A Thermodynamic Model for Gas Adsorption Isotherms

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In this paper based on the principle of solution thermodynamics for gas–solid equilibrium, a relation is developed to express gas adsorption isotherms. An activity coefficient model based on weight fraction of sorbate in the solid phase has been derived that well describes the behavior of various gases on different types of adsorbents. The proposed model has been evaluated and compared with four other models commonly used for gas adsorption isotherms in the literature. For 12 different systems at various isotherms for the temperature range −128 to 100°C and the pressure range 0.02 to 1219 kPa for 689 data points, the proposed model predicts equilibrium pressure with an average deviation of 5.3%, which is about half of the error obtained from other methods. The proposed model clearly outperforms other available methods such as the vacancy solution theory, the ideal adsorption solution model, and other various modified forms of the Langmuir isotherm. Unique features of the proposed model are its simplicity, generality, and accuracy over the entire pressure and temperature ranges. © 1999 Academic Press

Key Words: gas adsorption isotherm; thermodynamic model; solid activity coefficient.

INTRODUCTION

Environmental concerns have brought about strict regulations to limit contaminant emission. Common gases such as carbon monoxide, carbon dioxide, and hydrogen sulfide are presently removed by temperature swing adsorption (TSA) and/or pressure swing adsorption (PSA). Molecular sieves and selective membranes have made adsorption a most economical and viable unit operation for separation of gaseous mixtures. The complexity of adsorption phenomena and the lack of accurate and complete experimental adsorption data have been major factors influencing the development and application of adsorption technology.

The variation in solid phase concentration of the sorbate, q (mol/kg of adsorbent), as a function of the vapor/gas phase equilibrium pressure, P (concentration of the sorbate, kPa), is expressed by an isotherm. Langmuir (1) has considered simple kinetics and developed the isotherm equation

$$P = \frac{1}{b_0} \frac{\theta}{1 - \theta}, \qquad [1]$$

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where b is a constant for a sorbate–adsorbent system at a given temperature. Parameter θ is the fraction of surface covered by gas molecules. θ is defined as

$$\theta = \frac{q}{q_0}, \qquad [2]$$

where q_0 is the maximum amount of gas adsorbed for full surface coverage and it is a constant for a sorbate–adsorbent system at a given temperature. Combining Eqs. [1] and [2] gives another form for the Langmuir isotherm,

$$q = \frac{q_0 b_0 P}{1 + b_0 P}, \qquad [3]$$

where q_0 and b_0 are the two parameters that must be determined from experimental data.

There are a number of modified forms of the above expression (Eq. [1] or Eq. [3]) to account for the nonideal behavior of sorbates and the structure of adsorbents. The vacancy solution theory (VST) has been presented by Suwanayuen and Danner (2) based on the Wilson activity coefficient model for the nonideality from the Langmuir isotherm. The VST has the form

$$P = \left[\frac{1}{b_0} \frac{\theta}{1 - \theta} \right] \left[\Lambda_{12} \frac{1 - (1 - \Lambda_{21})\theta}{\Lambda_{12} + (1 - \Lambda_{12})\theta} \right]$$
$$\times \exp\left[\frac{-\Lambda_{21}(1 - \Lambda_{21})\theta}{1 - (1 - \Lambda_{21})\theta} - \frac{(1 - \Lambda_{12})\theta}{\Lambda_{12} + (1 - \Lambda_{12})\theta} \right], \quad [4]$$

where Λ_{12} and Λ_{21} are the Wilson parameters. When these parameters are equal to unity, Eq. [4] reduces to the Langmuir isotherm, Eq. [1]. Therefore, the VST model is a four-parameter correlation (b_0, q_0, Λ_{12}, and Λ_{21}) and these parameters must be determined from nonlinear regression of experimental data on P versus q. In this model convergence in some cases is a problem in obtaining the correlation parameters as discussed by Cochran *et al.* (3).

The ideal adsorption solution (IAS) theory, proposed by Myers and Prausnitz (4), for mixed-gas adsorption is based on

