional adsorption thermodynamics (Young and Crowell, 1962) deals with molar properties of the adsorbed vapor such as free energy $(g)$, enthalpy $(h)$, and entropy $(s)$. We introduce a new set of extensive thermodynamic variables called *excess properties* as follows: for any molar extensive property of the adsorbed vapor $(z)$, an associated excess property $(\Delta Z^e)$ is defined by:

$$\Delta Z^e = n(z - z_o) \tag{20}$$

$z_o$ is the molar value of $Z$ for adsorbate in the state of pure, saturated liquid at the system temperature. Both $n$ and $z$ are functions of $T$ and $P$, but $z_o$ is a function of $T$ alone. Therefore $\Delta Z^e$ is also a function of $T$ and $P$ (or $n$ and $T$). $\Delta Z^e$ is equal to zero at zero pressure and has a finite value at saturation $(P = P_o)$. The finite limit is obvious for type I isotherms for which $n = m$ at saturation. For type II isotherms, on the other hand, $n$ tends to infinity as $P \rightarrow P_o$ and $z \rightarrow z_o$, but with a finite product $n(z - z_o)$. This limit, defined by: $\Delta Z = \lim_{P \rightarrow P_o} \Delta Z^e$ is called the immersional property (free energy of immersion, enthalpy of immersion, entropy of immersion, etc.) because it is the value of $\Delta Z^e$ associated with immersing clean adsorbent in pure liquid adsorbate.

It follows from their definition that the relations between excess properties are the same as those for homogeneous bulk phases:

$$\Delta G^e = \Delta H^e - T\Delta S^e \tag{21}$$

$$\left[\frac{\partial \Delta G^e}{\partial T}\right]_n = -\Delta S^e \tag{22}$$

$$\left[\frac{\partial \Delta G^e/T}{\partial T}\right]_n = \frac{-\Delta H^e}{T^2} \tag{23}$$

with similar formulas for the immersional properties $(\Delta G, \Delta H, \Delta S)$.

These excess and immersional properties can be calculated from adsorption isotherms. The Gibbs free energy of the adsorbed phase is defined by:

$$G = U + PV - TS = -\Pi A + n\mu \tag{24}$$

This is the free energy of the entire condensed phase (adsorbate plus adsorbent) relative to the free energy of the clean adsorbent. As shown by Eq. 24, the free energy is composed of two parts: that due to the adsorbate $(n\mu)$ and that due to the adsorbent $(\Pi A)$. $\mu$ is the chemical potential of the adsorbate, $\Pi$ is the spreading pressure of the gas-solid interface, and $A$ is the surface area per unit mass of adsorbent. In the case of microporous adsorbents, the meaning of $A$ loses some of its significance but the product $(\Pi A)$ is a measurable quantity (Bering et al., 1970) even when the adsorbent is not inert.

At equilibrium, the chemical potential of the adsorbate in the adsorbed phase is equal to its chemical potential in the vapor phase $(\mu)$:

$$\mu = \mu^o(T) + RT \ln x \tag{25}$$

where $\mu^o(T)$ is the reference chemical potential in the state of pure, saturated liquid. Substitution of Eqs. 24 and 25 into Eq. 20 gives:

$$\Delta G^e = -\Pi A + nRT \ln x \tag{26}$$

The $(\Pi A)$ product is obtained from the Gibbs adsorption isotherm (Myers and Sircar, 1972):

$$d(\Pi A) = n d\mu = nRTd \ln x \tag{27}$$

Integrating at constant temperature:

$$\Pi A = RT \int_{x=0}^{x} n d \ln x \tag{28}$$

Substitution of Eq. 28 in Eq. 26, followed by integration by parts, yields an integral equation for the excess Gibbs free energy:

$$\Delta G^e = RT \int_{n=0}^{n} \ln(x) dn \tag{29}$$

In spite of the discontinuity of the integrand at zero coverage, the limit of this improper integral exists and $\Delta G^e$ is a well-defined thermodynamic quantity.

Application of Eqs. 22 and 23 to Eq. 29 gives expressions for the other excess functions:

$$\Delta H^e = R \int_{n=0}^{n} \left[\frac{\partial \ln x}{\partial(1/T)}\right]_n dn \tag{30}$$

$$\Delta S^e = -\int_{n=0}^{n} \left[\frac{\partial RT \ln x}{\partial T}\right]_n dn \tag{31}$$

Thus excess functions defined relative to the saturated liquid are simple integrals of the adsorption isotherm and its temperature derivative. Immersional properties $(\Delta G, \Delta H, \Delta S)$ are obtained by extending the upper limit of integration to saturation.

