Corrected Horváth-Kawazoe Equations for Pore-Size Distribution

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The Horváth-Kawazoe (HK) model is a widely used method for determining pore-size distribution in a microporous material from a single adsorption isotherm. The original model, however, suffers from conceptual flaws. The total interaction energy of the adsorbate is underestimated since the adsorbate-adsorbate interaction is incorrecty calculated. New corrected HK models proposed here for three pore geometries (slit, cylindrical, and spherical) can overcome these defects. Two other improvements have also been made in the new models. These assume that a filled micropore is composed of layers of adsorbate molecules which interact only with the molecular layers in the immediate vicinity. A better estimate of adsorbate-adsorbate-adsorbent interaction is obtained by utilizing actual distances between interacting molecules. The average interaction energy is calculated by a population-weighted average of the energy potential of the layers rather than by integration. This average potential approaches a nonzero value at large pore size, unlike that in the original model. Pore-size distributions predicted by the corrected HK models agreed significantly better with crystallographic data compared to the original model for both microporous and mesoporous sorbents.

Introduction

The quantitative estimation of pore-size distribution (PSD) of materials remains a crucial problem in the characterization of microporous materials. Although several techniques exist for characterization of pore size of mesoporous and macroporous materials such as the Kelvin equation (Brunauer et al., 1967), the BET equation (Brunauer et al., 1940), the BJH method (Barrett et al., 1951), and the Dubinin-Radushkevich equation (Dubinin and Radushkevich, 1947), extension of these methods to microporous materials does not yield satisfactory results. This is primarily so because the adsorbate molecules can no longer be treated in a fluid state as the pore size approaches very low values (less than 20 Å), and the consideration of attractive forces on a molecular level becomes necessary. This problem is further coupled with the urgency for a simple and rapid technique for pore-size evaluation due to an increasing demand for new microporous materials for gas adsorption and catalysis. As a result, exhaustive research has been devoted to this area in recent times.

As an outcome of this research, several approaches have emerged with respect to the estimation of micropore-size distribution. One of the earliest methods was the experimental measurement of the adsorbed saturated amounts of probe molecules of different dimensions. This method was found to be cumbersome to perform and there was an uncertainty about the results due to the networking effects of pores such as a large pore accessible through small pores which are smaller than the probe molecule. Another approach was to obtain the PSD from a single adsorption isotherm (Jaroniec and Madey, 1988). The basis of this method involved an isotherm $w(L, P)$ dependent upon pore size (L) and pressure (P). Thus, the amount adsorbed could be found by integrating the above isotherm over the entire range of pore size by coupling it with a PSD function $f(L)$. By assuming a known mathematical distribution function for $f(L)$ and using an empirical relationship (Stoeckli, 1977) to obtain $w(L, P)$, it was possible to obtain the PSD function by solving for its parameters (Jaroniec and Madey, 1988; Yang and Baksh, 1991; Baksh and Yang, 1992). However, despite its experimental simplicity, this procedure was undermined by the empiricism and assumptions involved. Based on these lines, recently new statistical mechanics approaches using either Monte Carlo techniques or the density functional theory have been proposed

and are steadily gaining acceptance. These techniques enable the calculation of the isotherm (dependent on pore size and geometry) in conjunction with PSD functions with assumed mathematical forms. A large amount of literature has been published regarding the application of this theory for studying gas adsorption, and, in particular, evaluation of PSD of materials (Seaton et al., 1989; Lastoskie et al., 1993; Olivier, 1995; Webb and Orr, 1997; Ravikovitch et al., 1988). The advantage of the technique is that it is a unified method applicable to both microporous, as well as mesoporous type of materials. However, the empirical parameters used in these models are difficult to obtain from literature with the exception of a few well-studied systems. Besides, the calculations involved are highly intensive requiring an elaborate computer code.

A simple and popular method for evaluating PSD of microporous materials is the method proposed by Horváth and Kawazoe (1983). This technique has been successfully used for the determination of PSD in microporous sorbents such as activated carbons and zeolites over the last decade (Seifert and Emig, 1987; Venero and Chiou, 1988; Davis et al., 1988, 1989; Beck et al., 1992; Horváth et al., 1998; Kane et al., 1998). This technique utilizes adsorption isotherm data at a temperature below or equal to the critical temperature of the adsorbate, which is typically nitrogen (at 77 K), argon (at 87 K), or an organic vapor (such as CH_3Cl) at ambient temperature (Mariwala and Foley, 1994). By assuming micropore-filling and equating the free-energy change upon adsorption to the average interaction energy of the adsorbing molecules, the "step" in the isotherm data is translated into a PSD. The model assumes that entropic effects are negligible for small adsorbate molecules and networking effects are insignificant if the adsorbate used in the analysis is smaller than the adsorbent channels. The mathematical expression relating relative pressure of the adsorbing gas to the pore size of the adsorbent has come to be known as the Horváth-Kawazoe (HK) equation.

The original HK equation considered a slit-shaped pore with an implicit assumption that the adsorption isotherm follows Henry' law. In order to correct for the deviation of isotherm data from Henry's law at higher relative pressures, Cheng and Yang (1994) proposed a correction factor, which incorporated a Langmuir isotherm fit to the data. Also, new models have been proposed based on the same principles to include pores with curved surfaces. Prominent among them are the cylindrical-pore model of Saito and Foley (1991) and the spherical pore model of Cheng and Yang (1994). Instruments incorporating these models have now been commercialized.

Despite the immense utility of the HK-model, there exist certain conceptual defects in the same. The derivation of the HK-model proceeds by the calculation of the energy potential of a single adsorbate molecule with a layer of sorbent molecules along the periphery of a pore of a particular geometry using the Lennard-Jones 6-12 potential. This potential is calculated by incorporating the adsorbate-adsorbent dispersion term as calculated by the Kirkwood-Müller formalism in the potential energy minimum ϵ^* (Horváth and Kawazoe, 1983). In order to include the adsorbate-adsorbate interactions, the adsorbate-adsorbate dispersion constant is appended to the adsorbate-adsorbent dispersion term in the

potential energy minimum, as will be shown in detail later. However, no clear explanation is provided for doing so. Moreover, the energy potential due to adsorbate-adsorbate interactions in a filled pore can be interpreted as the energy profile due to the adsorbate molecules placed, rather unrealistically, at the same position as the adsorbate molecules. This is because, according to the original model, the distance z of a sorbate molecule from another sorbate molecule is the same as that between a sorbate molecule and a sorbent molecule. Furthermore, the average interaction energy is calculated by integration of this energy profile over the entire pore characteristics length (pore width for slit-pores or radius in case of curved geometries). This implies that in a filled pore there is a continuous distribution of molecules along the characteristic length. However, micropores have dimensions comparable to molecular widths, and hence, the molecules in a filled pore can occupy only discrete positions relative to each other, if minor thermal vibrations are to be neglected. The original HK model has also been criticized for not taking the distribution of energy into account while calculating the average interaction energy (Webb and Orr, 1997). As a result of these shortcomings and others, it has been observed that pore sizes estimated by the HK method for materials in the higher micropore size range (8–20 Å) to be unrealistically low in some cases (Carrott et al., 1998).

The above listed shortcomings in the existing model provides the motivation for developing a new model based on an improved energy profile for a micropore filled with adsorbate molecules. The new model proposed in this work considers molecules to occupy discrete positions in the adsorbate-filled micropore, and the interaction energy of a molecule is calculated using an intermolecular spacing corresponding to a minimum energy potential between that molecule and the immediate neighboring molecules. The average interaction energy is obtained by a population-weighted average of energy potentials rather than by integration. New models for PSD, based on the Horváth-Kawazoe principle, have been proposed for slit, cylindrical, as well as spherical, shaped micropores. Comparison of the average interaction energy vs. pore-size profiles for the original and modified models showed a good agreement for small pore widths, but a considerable deviation was observed at pore widths measuring more than two adsorbate molecule diameters. PSD using the modified energy profile have been obtained using isotherm data in literature for all three pore geometries, and the results are compared with that obtained using the original model.

Review of the Original-HK Slit-shaped Pore Model

The basis for obtaining the energy profile in a pore is the Lennard-Jones 6-12 potential

$$\epsilon_{12}(z) = 4\epsilon_{12}^* \left[\left(\frac{\sigma}{z} \right)^{12} - \left(\frac{\sigma}{z} \right)^6 \right] \tag{1}$$

Halsey and coworkers gave the interaction energy of one adsorbate molecule with a single infinite-layer plane of adsor-

bent molecules to be as follows (Sams et al., 1960)

$$\epsilon(z) = \frac{N_s A_s}{2\sigma^4}\left[-\left(\frac{\sigma}{z}\right)^4 + \left(\frac{\sigma}{z}\right)^{10}\right] \quad (2)$$

Everett and Powl (1976) extended the above result to two parallel infinite lattice planes whose nuclei are spaced at distance L apart

$$\epsilon(z) = \frac{N_s A_s}{2\sigma^4}\left[-\left(\frac{\sigma}{z}\right)^4 + \left(\frac{\sigma}{z}\right)^{10} - \left(\frac{\sigma}{L-z}\right)^4 + \left(\frac{\sigma}{L-z}\right)^{10}\right]$$
$$(3)$$

where the internuclear distance at zero-interaction energy (Å): $\sigma = (2/5)^{1/6} d_o$, d_o being the average of the adsorbate and adsorbent molecule diameters $((d_o + d_A)/2)$. N_s is the number of sorbent molecules per unit area, and z is the internuclear distance between the adsorbate and adsorbent molecules (Å). The dispersion constants A_s and A_A are calculated by the Kirkwood-Muller formulae (erg·cm^6) as follows

$$A_s = \frac{6 mc^2 \alpha_s \alpha_A}{\dfrac{\alpha_s}{\chi_s} + \dfrac{\alpha_A}{\chi_A}} \quad (4a)$$

$$A_A = \frac{3}{2} mc^2 \alpha_s \alpha_A$$

Further, Horváth and Kawazoe (1983) proposed that the potential is increased by the interaction of adsorbate molecules within the pore. They included this additional interaction by adding an adsorbate dispersion term $(N_A A_A)$ term in the numerator of the depth of the potential energy minimum $(N_s/2\sigma^4)$ in Eq. 3 as follows

$$\epsilon(z) = \frac{N_s A_s + N_A A_A}{2\sigma^4}\left[-\left(\frac{\sigma}{z}\right)^4 + \left(\frac{\sigma}{z}\right)^{10} - \left(\frac{\sigma}{L-z}\right)^4\right.$$
$$\left. + \left(\frac{\sigma}{L-z}\right)^{10}\right] \quad (5)$$

However, no clear justification could be found in literature for incorporating the adsorbate-adsorbate-adsorbent interaction in this manner. Further, $\epsilon(z)$ in Eq. 4 may be split as follows

$$\epsilon(z) = \epsilon_{A-S}(z) + \epsilon_{A-A}(z)$$

$$= \frac{N_s A_s}{2\sigma^4}\left[-\left(\frac{\sigma}{z}\right)^4 + \left(\frac{\sigma}{z}\right)^{10} - \left(\frac{\sigma}{L-z}\right)^4 + \left(\frac{\sigma}{L-z}\right)^{10}\right]$$

$$+ \frac{N_A A_A}{2\sigma^4}\left[-\left(\frac{\sigma}{z}\right)^4 + \left(\frac{\sigma}{z}\right)^{10} - \left(\frac{\sigma}{L-z}\right)^4 + \left(\frac{\sigma}{L-z}\right)^{10}\right] \quad (6)$$

The first term $\epsilon_{A-S}(z)$ gives the adsorbate-surface interaction and the second term $\epsilon_{A-A}(z)$ gives the adsorbate-adsorbate interaction. Since the distance z of the gas molecule is the same in both $\epsilon_{A-S}(z)$, as well as $\epsilon_{A-A}(z)$, Eq. 6 gives an erroneous interpretation that the adsorbate-adsorbate interaction is caused between a gas molecule and two parallel infinite sheets of gas molecules, impractically placed at the *same* position as the sorbent molecules. Besides, the internuclear distance at zero interaction energy (σ) to be used in $\epsilon_{A-A}(z)$ is expected to be different from that used in the $\epsilon_{A-S}(z)$ expression, but the original model does not take this fact into account.