System	Adsorbate gas	Adsorbent	Temperature (°C)	Pressure range (kPa)	Amount adsorbed (range, mol/kg)	No. of data points	Data source
1	Carbon dioxide	Mordenite	10	0.32–60.76	0.38–2.36	18	
			30	0.37–138.7	0.25–2.38	41	Talu and Zwiebel (13)
			50	0.63–292.7	0.21–2.44	34	
2	Hydrogen sulfide	Mordenite	10	0.41–9.830	1.13–2.27	17	
			30	0.49–27.62	0.89–2.28	22	Talu and Zwiebel (13)
			65	0.48–79.18	0.39–2.24	23	
			95	3.19–101.9	0.64–1.95	7	
3	Propane	Mordenite	10	0.02–115.0	0.10–1.26	30	
			30	0.10–206.8	0.09–1.24	34	Talu and Zwiebel (13)
			51	0.51–207.5	0.17–1.10	28	
4	Ethane	Molecular sieve 13-X	0	0.40–97.04	0.12–2.61	27	
			25	0.54–137.8	0.04–2.29	31	Danner and Choi (14)
			50	2.12–137.8	0.08–1.89	20	
			100	3.30–121.4	0.03–0.86	25	
5	Ethylene	Molecular sieve 13-X	25	0.27–137.8	0.41–2.81	29	
			50	0.67–137.8	0.25–2.50	25	Danner and Choi (14)
			100	1.05–137.8	0.07–1.74	29	
6	Carbon dioxide	Molecular sieve 13-X	25	0.34–137.8	0.44–4.02	20	Huyn and Danner (15)
			50	0.44–137.8	0.21–3.44	17	
7	Isobutane	Molecular sieve 13-X	25	0.1–137.8	0.75–1.88	16	
			50	0.4–137.8	0.70–1.65	16	Huyn and Danner (15)
			100	0.64–107.2	0.17–1.33	16	
8	Carbon monoxide	Molecular sieve 5-A	−128	0.30–110.0	2.00–5.00	17	Danner and Wenzel (16)
9	Carbon monoxide	Molecular sieve 10-X	−128	0.40–150.5	1.80–5.80	16	Danner and Wenzel (16)
10	Oxygen	Molecular sieve 5-A	−128	1.00–213.0	0.30–5.30	18	Danner and Wenzel (16)
11	Propadiene	Activated carbon	5	2.60–292.8	2.80–6.70	11	
			15	1.30–428.4	2.40–6.50	10	Olivier et al. (17)
			20	1.10–382.4	2.60–6.20	10	
			30	5.10–436.9	2.50–5.95	12	
12	Propylene	Activated carbon	5	5.20–531.0	2.10–5.50	16	
			15	8.80–812.2	2.60–5.60	16	Olivier et al. (17)
			20	11.0–936.2	2.70–5.40	18	
			30	12.1–1219.3	2.00–5.30	20	
Total	H₂S, CO₂, CO, O₂, C₂H₃, C₂H₆, C₃H₈, C₃H₄, C₃H₆, iC₄H₁₀	Zeolite, mordenite activated carbon	−128 to 100	0.02–1219.3	0.03–6.70	689	

the concept of an ideal adsorbed solution, and by using classical surface thermodynamics, an expression analogous to Raoult's law was obtained. Moon and Tien (5) have suggested a method for calculating multicomponent gas adsorption equilibria from pure component data based on the IAS theory. The single component isotherm data can be expressed by a modified form of the Langmuir equation as

$$q = \frac{q_1 b_1 P}{1 + b_1 P} + \frac{\sigma_1^2 q_1 b_1 P(1 - b_1 P)}{2(1 - b_1 P)^3}, \qquad [5]$$

where q_1, b_1, and σ_1 are the three constants for each isotherm. When σ_1 is zero this equation reduces to Eq. [3], the Langmuir isotherm.

Khan et al. (6) have suggested a generalized isotherm for bisolute adsorption from dilute aqueous solution. This correlation has a unique characteristic, covering both extremes: the Langmuir isotherm and the Freundlich isotherm. Khan et al. (7) have simplified their generalized equation for pure component adsorption isotherms as follows:

$$q = \frac{q_2 b_2 P}{(1 + b_2 P)^{\sigma_2}}. \qquad [6]$$

In this correlation three parameters q_2, b_2, and σ_2 must be determined for each isotherm. When σ_2 is equal to unity, Eq. [5] reduces to the Langmuir isotherm (Eq. [3]). There are many other modified versions of the Langmuir isotherm such as the