Isosteric heat of adsorption is defined by (Young and Crowell, 1962):

$$q_{st} = RT^2 \left[\frac{\partial \ln P}{\partial T}\right]_n \tag{32}$$

It follows from this definition and Eq. 30 that excess enthalpy is the integral of the isosteric heat of adsorption less the heat of vaporization of saturated liquid $(\lambda_o)$:

$$\Delta H^e = -\int_{n=0}^{n} (q_{st} - \lambda_o) dn \tag{33}$$

Thus Eqs. 30 and 33 provide two expressions for evaluating the excess enthalpy, the first from the adsorption isotherm and the second by calorimetric measurement of the differential heat of adsorption $(q_d)$ of the vapor $(q_{st} = q_d + RT)$. At saturation, the excess enthalpy equals the heat of immersion $\Delta H$, which can be determined calorimetrically by immersing fresh adsorbent in liquid adsorbate.

## CHARACTERISTIC ADSORPTION ISOTHERM

The thermodynamic equations derived above are next applied to Eq. 18 for a heterogeneous surface. Substitution of Eq. 18 into Eq. 29 yields:

$$\Delta G^e = mRTJ \int_0^{\theta} \psi(\theta) d\theta \tag{34}$$

The free energy of immersion for type I isotherms is $(\theta \rightarrow 1$ as $x \rightarrow 1)$:

$$\Delta G = mRTJ \int_0^1 \psi(\theta) d\theta \tag{35}$$

Since the values of $m$ and $J$ are different for each adsorbate, excess Gibbs free energy is not a characteristic function. However $m$ and $J$ vanish from the quotient:

$$\frac{\Delta G^e}{\Delta G} = \frac{\int_0^\theta \psi(\theta)d\theta}{\int_0^1 \psi(\theta)d\theta} \tag{36}$$

The derivative of this quotient is the normalized function $\psi$ of Eq. 19:

$$\frac{d}{d\theta}\left[\frac{\Delta G^e}{\Delta G}\right] = \frac{\psi(\theta)}{\int_0^1 \psi(\theta)d\theta} \equiv P(\theta) \tag{37}$$

$P(\theta)$ is a characteristic equation because it depends only on $\theta$. Substitution of Eqs. 18 and 35 into Eq. 37 gives the key result:

$$P(\theta) = \frac{mRT \ln x}{\Delta G} \tag{38}$$

The free energy of immersion $\Delta G$ is a negative quantity and $P(\theta)$ therefore has a positive sign. This result is related to the Polanyi potential $(-RT \ln x)$. According to our theory of heterogeneous surfaces, the factor $(\Delta G/m)$, which is the molar free energy of immersion of the adsorbate vapor, transforms the Polanyi potential into a dimensionless function that is the same for all adsorbates. It differs in two ways from the DR equation: first, it does not specify the functionality $P(\theta)$ and second, the affinity coefficient $\beta$ of Dubinin is shown here to be proportional to a well-defined physical quantity, the free energy of immersion.

It is interesting that the spreading pressure can likewise be transformed into a characteristic function. From Eqs. 18, 28, and 35 it follows that:

$$\frac{\Pi A}{-\Delta G} = \frac{\int_0^\theta F(\theta)d\theta - \theta F(\theta)}{\int_0^1 F(\theta)d\theta} \tag{39}$$

The ratio $\pi A/(-\Delta G)$ should be the same function of $\theta$ for different vapors on a given adsorbent. This result would be useful for the prediction of mixture equilibria using IAS as mentioned earlier.

Equation 38 can be used to predict type I pure-vapor isotherms as follows. First, the adsorbent of interest is characterized by the adsorption isotherm of a reference substance to establish the function $P(\theta)$. The free energy of immersion is determined by integrating this isotherm from zero coverage to saturation using Eq. 29. The saturation capacity ($m$) of the reference substance is found by extrapolating the loading to saturation. Predictions for other vapors using $P(\theta)$ require values of $m$ and $\Delta G$. $m$ can be estimated using Gurvitsch's rule (Gregg and Sing, 1967). According to this rule, which is fairly accurate for microporous adsorbents, the saturation capacity ($V$) expressed as volume of liquefied adsorbate is a constant:

$$V = mv_o = \text{constant} \tag{40}$$

where $v_o$ is the molar volume of saturated liquid at the temperature of the adsorption isotherm. Therefore, $m$ is inversely proportional to molar volume and can be predicted from the value for the reference substance.