The next step in the derivation was obtaining the average interaction energy by integrating the above profile over the free space in the slit-pore

$$\bar{\epsilon}(z) = \frac{\displaystyle\int_{d_o}^{L-d_o} \epsilon(z)\,dz}{\displaystyle\int_{d_o}^{L-d_o} dz} \quad (7)$$

This implies that a gas molecule has a continuous distribution of positions in the filled micropore, which it is free to occupy. In reality, however, the gas molecule has only fixed positions at which it can exist when the pore is filled to capacity, especially when the pore width is only a few multiples of the adsorbate molecule diameter. Besides, the Boltzmann law of distribution of energy requires that the above average be instead computed by weighing the energy terms with the probability of a molecule to possess that energy, namely $e^{-\epsilon/kT}$. In other words, the molecule is expected to occupy a position at which the energy potential is minimum. This aspect was not considered in the original work. In the present work, a discretized average is proposed which attempts to incorporate the above features in the model.

Finally, the average potential energy so calculated was related to the free energy change upon adsorption $RT\ln(P/P_o)$. The resulting slit-pore HK model is as follows

$$RT\ln\left(\frac{P}{P_o}\right) = N_{Av}\cdot\bar{\epsilon}(z) = N_{Av}\frac{N_s A_s + N_A A_A}{\sigma^4(L - 2d_o)}$$

$$\times\left[\frac{\sigma^4}{3(L-d_o)^3} - \frac{\sigma^{10}}{9(L-d_o)^9} - \frac{\sigma^4}{3d_o^3} + \frac{\sigma^{10}}{9d_o^9}\right] \quad (8)$$

As can be seen from Eq. 8, the interaction energy of a molecule is *indeterminate* when $L = 2d_o$, that is, then the free space of the pore $(L - d_s)$ equals the diameter of an adsorbate molecule (d_A). However, a finite value for the potential exists for a molecule of this size as is obvious from Eq. 5. This anomaly is overcome in the modified model.

An implicit assumption in the original derivation by Horváth and Kawazoe (1983) was that the isotherm followed Henry's law. It is well known that most isotherm data show a considerable deviation from Henry's law at pressures near the saturation pressure of the adsorbate, and the equilibrium loading usually follows a Langmuir-type behavior. Cheng and

Yang (1994) introduced a correction term to incorporate the Langmuir isotherm in the model and the corrected model (referred henceforth as the HK-CY model) was given as

$$RT\ln\left(\frac{P}{P_o}\right) + RT\left[1 + \frac{1}{\theta}\ln(1-\theta)\right]$$

$$= N_{Av}\cdot\bar{\epsilon}(z) = N_{Av}\frac{N_S A_s + N_A A_A}{\sigma^4(L-2d_o)}$$

$$\times\left[\frac{\sigma^4}{3(L-d_o)^3} - \frac{\sigma^{10}}{9(L-d_o)^9} - \frac{\sigma^4}{3d_o^3} + \frac{\sigma^{10}}{9d_o^9}\right] \quad (9)$$

The Langmuir isotherm is typically represented as follows

$$\theta = \frac{K\left(\dfrac{P}{P_o}\right)}{1 + K\left(\dfrac{P}{P_o}\right)} \quad (10)$$

Taking a limit of Eq. 10 as P approaches the saturation pressure P_o, we have $\theta = K/(1+K)$. Now, applying the above limit of P/P_o tending to 1 to Eq. 9, we obtain the following

$$\lim_{P\to P_o} N_{Av}\cdot\bar{\epsilon}(z) = RT\left[1 - \frac{K+1}{K}\ln(K+1)\right] \quad (11)$$

Thus, at high pressures, the average interaction energy should tend to the value given by Eq. 11. Near the saturation pressure, the size of the largest pore, which can be filled with adsorbate, tends towards infinity. As can be seen from Eq. 8, as $L\to\infty$, the average interaction energy tends towards zero. Also, intuitively, is apparent that there will always be some

adsorbate-adsorbate interaction and the limiting interaction energy cannot go to zero even at large pore size. Thus, the original model for average interaction energy in the pore is inconsistent with the HK equation with the Cheng-Yang correction. The proposed model is found to have a better agreement in this regard. The physical parameters used in the micropore size distribution calculations in this work are given in Table 1.

Modified HK Model for Slit-shaped Pores

The general strategy for obtaining the PSD for the three pore geometries, namely, slit, cylindrical, and spherical pores is basically the same. The modified model for calculating the average interaction energy in a filled micropore proceeds by first estimating the number of gas adsorbate molecule layers within the filled micropore. Each gas molecule is assumed to rest preferentially at a position at which its energy potential within the pore would be minimum in accordance with the Boltzmann law of energy distribution. Furthermore, a gas molecule is assumed to interact most effectively with only its laterally immediate molecular layer. This fact is in agreement with experimental observations which show that the energy of adsorption of a monolayer of adsorbate molecules on a clean sorbent surface is the highest and that on subsequently adsorbed layers of gas molecules is a nearly constant lower value. Any interaction with molecules not in the immediate proximity of the molecule or with those lying above or below the molecule in the same layer is assumed to be negligible. The average interaction energy is then calculated by averaging the energy potentials of the individual gas molecule layers weighted by an approximate molecular population of each layer.

Consider a slit pore with the nuclei of the sorbent molecules in the lattice planes forming the pore-wall spaced at a distance L apart. If the diameter of the sorbent molecules is denoted as d_S and that of the adsorbent molecules as d_A, then the number of molecule layers M that can be accommo-

Table 1. Physical Parameters Used in Micropore Size Distribution Calculations

Parameter	Adsorbent			Adsorbate	
	Carbon	Aluminosilicate Oxide Ion	Aluminophosphate Oxide Ion	Nitrogen	Argon
Dia. (Å)	3.40[*]	2.76[**]	2.60[**]	3.00[*] 372[‖‖,‖]	3.82[††,‡,‡‡,‖] 2.95[†§§]
Polarizability, α (cm^3)	$1.02\times10^{-24*}$	$2.5\times10^{-24**}$	$2.5\times10^{-24**}$	$1.46\times10^{-24*}$	$1.63\times10^{-24**}$
Magnetic Susceptibility, χ (cm^3)	$1.35\times10^{-28*}$	$1.3\times10^{-29**}$	$1.3\times10^{-29**}$	$2.0\times10^{-29*}$	$3.24\times10^{-29**}$
Molec. Surface density (Molecule/cm^2)	$3.85\times10^{15*}$	$3.75\times10^{15†,§§}$ $1.00\times10^{15††,§}$ $8.48\times10^{14‡,**}$ $8.73\times10^{14‡‡,**}$ $3.27\times10^{14‖‖,§}$	$1.0\times10^{15§}$	$6.7\times10^{14*}$	$8.52\times10^{14**}$

[*]Horváth and Kawazoe (1983).
[**]Cheng and Yang (1994).
[†]Faujasite, Slit-pore model.
[††]ZSM-5, Cylindrical-pore model.
[‡]Faujasite, Spherical-pore model.
[‡‡]A Zeolite, Spherical-pore model.
[§]Estimated in this work.
[§§]ASAP 2010 Manual, Micromeritics Inc. (1995).
[‖]Razmus and Hall (1991).
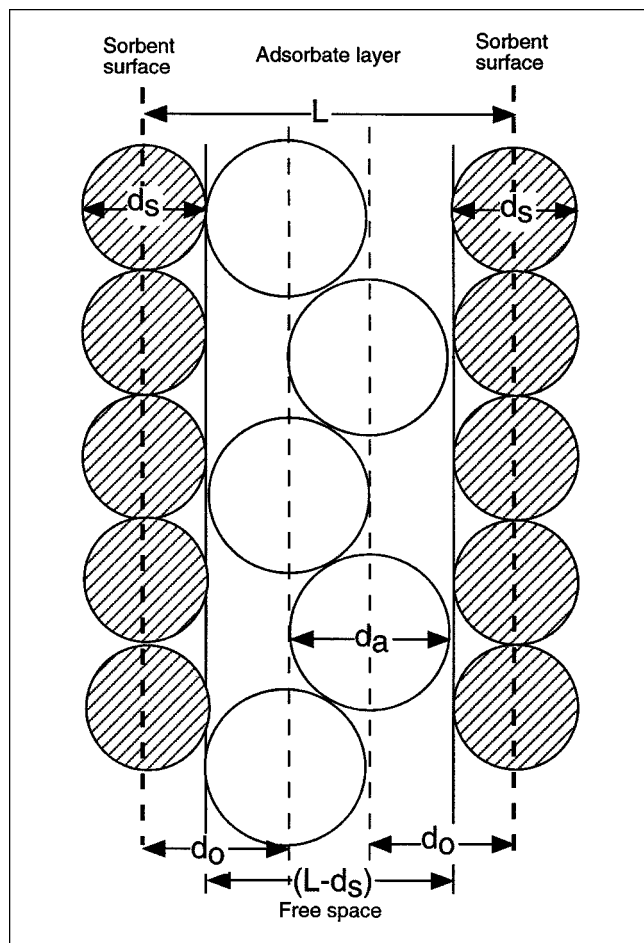[‖‖]MCM-41, Cylindrical-pore model.

Figure 1. Single layer of adsorbate molecules in a slit-shaped adsorbent pore of width *L*.

dated laterally as the pore gets filled up can be estimated as

$$M = \frac{L - d_S}{d_A} \qquad (12)$$

It should be noted that M can be a whole number or it may also be a fraction. The physical interpretation of a fractional number of layers is that the molecules in the layers are not arranged with their centers oriented in the same straight line, but are slightly skewed with respect to each other so as to afford a greater packing of molecules. Such a packing arrangement will, of course, result in a decrease in molecular density in the neighboring layers, but the resulting decrease in interaction energy will be accounted for when taking the average of the energy potentials.