TABLE 2
Constants in Eq. [16] (Proposed Model) for Systems Listed in Table 1

System	Adsorbate gas	Adsorbent	Temperature (°C)	a	b	c	n
1	Carbon dioxide	Mordenite	10	1.92718	77.26676	−160.650	2
			30	3.15151	68.72585	−96.0886	2
			50	4.07539	73.33106	−155.997	2
2	Hydrogen sulfide	Mordenite	10	0.29714	47.99053	389.6589	2
			30	0.63493	70.61579	226.6718	2
			65	2.64066	59.65608	273.7888	2
			95	3.57241	73.06591	82.19116	2
3	Propane	Mordenite	10	1.22117	66.28906	1457.948	2
			30	2.96448	27.05728	1919.507	2
			51	3.80452	28.99118	2004.173	2
4	Ethane	Molecular sieve 13-X	0	4.98978	16.76293	1.05571×10^6	5
			25	6.01932	20.58848	1.18520×10^6	5
			50	6.86054	25.13723	1.22832×10^6	5
			100	8.20153	25.36461	1.57240×10^7	5
5	Ethylene	Molecular sieve 13-X	25	2.89603	52.70540	8.51070×10^5	5
			50	4.18591	52.30213	7.59237×10^5	5
			100	6.06955	53.53808	8.52098×10^5	5
6	Carbon dioxide	Molecular sieve 13-X	25	2.22032	35.46964	2.26675×10^4	5
			50	3.55350	34.93181	2.68839×10^4	5
7	Isobutane	Molecular sieve 13-X	25	−1.0955	56.37733	4.79047×10^5	5
			50	2.02208	14.30054	1.13016×10^6	5
			100	4.10674	14.98012	1.58148×10^6	5
8	Carbon monoxide	Molecular sieve 5-A	−128	6.00753	−77.4925	4.42006×10^5	5
9	Carbon monoxide	Molecular sieve 10-X	−128	−0.5403	53.08155	4.75098×10^4	5
10	Oxygen	Molecular sieve 5-A	−128	3.60867	19.84463	5.26883×10^4	5
11	Propadiene	Activated carbon	5	2.06450	−8.38363	257.3726	2
			15	2.03669	−10.4124	290.5052	2
			20	−1.4495	33.85509	163.4337	2
			30	4.59575	−28.7108	345.5243	2
12	Propylene	Activated carbon	5	8.01975	−86.2942	580.6494	2
			15	4.85236	−37.7692	430.8271	2
			20	5.34745	−42.9296	457.9448	2
			30	7.98201	−71.0203	562.9058	2

correlation suggested by Toth as given by Valenzuela and Myers (8). The Toth equation has a form similar to that of Eq. [6], but as Khan *et al.* (7) have discussed Eq. [6] is more accurate than any other forms of the modified Langmuir isotherm.

Martinez and Basmadjain (9) have introduced a few parameters to the Langmuir equation to account for sorbate size, loss of symmetry, and molecular interaction in gas–solid adsorption. Their equation for a single-solute case is

$$P = m \frac{\theta^s}{(1 - \theta)^r} \exp\left(- \frac{rW\theta}{KT} \right). \qquad [7]$$

This equation contains five parameters m, r, s, W, and q_0. Equation [7] is a modification of the Langmuir equation; when $W = 0$ and $r = s = 1$, Eq. [7] reduces to the Langmuir isotherm (Eq. [1]).

The Langmuir isotherm (Eq. [3]) and all its modified versions (Eqs. [4]–[7]) fail to perform well at low pressures where $\theta \to 0$. In addition, the optimization procedure for some of these models, such as the VST model, is tedious in order to obtain the four parameters involved in the correlation. In some occurrences convergence may never be obtained (Cochran *et al.* (3)). The main objective of this work is to propose a simple, accurate, and generalized model for gas adsorption isotherms based on the gas–solid equilibrium principles.