There are two methods of obtaining $\Delta G$ from experimental data. The first and most direct approach is to measure one point on the adsorption isotherm of the pure vapor. $\Delta G$ can then be calculated from the estimated value of $m$ and the equality of $P(\theta)$ for the vapor and reference substance according to Eq. 38. This value of $\Delta G$ may then be used to predict the rest of the adsorption isotherm. The second and most sensitive method is to measure differences in free energy of immersion $(\Delta G_2 - \Delta G_1)$ between the adsorbate and the reference substance using surface excess data for adsorption from the binary liquid mixture (Myers and Sircar, 1972):

$$\Delta G_2 - \Delta G_1 = RT \int_{x_1=0}^{1} \frac{n_1^e}{\gamma_1 x_1 x_2} d(\gamma_1 x_1) \tag{41}$$

where $n_1^e$ is the surface excess of component 1 in the liquid mixture. $x_i$ and $\gamma_i$ are the mole fraction and activity coefficient, respectively, of the $i$th component in the binary, bulk liquid mixture. Activity coefficients are available from experimental vapor-liquid equilibrium (VLE) data. This indirect method of obtaining $\Delta G$ is attractive because adsorption measurements are easier for liquids than for gases.

## COMPARISON WITH EXPERIMENT

Equation 38 was tested using measurements of adsorption of vapors of benzene, cyclohexane, $n$-heptane, and 1,2-dichloroethane on silica gel (Davision PA 400) at 30°C (Sircar, 1970). These substances were selected because of their dissimilarity in structure and molecular size and shape, in order to provide a stringent test of the theory. Figure 3 shows the isotherms plotted as $nv_o$ vs. $(RT/v_o) \ln x$ according to the conventional Polanyi model. The isotherms for cyclohexane and $n$-heptane coincide but those for benzene and 1,2-dichloroethane do not.

Equation 38 works significantly better, as illustrated in Figure 4. The saturation adsorptive capacity for these type I vapors is reported in Table 2. The pore volume of the adsorbent from Eq. 40 is $V = 0.34 \pm 0.02\, cm^3/g$. Free energies of immersion of

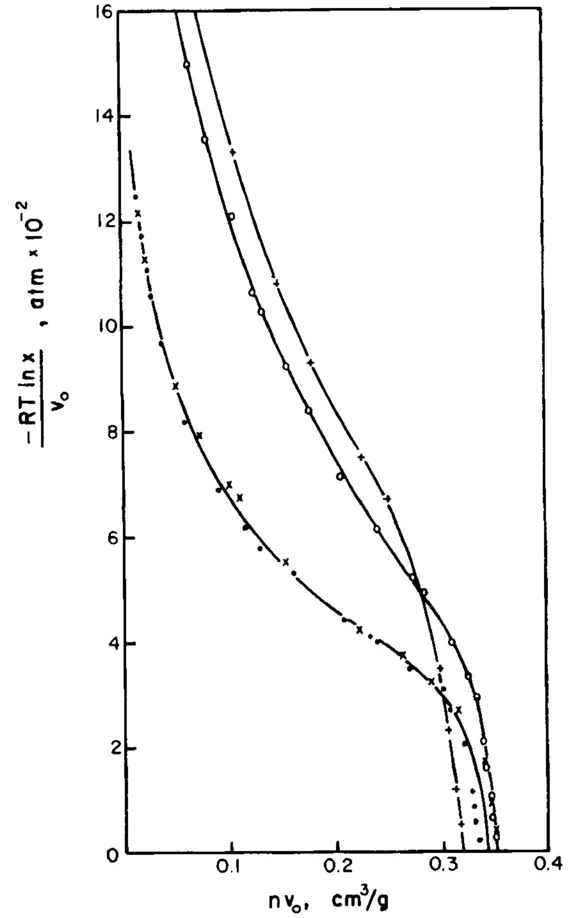

**Figure 3. Test of Polanyi-type model for adsorption of different vapors on silica gel at 30 C. O: benzene; ●: cyclohexane; X: $n$-heptane; +: 1,2-dichloroethane.**