When $1 \leq M < 2$, only one layer of molecules can be accommodated within the slit pore, as shown in Figure 1. In this case, each adsorbate molecule will interact with the two lattice planes forming the pore wall of the sorbent. The interaction energy of this monolayer, denoted as $\epsilon_1(z)$, is given by an expression similar to Eq. 3. An examination of Eq. 3 reveals that the minimum energy potential exists at a distance of d_o from either sorbent lattice planes. Since the Boltzmann

law of energy distribution law suggests that the molecule will most probably rest at a position at which the energy potential is the minimum, each molecule is assumed to exist at a distance of d_o from one of the two sorbent lattice planes. The interaction energy would then be

$$\epsilon_1(z) = \frac{N_s A_s}{2\sigma_s^4}\left[-\left(\frac{\sigma^s}{d_o}\right)^4 + \left(\frac{\sigma_s}{d_o}\right)^{10} - \left(\frac{\sigma_s}{L-d_o}\right)^4 \right.$$
$$\left. + \left(\frac{\sigma_s}{L-d_o}\right)^{10}\right] \qquad (13)$$

Note that the internuclear distance at zero interaction energy for an adsorbate-sorbent system is now denoted as σ_s to differentiate it from σ_A, which is the zero interaction energy distance for an adsorbate-adsorbate system. The expressions for σ_S and σ_A are as follows

$$\sigma_S = (2/5)^{1/6} d_o \qquad (14)$$

$$\sigma_A = (2/5)^{1/6} d_A \qquad (15)$$

The average energy of a slit pore having $1 < M < 2$ is the same as $\epsilon_1(z)$ since, irrespective of M, the molecules are assumed to rest at a distance if d_o from either pore walls. The situation is slightly different when $M \geq 2$. Three cases for this situation are depicted in Figures 2–4, wherein two different types of layers can be visualized: the first type consisting of the two layers in the immediate vicinity of the two pore walls, and at a distance of d_o from them, and the second type of molecules present in the interior of the pore sandwiched between two adjoining adsorbate layers. The first type of molecules (marked A in the figure) will interact with the sorbent molecules on one side and with adsorbate molecules on the other. The distance between the two adsorbate molecules would be approximately d_A by the same argument as discussed above. The interaction energy of this layer of molecules, denoted as $\epsilon_2(z)$ is given by

$$\epsilon_2(z) = \frac{N_s A_s}{2\sigma_s^4}\left[-\left(\frac{\sigma_s}{d_o}\right)^4 + \left(\frac{\sigma_s}{d_o}\right)^{10}\right]$$
$$+ \frac{N_A A_A}{2\sigma_A^4}\left[-\left(\frac{\sigma_A}{d_A}\right)^4 + \left(\frac{\sigma_A}{d_A}\right)^{10}\right] \qquad (16)$$

The second type of molecules (marked B in the figure), comprising $(n-2)$ number of layers, will interact effectively only with two parallel planes of gas molecules at a distance of d_A on either side of the molecule and its interaction energy $\epsilon_3(z)$ will be given by

$$\epsilon_3(z) = 2 \cdot \frac{N_A A_A}{2\sigma_A^4}\left[-\left(\frac{\sigma_A}{d_A}\right)^4 + \left(\frac{\sigma_A}{d_A}\right)^{10}\right] \qquad (17)$$

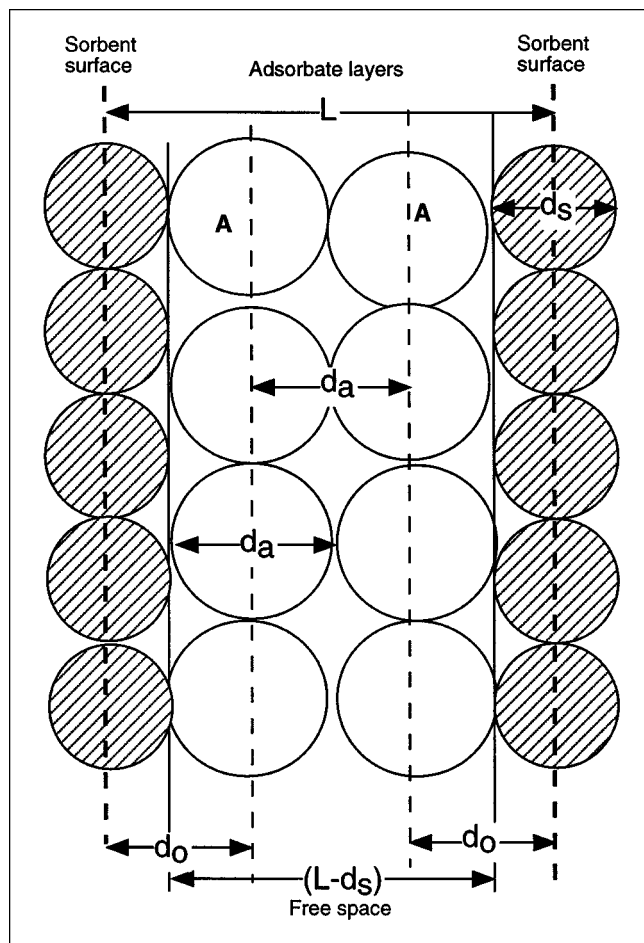The average interaction energy for $M > 2$ can be calculated by weighing the energy potentials of the molecules by

Figure 2. Two layers of adsorbate molecules in a slit-shaped adsorbent pore of width _L_.
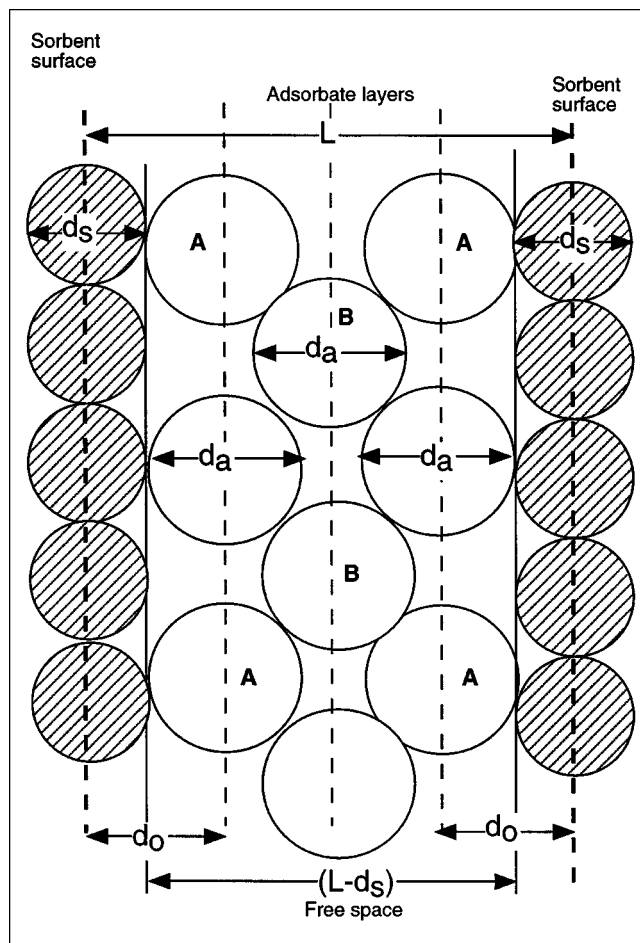

Figure 3. Three layers of adsorbate molecules in a slit-shaped adsorbent pore of width _L_.

the actual number of layers of molecules possessing the corresponding energy

$$\bar{\epsilon} = \frac{2\,\epsilon_2 + (M-2)\epsilon_3}{M} \qquad (18)$$

Here, M, the number of layers accommodated within the pore, is given by Eq. 12. The above method of averaging does away with integration, which assumes that a gas molecule in a filled micropore is free to assume a continuous distribution of positions within the slit pore free space. When M is not a whole number, the picture will be something between the two whole numbers enclosing M. For example, Figure 2 shows the molecule layers for $M = 2$ and Figure 3 shows the case when $M = 3$. For $2 < M < 3$, Figure 4 shows a likely configuration. Since the centers of the sorbate molecules will no longer be collinear, the density of the molecules adjacent to the middle layer will be decreased and its interaction energy will be lower. This factor is taken into account by using the interpolating Eq. 18, which will consider only a fraction of the adsorbate-adsorbate potential $\epsilon_3(z)$ for this molecule in the final average. Equation 18 will thus be exact when M is a whole number, and will be an interpolated approximation when M lies between two whole numbers.

The pore-size distribution can now be determined following the methodology outlined by Horváth and Kawazoe (1983). As was explained in the previous section regarding the original HK model, the free energy change upon adsorption, $RT\ln(P/P_o)$, is equated to the molar average interaction energy $N_{Av}\cdot\bar{\epsilon}$. Thus, the modified-HK equation can be written as

$$RT\ln\left(\frac{P}{P_o}\right) = N_{Av}\cdot\bar{\epsilon} \qquad (19)$$

On applying the correction for isotherm nonlinearity given by Cheng and Yang (1994), the modified HK-CY equation is obtained as

$$RT\ln\left(\frac{P}{P_o}\right) + RT\left[1 + \frac{1}{\theta}\ln(1-\theta)\right] = N_{Av}\cdot\overline{\in} \qquad (20)$$

In Eqs. 19 and 20 above

$$\bar{\epsilon} = \epsilon_1 \qquad \text{when } 1 \le M < 2$$

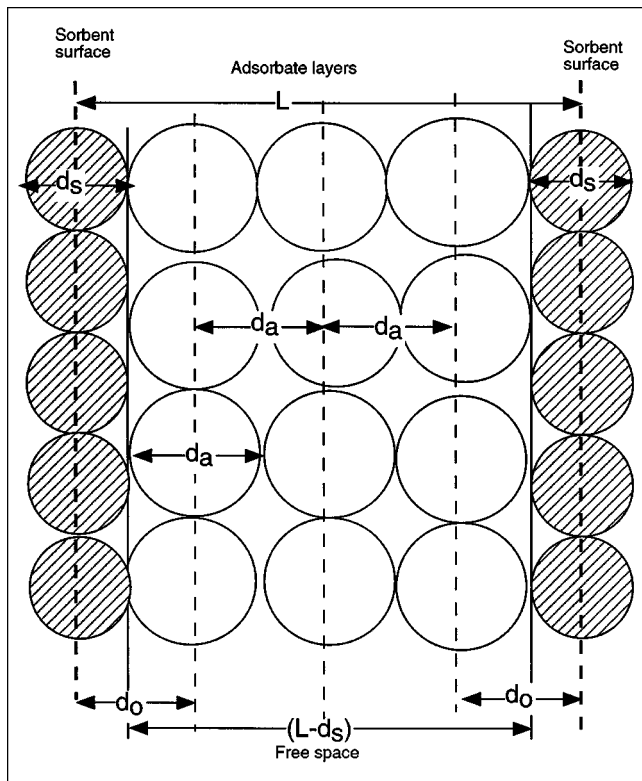$$= \frac{2\,\epsilon_2 + (M-2)\epsilon_3}{M} \qquad \text{when } M \ge 2 \qquad (21)$$

Figure 4. Possible configuration of adsorbate molecules in a slit-shaped adsorbent pore measuring between 2 to 3 adsorbate molecule diameters in width.

The above model is simple and can be easily implemented using a programming code or a spreadsheet. A slight discontinuity in $\bar{\epsilon}$ may occur at $M = 2$ as a result of the above two interpolating functions, but the difference in the values was found to be negligibly small for the examples studied in this work. The algorithm for determining pore size using the corrected HK equation is summarized in Table 2.

Review or Original HK Model for Cylindrical Pores

The interaction energy of a gas molecule in a cylindrical pore composed of a single layer of oxide ions was first obtained by Everett and Powl (1976) and is given as follows

$$
\epsilon(r) = \frac{5}{2}\pi\epsilon^* \left[\frac{21}{32}\left(\frac{d_o}{L}\right)^{10} \sum_{k=0}^{\infty} \alpha_k \left(\frac{r}{L}\right)^{2k} \right.
$$
$$
\left. - \left(\frac{d_o}{L}\right)^4 \sum_{k=0}^{\infty} \beta_k \left(\frac{r}{L}\right)^{2k} \right] \quad (22)
$$

In the above equation, the constants α_k and β_k are given by

$$
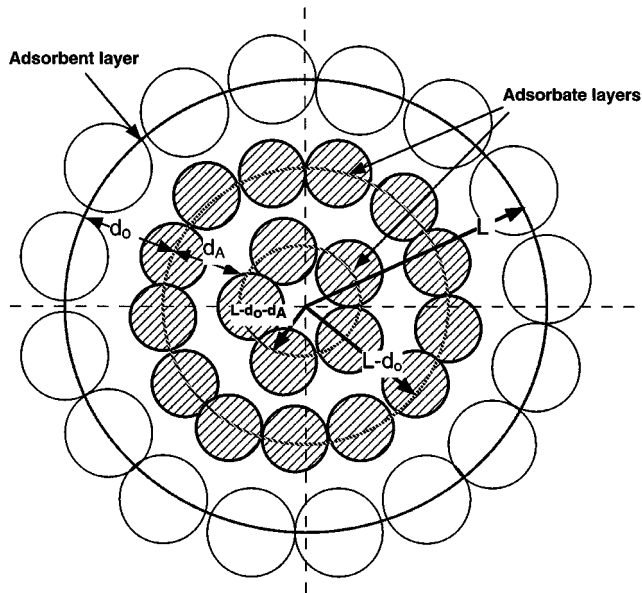\alpha_k = \left(\frac{-4.5 - k}{k}\right)^2 \alpha_{k-1} \quad (23a)
$$

Figure 5. Cross-sectional view of the configuration of adsorbate molecules in a cylindrical pore of radius L.

$$
\beta_k = \left(\frac{-1.5 - k}{k}\right)^2 \beta_{k-1} \quad (23b)
$$

where $\alpha_o = \beta_o = 1$. Here, r is the distance of the nucleus of gas molecule from the central axis of the cylinder and ϵ^* is the potential energy minimum given by

$$
\epsilon^* = \frac{3}{10} \frac{N_S A_S}{d_o^4} \quad (24)
$$

Using the result, Saito and Foley (1991) developed a PSD model using a method similar to that of Horváth and Kawazoe (1983). In their work also, the adsorbate-adsorbate-adsorbent interaction was incorporated in the model by modifying the potential energy minimum ϵ^* to the following

$$
\epsilon^* = \frac{3}{10} \frac{N_S A_S + N_A A_A}{d_o^4} \quad (25)
$$

The resulting radial energy potential profile was then averaged over the cylindrical cross-sectional area to give the following original-HK equation for cylindrical pores

$$
\ln\left(\frac{P}{P_o}\right) = \frac{3}{4}\pi N_{Av} \frac{N_s A_s + N_A A_A}{d_o^4} \sum_{k=0}^{\infty} \left\{ \frac{1}{k+1}\left(1 - \frac{d_o}{L}\right)^{2k} \right.
$$
$$
\left. \times \left[\frac{21}{32}\alpha_k\left(\frac{d_o}{L}\right)^{10} - \beta_k\left(\frac{d_o}{L}\right)^4 \right] \right\} \quad (26)
$$

Table 2. Algorithm (Pseudo-Code) for Obtaining Effective Pore Size of Slit-Shaped Pores

(1) Guess slit width L corresponding to adsorbate relative pressure P/P_o.

(2) Calculate number of adsorbate molecular layers M (Eq. 12)

$$M = \frac{L - d_s}{d_A}$$

(3) Calculate ϵ_1, ϵ_2, and ϵ_3 (Eqs. 13, 16, and 17).

$$\epsilon_1(z) = \frac{N_s A_s}{2\sigma_s^4}\left[-\left(\frac{\sigma_s}{d_o}\right)^4 + \left(\frac{\sigma_s}{d_o}\right)^{10} \right.$$
$$\left. - \left(\frac{\sigma_s}{L - d_o}\right)^4 + \left(\frac{\sigma_s}{L - d_o}\right)^{10} \right]$$

$$\epsilon_2(z) = \frac{N_s A_s}{2\sigma_s^4}\left[-\left(\frac{\sigma_s}{d_o}\right)^4 + \left(\frac{\sigma_s}{d_o}\right)^{10} \right]$$
$$+ \frac{N_A A_A}{2\sigma_A^4}\left[-\left(\frac{\sigma_A}{d_A}\right)^4 + \left(\frac{\sigma_A}{d_A}\right)^{10} \right]$$

$$\epsilon_3(z) = 2 \cdot \frac{N_A A_A}{2\sigma_A^4}\left[-\left(\frac{\sigma_A}{d_A}\right)^4 + \left(\frac{\sigma_A}{d_A}\right)^{10} \right]$$

(4) If $M < 2$ then
$$\bar{\epsilon} = \epsilon_1$$
Else $(M > 2)$
$$\bar{\epsilon} = \frac{2\epsilon_2 + (M - 2)\epsilon_3}{M}$$

(5) If $[RT \ln(P/P_o) = N_{AV}\bar{\epsilon}]$ then
Effective pore width $= (L - d_s)$
Else
Guess new L and iterate from (1) again.

On applying the Cheng-Yang correction discussed above, the original HK-CY equation is obtained as follows

$$\ln\left(\frac{P}{P_o}\right) + RT\left[1 + \frac{1}{\theta}\ln(1 - \theta)\right] = \frac{3}{4}\pi N_{A\nu}\frac{N_s A_s + N_A A_A}{d_o^4}$$

$$\times \sum_{k=0}^{\infty}\left[\frac{1}{k+1}\left(1 - \frac{d_o}{L}\right)^{2k}\left(\frac{21}{32}\alpha_k\left(\frac{d_o}{L}\right)^{10} - \beta_k\left(\frac{d_o}{L}\right)^4\right)\right]$$

(27)

This model also suffers from the same drawbacks as those discussed for the slit-pore model, namely, an erroneous method to calculate the adsorbate-adsorbate interaction which underestimates the energy potential for large pore diameters.

Modified HK Model for Cylindrical Pores

The derivation for the modified HK model for pores with cylindrical geometry follows the same procedure as that for the slit-pore model. The total number of concentric layers of adsorbate molecules that can be accomodated in the cylinder of radius L is first determined. The energy potential of the adsorbate molecules in each layer is then calculated using the appropriate equation corresponding to Eq. 22. The number of sorbate molecules in each sorbate layer is estimated using the sorbate molecule diameter and diameter of the corresponding concentric layers. The average interaction energy is

then determined by a population-weighted average of the individual layer potentials. One of the assumptions made by the model is that since adsorption will proceed from the extreme periphery of the pore towards the center, the energy potential of each layer would correspond to only the field induced by the immediately surrounding outer layer of molecules. The interaction energy induced by the inside layer of molecules enclosed by the molecules for which the energy potential is being calculated is considered to be negligible.

Figure 5 shows a cross-sectional view of a cylindrical pore. The total number of concentric molecular layers M that can be accommodated within a free space diameter of $(2L - d_s)$ is given by

$$M = \text{int}\left[\frac{\left(\frac{2L - d_s}{d_A} - 1\right)}{2}\right] + 1 \qquad (28)$$

Note that "int" is a mathematical function which truncates the decimal part of a value and retains only the integer part.

The first layer of molecules will be enclosed by a layer of molecules belonging to the sorbent material (such as oxide ions). Since it is assumed that molecules in a layer will preferentially occupy positions at which the energy potential is minimum, the first layer of molecules is supposed to exist at a radius of $(L - d_o)$ from the center. Thus, making the required substitution, the energy potential of the first layer (ϵ_1) is obtained as

$$\epsilon_1 = \frac{3}{4}\pi\frac{N_s A_s}{d_o^4}\left[\frac{21}{32}a_1^{10}\sum_{k=0}^{\infty}\alpha_k\left(b_1^{2k}\right) - a_1^4\sum_{k=0}^{\infty}\beta_k\left(b_1^{2k}\right)\right] \quad (29a)$$

where a_1 and b_1 are given

$$a_1 = \frac{d_o}{L} \qquad b_1 = \frac{L - d_o}{L} \qquad (29b)$$

As can be inferred from Eq. 29b, the constant a_1 (and, in general, a_1) corresponds to a ratio of internuclear spacing d_o to the radius of the enclosing layer of molecules, while b_1 (and, in general, b_i) is the ratio of distance of the layer from the central axis of the pore to the radius of the enclosing layer of molecules. Note that, in the following discussion, the layers are numbered in increasing numbers starting from the outermost layer to the innermost.

The second layer of molecules will be encircled by a cylindrical shell of adsorbate molecules. The depth of energy potential minimum will thus be different from that used in Eq. 29a. Moreover, the internuclear spacing between the molecules is expected to be d_A rather than d_o and the layer of molecules is consequently located at a radius of $(L - d_o - d_A)$ from the central axis. Thus, the energy potential of the second layer is given analogous to Eqs. 29a and 29b and as follows

$$\epsilon_2 = \frac{3}{4}\pi\frac{N_A A_A}{d_A^4}\left[\frac{21}{32}a_z^{10}\sum_{k=0}^{\infty}a_k\left(b_2^{2k}\right) - a_2^4\sum_{k=0}^{\infty}\beta_k\left(b_2^{2k}\right)\right]$$

(30a)

where

$$a_2 = \frac{d_A}{L - d_o} \qquad b_2 = \frac{L - d_o - d_A}{L - d_o} \qquad (30b)$$

Similarly, the third layer will exist at a distance of $(L - d_o - 2 d_A)$ from the axis enclosed by a cylindrical shell of radius $(L - d_o - d_A)$. Hence

$$\epsilon_3 = \frac{3}{4} \pi \frac{N_A A_A}{d_A^4} \left[\frac{21}{32} a_3^{10} \sum_{k=0}^{\infty} \alpha_k(b_3^{2k}) - a_3^4 \sum_{k=0}^{\infty} \beta_k(b_3^{2k}) \right] \tag{31a}$$

where

$$a_3 = \frac{d_A}{L - d_o - d_A} \qquad b_3 = \frac{L - d_o - 2 d_A}{L - d_o - d_A} \qquad (31b)$$

Genearlizing the above equations, one can write down the equation for the energy potential for the ith layer $(i > 1)$ as follows

$$\epsilon_i = \frac{3}{4} \pi \frac{N_A A_A}{d_A^4} \left[\frac{21}{32} a_i^{10} \sum_{k=0}^{\infty} \alpha_k(b_i^{2k}) - a_i^4 \sum_{k=0}^{\infty} \beta_k(b_i^{2k}) \right] \tag{32a}$$

and the constants a_i and b_i are given by

$$a_i = \frac{d_A}{L - d_o - (i-2) d_A} \qquad b_i = \frac{L - d_o - (i-1) d_A}{L - d_o - (i-2) d_A} \tag{32b}$$

The maximum number of molecules of diameter $d(\text{Å})$ that can be accommodated with their centers along the circumference of a circle of diameter D is given by $N = \text{int}[\pi/\text{Sin}^{-1}(d/D)]$ for $d \leq D$ and $N = 1$ for $d > D$. For the ith layer of adsorbate molecules within the pore, the molecules lie along a circle of diameter $2[L - d_o - (i-1) d_A]$, and, hence, the maximum number of molecules of diameter d_A that are present in a horizontal cross-section of the ith layer (when $d_A \leq 2[L - d_o - (i-1) d_A)$ can be written as

$$N_i = \frac{\pi}{\sin^{-1}\left[\dfrac{d_A}{2(L - d_o - (i-1) d_A)} \right]} \tag{33}$$

However, if $d_A > 2[L - d_o - (i-1) d_A]$, $N_i = 1$.