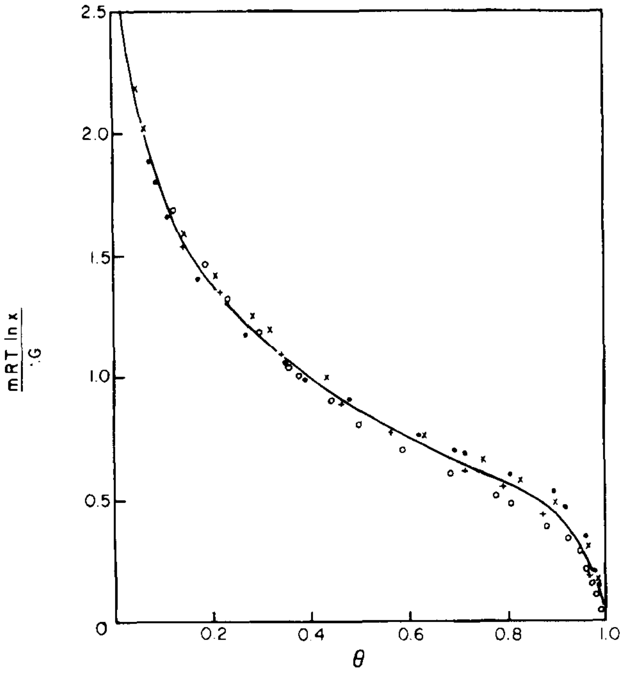

**Figure 4. Test of Eq. 38 for adsorption of different vapors on silica gel at 30°C; symbols as in Fig. 3.**

the silica gel in all four liquids were calculated using Eq. 29 and then checked for thermodynamic consistency using surface excess experiments on the binary liquid mixtures in conjunction with Eq. 41; results are reported in Table 2. It is seen that benzene and 1,2-dichloroethane have free energies of immersion nearly twice as large as that of cyclohexane and *n*-heptane. The maximum deviation from the solid curve for all four adsorbates is only 5%, an amount that is within the accuracy of our experimental data.

## NOTATION

$A$ = specific surface area
$B_{1s}$ = adsorption second virial coefficient, Eq. 1
$C(T)$ = constant, Eq. 4
$C_o$ = constant, Eq. 11
$E$ = decrease in energy upon adsorption from gas phase, per mole
$\bar{E}$ = average energy of adsorption
$f(z)$ = energy density function, Eq. 15
$F(z)$ = cumulative energy distribution function
$G$ = Gibbs free energy per unit mass of adsorbent
$\Delta G$ = free energy of immersion per unit mass of adsorbent
$H$ = enthalpy per unit mass of adsorbent
$\Delta H$ = enthalpy of immersion per unit mass of adsorbent
$J(T)$ = function of temperature, Eq. 18
$m$ = moles adsorbed at saturation per unit mass of adsorbent
$n$ = moles adsorbed per unit mass of adsorbent
$n^e$ = surface excess per unit mass of adsorbent, Eq. 41
$P$ = pressure
$P_o$ = vapor pressure of saturated liquid
$P(\theta)$ = characteristic function, Eq. 38
$q_d$ = differential heat of adsorption per mole of adsorbate
$q_{st}$ = isosteric heat of adsorption per mole of adsorbate
$R$ = gas constant
$T$ = absolute temperature
$T_r$ = reduced temperature ($T/T_c$)
$v_o$ = molar volume of saturated liquid
$V$ = volumetric capacity of adsorbed phase per unit mass of adsorbent
$x$ = reduced vapor pressure ($P/P_o$)
$x_i$ = mole fraction of $i$th component in bulk liquid
$Z$ = arbitrary extensive thermodynamic property, per unit mass of adsorbent
$z$ = ($E - E_{min}$), Eq. 13

### Greek Letters

$\gamma$ = activity coefficient in bulk liquid phase
$\theta$ = reduced amount adsorbed ($n/m$)
$\lambda_o$ = enthalpy of vaporization of bulk liquid
$\mu$ = chemical potential of adsorbate
$\Pi$ = spreading pressure
$\sigma$ = $E_{max} - E_{min}$, Eq. 6
$\psi(\theta)$ = arbitrary function, Eq. 18

### Subscripts

$i$ = $i$th component
$o$ = value at saturation of vapor
$R$ = reference substance

### Superscripts

$^{\circ}$ = a reduced (dimensionless) quantity
$e$ = excess function, Eq. 20

TABLE 2. PROPERTIES OF ADSORBATES FOR ADSORPTION ON SILICA GEL AT 30°C

| Compound | $v_o$ cm³/mol | $m$ mmol/g | $\Delta G$ cal/g | $V$ cm³/g |
|---|---|---|---|---|
| Benzene | 0.090 | 3.91 | −8.73 | 0.351 |
| Cyclohexane | 0.109 | 3.05 | −4.76 | 0.335 |
| *n*-heptane | 0.148 | 2.38 | −4.76 | 0.353 |
| 1,2-dichloroethane | 0.080 | 3.96 | −9.34 | 0.316 |

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