Thus, the average interaction energy $\bar{\epsilon}$ can now be written down by a population-weighted average as follows

$$\bar{\epsilon} = \frac{\displaystyle\sum_{i=1}^{M} N_i \epsilon_i}{\displaystyle\sum_{i=1}^{M} N_i} \tag{34}$$

The PSD for the cylindrical pore model can now be easily determined using either the HK Eq. 19, or the HK-CY Eq. 20. The algorithm for determining pore-size using the cor-

Table 3. Algorithm (Pseudo-Code) for Obtaining Effective Pore Diameter of Cylindrical Pores

(1) Guess pore *radius L* corresponding to adsorbate relative pressure P/P_o.

(2) Calculate number of concentric adsorbate molecular layers M (Eq. 28)

$$M = \text{int} \left[\frac{\left(\dfrac{2 L - d_s}{d_A} - 1 \right)}{2} \right] + 1$$

(3) Calculate ϵ_1 (Eqs. 29 a, b)

$$\epsilon_1 = \frac{3}{4} \pi \frac{N_s A_s}{d_o^4} \left[\frac{21}{32} a_1^{10} \sum_{k=0}^{\infty} \alpha_k(b_1^{2k}) - a_1^4 \sum_{k=0}^{\infty} \beta_k(b_1^{2k}) \right]$$

$$a_1 = \frac{d_o}{L} \qquad b_1 = \frac{L - d_o}{L}$$

(4) Calculate ϵ_1 for $i = 2$ to M (Eqs. 32 a, b)

$$\epsilon_i = \frac{3}{4} \pi \frac{N_A A_A}{d_A^4} \left[\frac{21}{32} a_i^{10} \sum_{k=0}^{\infty} \alpha_k(b_i^{2k}) - a_i^4 \sum_{k=0}^{\infty} \beta_k(b_i^{2k}) \right]$$

$$a_i = \frac{d_A}{L - d_o - (i-2) d_A} \qquad b_i = \frac{L - d_o - (i-1) d_A}{L - d_o - (i-2) d_A}$$

(5) Calculate the population of the layers: N_i, for $i = 1$ to M (Eqs. 33)

If $(d_A \leq 2[L - d_o - (i-1) d_A])$ then

$$N_i = \frac{\pi}{\sin^{-1}\left[\dfrac{d_A}{2(L - d_o - (i-1) d_A)} \right]}$$

Else $(d_A > 2[L - d_o - (i-1) d_A])$

$N_i = 1$

(6) Calculate $\bar{\epsilon}$ (using Eq. 34)

$$\bar{\epsilon} = \frac{\displaystyle\sum_{i=1}^{M} N_i \epsilon_i}{\displaystyle\sum_{i=1}^{M} N_i}$$

(7) If $[RT \ln(P/P_o) = N_{AV} \bar{\epsilon}]$ then

Effective pore diameter $= (2 L - d_s)$

Else

Guess new L and iterate from (1) again.

rected HK equation for cylindrical pores is outlined in Table 3.

Review of Original HK Model for Spherical Pores

The interaction between an adsorbate molecule and a single layer of sorbent molecules located along the wall of a spherical cavity has been studied in detail in literature (Walker, 1966; Soto et al., 1981; Baksh and Yang, 1991). If L is the radius of the cavity, r is the radial distance of a gas molecule from the center of the cavity, and N is the number of molecules on the enveloping cavity surface, the energy potential $\epsilon(r)$ is given as

$$\epsilon(r) = 2 N \epsilon_{12}^* \left[-\left(\frac{d_o}{L} \right)^6 \frac{1}{4\left(\dfrac{r}{L} \right)} \left(\frac{1}{\left(1 - \dfrac{r}{L} \right)^4} - \frac{1}{\left(1 + \dfrac{r}{L} \right)^4} \right) \right.$$

$$\left. + \left(\frac{d_o}{L} \right)^{12} \frac{1}{10\left(\dfrac{r}{L} \right)} \left(\frac{1}{\left(1 - \dfrac{r}{L} \right)^{10}} - \frac{1}{\left(1 + \dfrac{r}{L} \right)^{10}} \right) \right] \tag{35}$$

Using the same approach of Horváth and Kawazoe (1983), the potential expression after taking into account the adsorbate-adsorbate interaction results in the following form

$$
\epsilon(r) = 2(N_l \epsilon_{12}^* + N_2 \epsilon_{22}^*) \left[-\left(\frac{d_0}{L}\right)^6 \frac{1}{4\left(\frac{r}{L}\right)} \right.
$$

$$
\times \left(\frac{1}{\left(1 - \frac{r}{L}\right)^4} - \frac{1}{\left(1 + \frac{r}{L}\right)^4} \right) + \left(\frac{d_o}{L}\right)^{12} \frac{1}{10\left(\frac{r}{L}\right)}
$$

$$
\left. \left(\frac{1}{\left(1 - \frac{r}{L}\right)^{10}} - \frac{1}{\left(1 + \frac{r}{L}\right)^{10}} \right) \right] \quad (36)
$$

$$
N_l = 4\pi L^2 N_s \quad (37)
$$

where

$$
N_2 = 4\pi(L - d_o)^2 N_A \quad (38)
$$

and the minimum energies are given as

$$
\epsilon_{12}^* = \frac{A_S}{4 d_o^6} \quad (39)
$$

$$
\epsilon_{22}^* = \frac{A_A}{4 d_A^6} \quad (40)
$$

By integrating over the volume of the spherical cavity, Cheng and Yang (1994) arrived at the following HK equation for spherical pores

$$
RT \ln\left(\frac{P}{P_o}\right) = N_{Av} \frac{6(N_l \epsilon_{12}^* + N_2 \epsilon_{22}^*) L^3}{(L - d_o)^3}
$$

$$
\times \left[-\left(\frac{d_o}{L}\right)^6 \left(\frac{1}{12} T_l - \frac{1}{8} T_2\right) + \left(\frac{d_0}{L}\right)^{12} \left(\frac{1}{90} T_3 - \frac{1}{80} T_4\right) \right],
$$

$$
(41)
$$

where

$$
T_1 = \frac{1}{\left(1 - \frac{L - d_o}{L}\right)^3} - \frac{1}{\left(1 + \frac{L - d_o}{L}\right)^3} \quad (42)
$$

$$
T_2 = \frac{1}{\left(1 + \frac{L - d_o}{L}\right)^2} - \frac{1}{\left(1 - \frac{L - d_o}{L}\right)^2} \quad (43)
$$

$$
T_3 = \frac{1}{\left(1 - \frac{L - d_o}{L}\right)^9} - \frac{1}{\left(1 + \frac{L - d_o}{L}\right)^9} \quad (44)
$$

$$
T_4 = \frac{1}{\left(1 + \frac{L - d_o}{L}\right)^8} - \frac{1}{\left(1 - \frac{L - d_o}{L}\right)^8} \quad (45)
$$

On applying the Cheng-Yang correction for nonlinearity of the isotherm, the following original HK-CY model is obtained

$$
RT \ln\left(\frac{P}{P_o}\right) - RT\left[1 - \frac{1}{\theta} \ln(1 - \theta)\right]
$$

$$
= N_{Av} \frac{6(N_1 \epsilon_{12}^* + N_2 \epsilon_{22}^*) L^3}{(L - d_o)^3} \left[-\left(\frac{d_o}{L}\right)^6 \left(\frac{1}{12} T_l - \frac{1}{8} T_2\right) \right.
$$

$$
\left. + \left(\frac{d_o}{L}\right)^{12} \left(\frac{1}{90} T_3 - \frac{1}{80} T_4\right) \right], \quad (46)
$$

where $T_1 - T_4$ are given by Eqs. 42–45. Again, as in the previous two models, there is room for improving the adsorbate-adsorbate interaction estimate by considering a more physically realistic picture of the molecular distribution in the pore.

Modified HK Model for Spherical Pores

The modified HK model for a spherical pore follows essentially the same logic as that for slit and cylindrical shaped pores. The total number of adsorbate layers in the form of spherical shells that can be accommodated within a pore of radius L is determined. The energy potential of each gas molecule is computed considering the interaction with the immediately enveloping spherical shell of molecules, which would be the sorbent in the case of the first shell, or the sorbate in the case of subsequent shells. As before, the interaction of the sorbate molecule with the molecules in its own layer, as well as with those in the layers in the interior of its shell, is neglected.

Similar to the cylindrical model, the number of adsorbate layers (M) that can be accommodated with a spherical pore of radius L, is given by

$$
M = \text{int}\left[\frac{\left(\frac{2L - d_s}{d_A} - 1\right)}{2} \right] + 1 \quad (47)
$$

The first layer of adsorbate molecules in the spherical cavity is enclosed by the sorbent molecules along the cavity wall of radius L. The molecules have a maximum probability of existing at a position of minimum potential, which corresponds to a radius of $(L - d_o)$ from the center. Using an expression similar to Eq. 33, the energy potential of the first layer can thus be written as

$$
\epsilon_1 = 2 N_o \epsilon_{12}^* \left[-\frac{c_1^6}{4 f_1} \left(\frac{1}{(1 - f_1)^4} - \frac{1}{(1 + f_1)^4} \right) \right.
$$

$$
\left. + \frac{c_1^{12}}{10 f_1} \left(\frac{1}{(1 - f_1)^{10}} - \frac{1}{(1 + f_1)^{10}} \right) \right] \quad (48)
$$

where N_o, the total number of sorbent molecules in the cavity wall single lattice plane, can be found from the density

(based on area) as follows

$$N_0 = 4 \pi L^2 N_s \qquad (49)$$

Note that since an adsorbate-adsorbent interaction is involved, the depth of energy potential is ϵ_{12}^*. The constant c_1 (and, in general, c_i) is the ratio of the internuclear distance between the interacting molecules under consideration and the radius of the outer enclosing shell of molecules, whereas f_1 (and, in general, f_i) is the ratio of the radius of the layer of molecules for which the energy potential is being calculated to the radius of the outer enclosing shell of molecules. For the first layer, therefore, these constants are given as

$$c_1 = \frac{d_o}{L} \qquad f_1 = \frac{L - d_o}{L} \qquad (50)$$

The number of molecules existing in the first spherical layer of sorbate molecules can be estimated as

$$N_1 = 4 \pi (L - d_o)^2 N_A \qquad (51)$$

The second layer of molecules exists at a radius of ($L\text{-}d_o\text{-}d_A$) will be enclosed by the first layer of sorbate molecules at a radius of ($L\text{-}d_o$). Also, since now an adsorbate-adsorbate interaction is involved, the depth of energy potential is ϵ_{22}^*. The energy of interaction can be written as

$$\epsilon_2 = 2 N_1 \epsilon_{22}^* \left[-\frac{c_2^6}{4 f_2} \left(\frac{1}{(1 - f_2)^4} - \frac{1}{(1 + f_2)^4} \right) \right.$$
$$\left. + \frac{c_2^{12}}{10 f_2} \left(\frac{1}{(1 - f_2)^{10}} - \frac{1}{(1 + f_2)^{10}} \right) \right] \qquad (52)$$

and the constants c_2 and f_2 are given as

$$c_2 = \frac{d_A}{L - d_o} \qquad f_2 = \frac{L - d_o - d_A}{L - d_o} \qquad (53)$$

The number of molecules in the second layer is

$$N_2 = 4 \pi (L - d_o - d_A)^2 N_A \qquad (54)$$

Likewise, the third layer of molecules is situated at a radial distance of ($L\text{-}d_o\text{-}2 d_A$) enclosed by an adsorbate layer of radius ($L\text{-}d_o\text{-}d_A$). Thus, its energy potential would be

$$\epsilon_3 = 2 N_2 \epsilon_{22}^* \left[-\frac{c_3^6}{4 f_3} \left(\frac{1}{(1 - f_3)^4} - \frac{1}{(1 + f_3)^4} \right) \right.$$
$$\left. + \frac{c_3^{12}}{10 f_3} \left(\frac{1}{(1 - f_3)^{10}} - \frac{1}{(1 + f_3)^{10}} \right) \right] \qquad (55)$$

The constants therein as well as the population of molecules inhabiting the third layer can be expressed as

$$c_3 = \frac{d_A}{L - d_o - d_A} \qquad f_3 = \frac{L - d_o - 2 d_A}{L - d_o - d_A}. \qquad (56)$$

$$N_3 = 4 \pi (L - d_o - 2 d_A)^2 N_A \qquad (57)$$

By an inspection of the above equations, one can write down a generalized equation for the ith layer ($i > 1$) of sorbate molecules as follows

$$\epsilon_i = 2 N_{i-1} \epsilon_{22}^* \left[-\frac{c_i^6}{4 f_i} \left(\frac{1}{(1 - f_i)^4} - \frac{1}{(1 + f_i)^4} \right) \right.$$
$$\left. + \frac{c_i^{12}}{10 f_i} \left(\frac{1}{(1 - f_i)^{10}} - \frac{1}{(1 + f_i)^{10}} \right) \right] \qquad (58)$$

$$c_i = \frac{d_A}{L - d_o - (i-2) d_A} \qquad f_i = \frac{L - d_o - (i-1) d_A}{L - d_o - (i-2) d_A} \qquad (59)$$

$$N_{i-1} = 4 \pi \left[L - d_o - (i-2) d_A \right]^2 N_A \qquad (60)$$

As before, the average interaction energy of the adsorbate molecule in the pore would be given by a population-weighted average of the energy potentials of individual molecule layers

$$\bar{\epsilon} = \frac{\displaystyle\sum_{i=1}^{M} N_i \epsilon_i}{\displaystyle\sum_{i=1}^{M} N_i} \qquad (61)$$

where M, the number of adsorbate layers present in the filled spherical pore, is estimated using Eq. 47. ϵ_i and N_i are given by Eqs. 48 and 58–61. The HK model (Eq. 19) or the HK-CY model (Eq. 20) can be now used to process the isotherm data in order to obtain the PSD. The algorithm for determining pore size using the corrected HK equation for spherical pores is given in Table 4.

In the subsequent sections, the new models would be compared vis-à-vis the original HK and HK-CY equations using isotherm data reported in literature.

Results and Discussion

In this section, the corrected HK model will be compared against the original HK model by studying the profiles of the average interaction energy variation with pore size, as well as by obtaining the PSD from the isotherm data reported in literature. Most of the examples considered in this work have been studied earlier by Chen and Yang (1994). The parameters used in the models have been summarized in Table 1. It should be noted that there are a few differences in the parameters used in this work and the previous work by Cheng and Yang (1994). A primary difference is the size of the argon molecule. A study of the literature employing the Horváth-Kawazoe equation showed that there is a wide disparity in the size of the argon molecule used ranging from 2.89 Å (Venero and Chiou, 1988) to 3.36 Å (Cheng and Yang, 1994). The value of the adsorbate molecular diameter chosen in past literature was actually a "fitting" parameter in order to obtain a better fit to the actual PSD of a material. In this work, however, an Ar molecular diameter of 3.82 Å has been used in most cases in this work which is also the more accepted value in literature (Breck, 1974; Razmus and Hall, 1991). However, for the PSD of faujasite using the slit-pore model, an Ar value of 2.95 Å was found to be more appropri-

Table 4. Algorithm (Pseudo-Code) for Obtaining Effective Pore Diameter of Spherical Pores

(1)	Guess pore *radius L* corresponding to adsorbate relative pressure P/P_o.
(2)	Calculate number of concentric adsorbate molecular layers M (Eq. 47)

$$M = \text{int}\left[\frac{\left(\dfrac{2L - d_s}{d_A} - 1\right)}{2}\right] + 1$$

(3)	Calculate ϵ_1 (Eqs. 48–50)

$$\epsilon_1 = 2N_0\epsilon_{12}^*\left[-\frac{c_1^6}{4f_i}\left(\frac{1}{(1-f_1)^4} - \frac{1}{(1+f_1)^4}\right) + \frac{c_1^{12}}{10f_1}\left(\frac{1}{(1-f_1)^{10}} - \frac{1}{(1+f_1)^{10}}\right)\right]$$

$$c_1 = \frac{d_o}{L} \quad f_1 = \frac{L - d_o}{L}$$

$$N_0 = 4\pi L^2 N_s$$

(4)	Calculate N_i for $i = 1$ to M (Eq. 60)
	$N_i = 4\pi[L - d_o - (i-1)d_A]^2 N_A$
(5)	Calculate ϵ_1 (Eqs. 58 and 59) for $i = 2$ to M

$$\epsilon_i = 2N_{i-1}\epsilon_{22}^*\left[-\frac{c_i^6}{4f_i}\left(\frac{1}{(1-f_i)^4} - \frac{1}{(1+f_i)^4}\right) + \frac{c_i^{12}}{10f_i}\left(\frac{1}{(1-f_i)^{10}} - \frac{1}{(1+f_i)^{10}}\right)\right]$$

$$c_i = \frac{d_A}{L - d_o - (i-2)d_A} \quad f_i = \frac{L - d_o - (i-1)d_A}{L - d_o - (i-2)d_A}$$

(6)	Calculate $\bar{\epsilon}$ (using Eq. 61)

$$\bar{\epsilon} = \frac{\displaystyle\sum_{i=1}^{M} N_i\epsilon_i}{\displaystyle\sum_{i=1}^{M} N_i}$$

(7)	If $[RT\ln(P/P_o) = N_{A\nu}\,\bar{\epsilon}]$ then
	Effective pore diameter $= (2L - d_s)$
	Else
	Guess new L and iterate from (1) again.

Figure 6. Variation of average interaction energy of N_2 molecules vs. pore size of molecular sieve carbon as predicted by original and modified HK models for slit-shaped pores.

ate. Also, there is a minor difference in the oxide ion surface density value for aluminophosphate materials. The value of 1.48×10^{15} molecules/cm² used by Cheng and Yang (1994) was arrived at by assuming a closed packed arrangement of oxide ions of diameter 2.6 Å. A study of the structure of aluminophosphates such as $AIPO_4 - 5$ and VPI-5 revealed, however, that, assuming an AL-O bond length of 1.73Å and a P-O bond length of 1.66 Å, the average oxide ion density on the cylindrical channel surface was closer to 1.0×10^{15} molecules/cm². Choosing the right physical parameters is critical for discriminating between Horváth-Kawazoe models, since the predicted pore size is known to be very sensitive to small variations in the physical parameters used (Saito and Foley, 1991).

Slit-shaped pore model

HGS-638 Molecular Sieve Carbon. The modified energy profile model developed in this work was compared vis-á-vis the original HK model. As a model system, adsorption of liquid nitrogen at 77 K on HGS 638 molecular sieve carbon
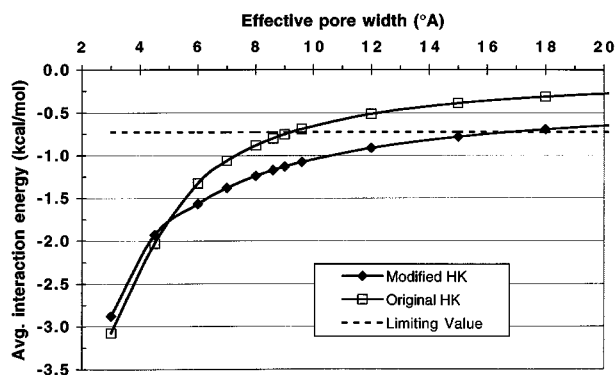
sorbent was considered which was the same system studied by Horváth and Kawazoe (1983). The physical parameters used in the model are summarized in Table 1. The comparison of the average interaction energy with respect to the slit pore size expressed in multiples of the N_2 molecular diameter (3.0 Å) is shown in Figure 6. From the figure, it can be inferred that the average interaction energy predicted by both the models is approximately the same for pore widths measuring 1 to 2 times the adsorbate molecular diameter. This is expected since the sorbate-sorbate interaction has a negligible contribution compared to the overlapping sorbate-sorbent energy potentials at very small pore sizes. However, beyond a pore size of $2\,d_A$, the modified model predicts a much lower energy potential than the original model. Thus, the pore size predicted by using the original HK model would be an underestimate of the actual pore size for pore widths exceeding $2\,d_A$. As was explained earlier, the system should tend to have a limiting maximum interaction energy equal to that given by Eq. 11. A Fit of Eq. 10 with the N2/HGS-638 MSC data given in the study by Horváth and Kawazoe (1983) gave a value of $K = 175$. Substituting this K value in the righthand side of Eq. 11 gives a limiting value of -0.73 kcal/mol. This should be the limiting magnitude of interaction energy in a pore of infinite width and is indicated as dotted line in Figure 6. It was interesting to note that while the interaction energy predicted by the original model tends towards zero at large pore widths, that predicted by the proposed model tends to a value closer to the limiting interaction energy. An inspection of Eq. 15 reveals that as $L \to \infty$ (that is, $M \to \infty$), the average interaction energy tends to $N_{A\nu}\epsilon_3(z)$. For the N_2/HGS-638 system, this limiting value was determined to be -0.3 kcal/mol. The two values are remarkably similar considering the fact that the limiting value given by Eq. 10 is purely from experimental isotherm data while that obtained from Eqs. 14 and 15 are purely from Lennard-Jones interaction parameters. Besides, the error is also likely to be caused due to an assumption in the HK derivation that the entropy of adsorption can be neglected compared to the enthalpy of adsorption, whereas the entropy change can be considerable at large pore sizes.

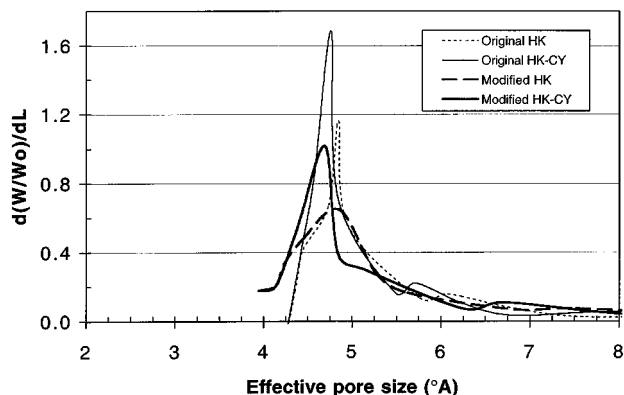The PSD of HGS-638 predicted by the original HK Eq. 8, original HK-CY Eq. 9, modified-HK Eq. 19 and the modified

Figure 7. PSD of HGS-638 molecular sieve carbon as predicted by original and modified HK models for slit-shaped pores.

HK-CY Eq. 20 is shown in Figure 7. It can be seen that there is virtually no shift in the peak pore size when the interaction energy model was changed. This is so because the peak pore size of HGS-638 lies in the 4–6°A range, which corresponds to roughly twice the adsorbate molecule (N_2) diameter. It is evident from Figure 6 that the interaction energy predicted by the two models is nearly the same until the slit width is about $2 d_A$ and, hence, the predicted pore widths are also similar in this size range. Also, it was observed that the points on the figure corresponding to the higher extreme of the pore width in the original model appeared at a still higher pore size in the new model. This again can be explained from the fact that, for the same interaction energy, the new model predicts a higher pore size compared to that predicted by the original model.

Faujasite zeolite

The adsorption isotherm of argon on faujasite zeolite at 87 K has been given by Borghard et al. (1991). This type of zeolite actually has a spherical cavity and the results using the modified HK model for spherical pores will be subsequently shown. The slit-pore model was tried in the case of faujasite,
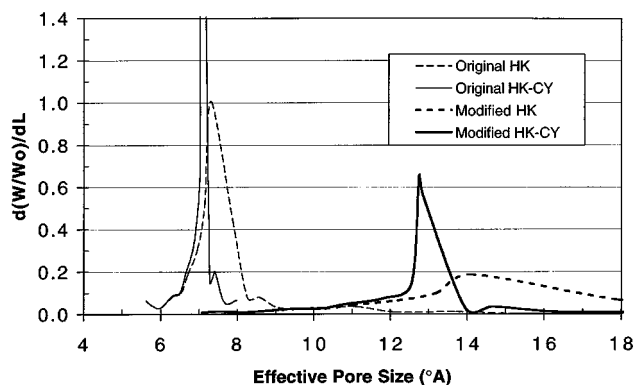
particularly since it has a comparatively larger pore structure than molecular sieve carbons and the differences between the model predictions will become obvious. It has been shown previously (Cheng and Yang, 1994) that the application of the original HK model gives a highly underestimated PSD. Figure 8 shows the prediction of the two original and two modified models. It can be seen that while the original models predicted a pore size of 7 Å, the modified models gave a peak at much higher pore size of 13 Å. It is interesting to note that the crystallographic channel size of Faujasite is 7.4 Å, while the actual cavity size of Faujasite is 13.7 Å. Thus, the modified model is seen to be more capable of determining the PSD in the higher range of pore size compared to the original model. This is a result of a more realistic picture for calculation of adsorbate-adsorbate interaction and an improved method of averaging interaction energy.

Cylindrical Pore Model
ZSM-5 zeolite

The zeolite ZSM-5 is an aluminosilicate with three-dimensional channels measuring 5.6×5.3 Å in width. The isothermal of argon on ZSM-5 zeolite at 87 K has been reported by Venero and Chiou (1988). Since the channels for this adsorbent are approximately cylindrical in nature, the cylinder-shaped pore model would be ideal for this example. Figure 9 shows the average interaction energy of an argon molecule at 87 K in ZSM-5 pore filled with adsorbate molecules at different pore diameters, as predicted by the original and modified HK cylindrical pore models. It can be seen that although the average energy within the pore predicted by the two models was reasonably close at low pore sizes (< 7Å), the difference became more pronounced in the higher size range. A fit of the isotherm data to Eq. 10 gave a value of $K = 770$. Using this value of K, a limiting interaction energy value of -0.98 kcal/mol was obtained at large pore sizes (Eq. 11), which is depicted in the form of a dotted line in Figure 9. From the prediction using the Lennard-Jones parameters, it can be seen that at large pore sizes, a limiting value of -0.70 kcal/mol is obtained. The reasonably good agreement of the two values,

Figure 8. PSD of faujasite zeolite as predicted by original and modified HK models for slit-shaped pores.
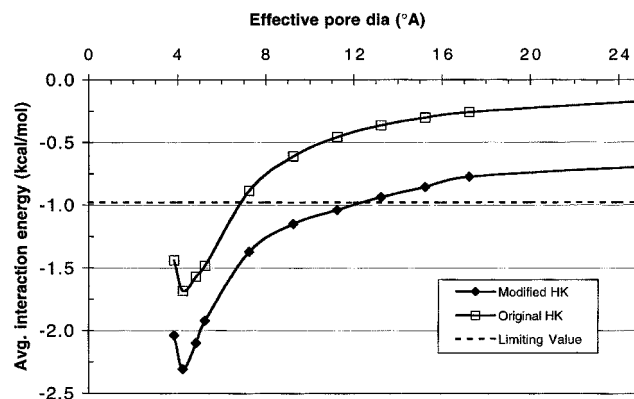

Figure 9. Variation of average interaction energy of argon molecules vs. pore size of ZSM-5 zeolite as predicted by original and modified HK models for cylindrical pores.
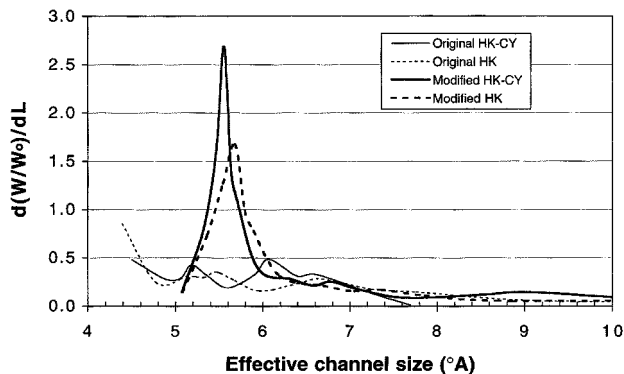
Figure 10. PSD of ZSM-5 zeolite as predicted by original and modified HK models for cylindrical pores.

Figure 11. PSD of MCM-41 material as predicted by original and modified HK models for cylindrical pores.

one from purely empirical data and the other from established interaction parameters, adds to the merit of the modified model.

The PSD of ZSM-5 predicted by the four models is shown in Figure 10. It was seen that for the parameters chosen (Table 1), no prominent peak was visible for both the original HK, as well as the HK-CY model since no solution for the pore size existed for the first few points of the isotherm. On the other hand, a peak was obtained at 5.7 Å using the modified HK model. On using the modified HK-CY model, a sharper peak was observed at 5.6 Å, which agrees well with the crystallographic dimension of the ZSM-5 channel.

MCM-41 molecular sieves

MCM-41 materials belong to the family of large pore (mesoporous) molecular sieves and are increasingly becoming popular as catalyst supports. These synthetic materials possess a regular array of hexagonal, uniform unidimensional mesopores, which can be systematically varied from $16 - 100$ Å. Due to their narrow PSD, minimal network effects, and well-known surface chemistry, they are ideal candidates for testing pore-size models. Numerous studies have been conducted for studying the PSD of MCM-41 materials using various techniques such as the BJH method (Ravikovitch et al., 1997; Sayari et al., 1999), X-ray diffraction (XRD) (Ravikovitch et al., 1995), H-NMR (Schmidt et al., 1995), and nonlocal density functional theory (NLDFT) (Ravikovitch et al., 1995, 1997).

In order to test the corrected HK model, N_2 adsorption data at 77.4 K on a MCM-41 material denoted "Sample C" in a previously published work (Ravikovitch et al., 1995) was used. The XRD results and the NLDFT simulation studies reported in the latter work show the pore size of the material to be 45 Å. Figure 11 shows the PSD for the MCM-41 material predicted from the N_2 adsorption data using the corrected and original HK cylindrical pore models. Since the isotherm does not follow Langmuirian behavior, the Cheng-Yang correction was computed by fitting the data to a Langmuir isotherm as much as possible. The figure shows that the corrected HK-CY equation accurately estimates the pore size of the material to be 45 Å. Using the same model parameters
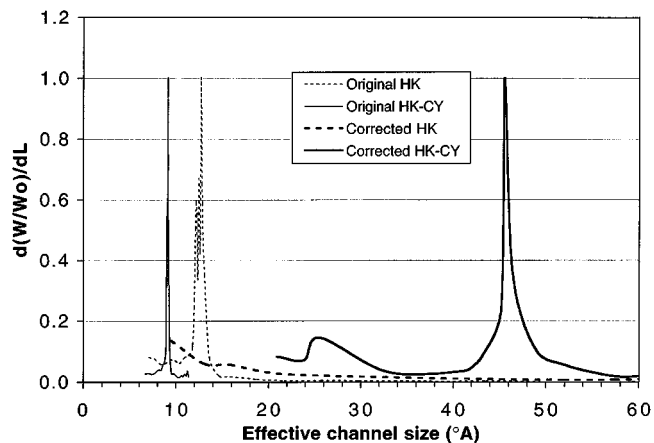
(shown in Table 1), the original HK and HK-CY models give a grossly underestimated pore size of 12 Å and 9 Å, respectively. It must be noted that the corrected HK equation without the Cheng-Yang correction gives a highly overestimated value of pore size (beyond the limits of Figure 11). This is because the inflexion on the curve occurs at a high P/P_s value (~ 0.4), and there is a severe deviation from Henry's law at this value. Further, Ravikovitch et al. (1997) have reported that the BJH method systematically underestimated the pore size of the MCM-41 materials studies by ~ 10 Å. Thus, the utility of the corrected HK-CY model in predicting PSD for materials in the mesoporous (> 20Å) size range is demonstrated.

$AlPO_4$ (Aluminophosphates)

Like zeolitic materials, aluminophosphates also poses well-defined structure and narrow PSD. Most aluminophosphates such as $AlPO_4$-11 and VPI-5 have a one-dimensional channel structure. Adsorption isotherms of argon on these materials have been reported by Davis et al. (1988).

The PSD of $AlPO_4$-11 is shown in Figure 12. The actual channel size reported in literature is 6.3 Å (Meier and Olson,
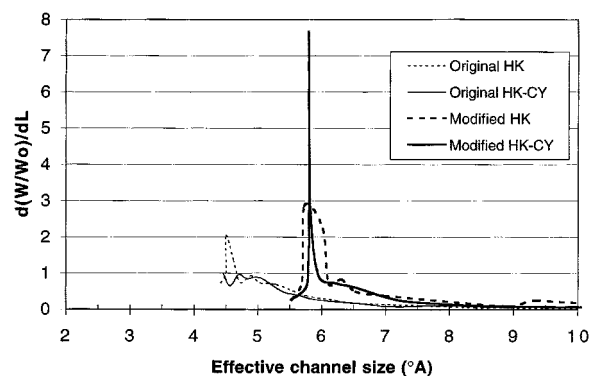

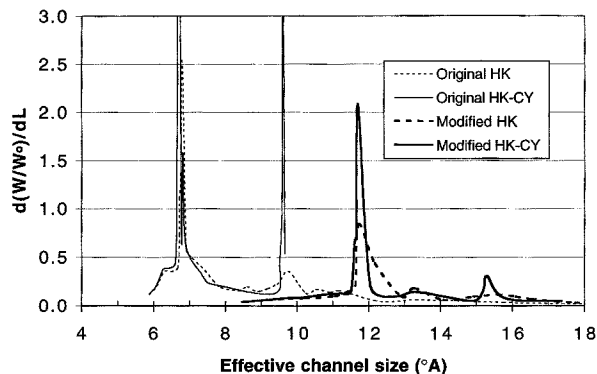Figure 12. PSD of $AlPO_4$-11 as predicted by original and modified HK models for cylindrical pores.

Figure 13. PSD of VPI-5 as predicted by original and modified HK models for cylindrical pores.
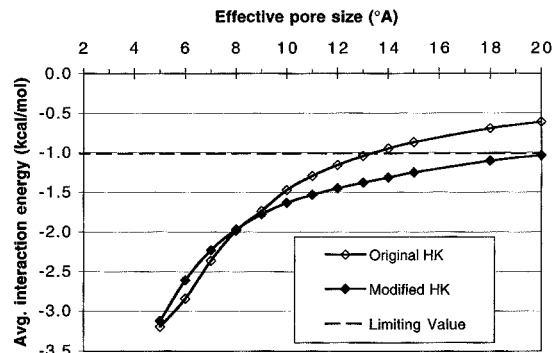

Figure 14. Variation of average interaction energy of argon molecules vs. pore size of faujasite zeolite as predicted by original and HK models for spherical pores.

1987). The modified HK-CY model gives a peak at a pore size of about 5.9 Å. The original model on the other hand gives a peak at a much lower pore size at 4.6 Å. Figure 13 shows the computed PSD of VPI-5 aluminophosphate, whose isotherm is seen to have two sigmoidal bends suggesting that it may have a bimodal PSD. The currently accepted pore size of VPI-5 is 12.1 Å (Davis et al., 1988). It was shown previously by Cheng and Yang (1994) that VPI-5 gives two peaks on employing the original HK-CY equation: a major peak at 8.6 Å and a minor one at 11.7 Å. In this work different parameters were used for the kinetic diameter of argon and the oxide ion density in the aluminophosphate framework. As a result, the new peaks obtained using the original model were situated at 6.8 Å and at 8.7 Å. With the modified HK-CY model, the major peak was observed at 11.8 Å and a minor peak was observed at 15.2 Å. Thus, the modified cylindrical HK-CY model has a better agreement with crystallographic data than the original model.

Spherical Pore Model
Faujasite zeolite

The PSD for faujasite zeolite using the slit pore model was shown in an earlier section. This zeolite is, however, known to have nearly spherical shaped cavities measuring 13.7 Å in diameter. Hence, it is apparent that the spherical pore model would be more appropriate to obtain the PSD for this material. The average interaction energy of an Ar molecule in an adsorbate filled Faujasite micropore predicted by the original and modified HK equations is shown in Figure 14. It can be seen from the figure that the predicted average energy potentials for both the models are nearly the same until an effective pore size of 8 Å. At higher pore diameters, a considerable difference in calculated average energy values was observed. As in previous examples of models with other pore geometries, the interaction energy calculated by the original HK model was seen to approach zero at large pore size, whereas that predicted by the new model was seen to asymptotically approach a value of about -0.75 kcal/mol. A fit of the isotherm data to Eq. 9 gave a value of $K = 920$, which on substitution in Eq. 10 resulted in a limiting value of -1.0 kcal/mol of the interaction energy (shown as a dotted line in the figure) at large pore size. As before, this is a good agree-

ment of a theoretical model prediction with an experimentally obtained value.

The spherical-shaped pore model was employed next to deduce the PSD of Faujasite from the argon isotherm data of Borghard et al. (1991). Figure 15 shows the distribution of pores as calculated by the four models. For the parameters chosen, the original HK-CY equation provided a peak at about 10.5 Å, whereas the modified HK-CY model calculated one at the expected value of 13.7 Å. The modified HK model without the correction for isotherm nonlinearity, however, provides a highly diminished peak at about 14.8 Å.

5A zeolite

The adsorption of argon on 5A zeolite at 87K was measured by Venero and Chiou (1988). On performing a PSD analysis of the isotherm data with the models discussed in this work, it was observed that the original model predicted a pore size of 8.8 Å, whereas the modified model predicts a pore size of 9.8 Å (Figure 16). In reality, 5A zeolite (also known as Ca-A) has a crystallographic channel size of 4.9 Å (Dyer, 1988) and a cavity size of 11.4 Å. Thus, the new model provides a reasonably better estimate of the pore size. Again, the difference in the calculated and the crystallographic value
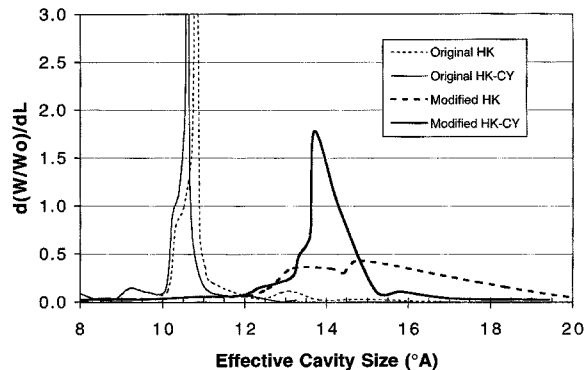

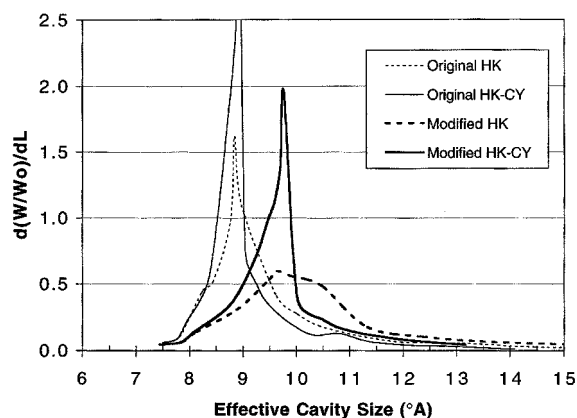Figure 15. PSD of faujasite zeolite as predicted by original and modified HK models for spherical pores.

Figure 16. PSD of 5A (Ca-A) zeolite as predicted by original and modified HK models for spherical pores.

can be attributed to the uncertainty in the model parameters used.

Conclusions

The conventional Horváth-Kawazoe equations for calculation of PSD in microporous sorbents have been shown to have certain errors associated in its derivation. The primary causes of error in the original model have been identified as an incorrect method of calculating adsorbate-adsorbate interaction within a filled micropore, an unrealistic picture of distribution of molecules in the micropores, and the lack of inclusion of an energy distribution while calculating the average interaction energy. In this work, new models have been proposed for the purpose of determination of PSD for slit, cylindrical as well as spherical shaped pores. Although the primary principle is the same as that of Horváth and Kawazoe (1983), the proposed model is different with respect to the method of calculation of average interaction energy. An improved method of calculating adsorbate-adsorbate interaction is demonstrated assuming that molecules occupy positions corresponding to lowest energy potentials. This is in accordance with the Boltzmann law of energy distribution which assigns the highest probability of a molecule to exist in a state for which its energy potential is minimum. The new model is simple to use and can be easily implemented using a programming code or a spreadsheet with a nonlinear regression capability. A study of the average interaction energy vs. pore-size profiles revealed that the original model is reasonably accurate for effective pore sizes measuring less than two adsorbate diameters, but, thereafter, a significant deviation was observed from the modified model. Various examples have been provided for all the three different pore geometries which show that the PSD provided by the corrected model is in better agreement with crystallographic data in literature than the original model. Moreover, the corrected HK model is shown to accurately predict PSD of even mesoporous materials like MCM-41 materials, which was not possible with the original HK model. Thus, the improved model can be used for the entire nanoporous size range up to the pore size at which the surface tension of the adsorbate in the pore becomes important, in which case the Kelvin equation should be used.

Notation

a_i, b_i = parameters in modified cylindrical pore model for ith layer of molecules

c = speed of light m/s

c_i, f_i = parameters in modified spherical pore model for ith layer of molecules

d_o = mean of the diameters of adsorbate and adsorbent molecules, Å

i = index for sorbate molecular layer numbered starting from outermost layer

k = summation counter for cylindrical pore energy profile equation, or Boltzmann constant

K = parameter in the Langmuir equation

L = internuclear distance between parallel layers of slit-shaped pores, likewise defined as the radius (not diameter) for cylindrical and spherical pore, Å

m = mass of an electron, kg

N = density of molecules based on surface area, (molecules/cm^2), or number of molecules in a layer

N_1 = number of sorbent molecules on cavity surface

N_2 = number of adsorbate molecules in layer

N_{Av} = Avogadro's number, molecules/mol

P = pressure of adsorbate in the gas phase, bar

P_o = saturation vapor pressure of adsorbate, bar

r = radial distance of an adsorbate molecule from the central axis for cylindrical pores and from center in case of spherical pores

R = gas constant, J/mol/K

T = absolute temperature, K

α = polarizability, cm^3

ϵ_{12} = interaction energy potential between molecule 1 and 2, erg/molecule

ϵ_{12}^* = depth of potential energy minimum for adsorbate-adsorbent interaction, erg/molecule

ϵ_{22}^* = depth of potential energy minimum for adsorbate-adsorbate interaction, erg/molecule

$\bar{\epsilon}$ = average interaction energy, erg

θ = degree of void filling in the sorbent

χ = magnetic susceptibility, cm^3

Subscripts

A = corresponding to adsorbate

S = corresponding to the adsorbent

A-S = adsorbate-sorbent interaction

A-A = adsorbate-adsorbate interaction

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