PROPOSED THERMODYNAMIC MODEL

In developing our thermodynamic model, we assume that the sorbate gas molecules are adsorbed on porous adsorbent with a constant void fraction providing a uniform distribution. The solid phase can be treated as solid solution of sorbate gas well distributed into the adsorbent having a large
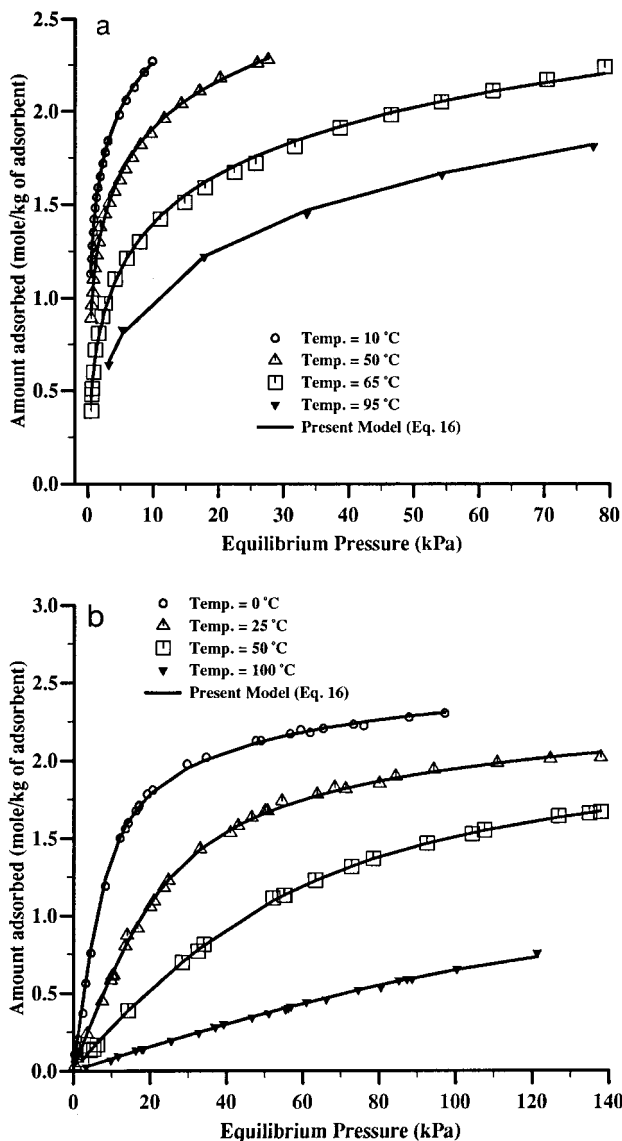
FIG. 1. Model predictions for gas adsorption isotherms. (a) System 2 (H_2S on mordenite); (b) System 4 (ethane on molecular sieve 13-X).

void fraction. Applying the principle of solution thermodynamic equilibrium relation between the gas phase and the solid phase based on the equality of fugacities of the sorbate in two phases gives

$$f_A^g = f_A^s, \qquad [8]$$

where f_A^g is the fugacity of sorbate (component A) in the gas phase and f_A^s is its fugacity in the solid phase. Now we define the solid activity coefficient of A (γ_A^s) based on the weight fraction of A in the solid phase, z_A,

$$\gamma_A^s = \frac{f_A^s}{z_A f_A^{0s}}, \qquad [9]$$

where f_A^{0s} is the fugacity of solid A at a standard state. We define this standard state at a later stage. The fugacity of A in the gas phase is given by the fugacity coefficient ϕ_A^g

$$f_A^g = y_A \phi_A^g P, \qquad [10]$$

where y_A is the mole fraction of A in the gas phase and P is the total pressure of the gas phase. Substituting Eqs. [6] and [7] into Eq. [5] gives

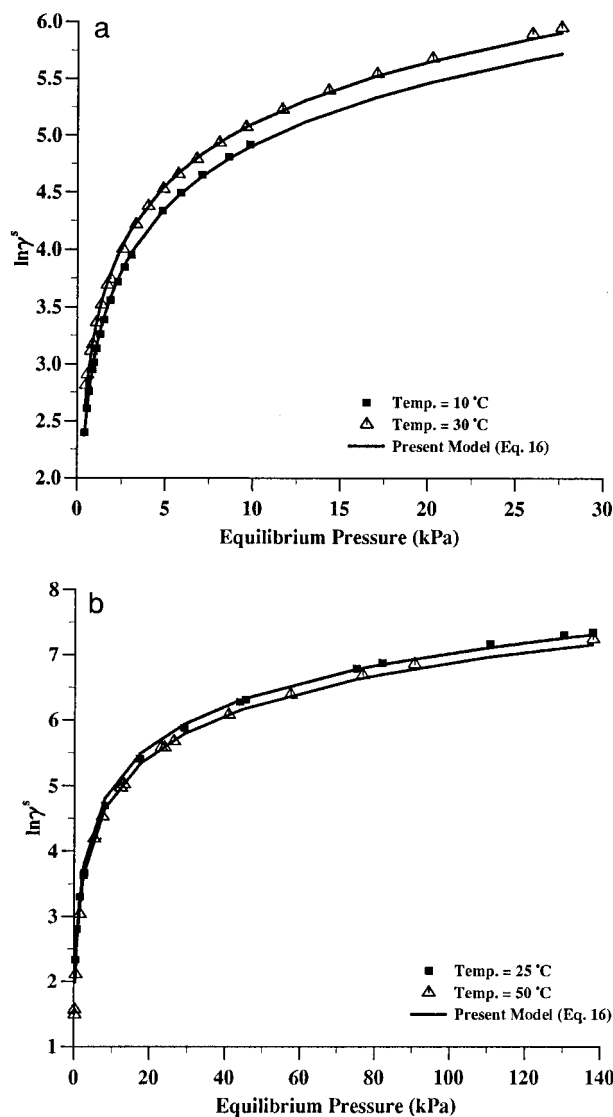$$y_A \phi_A^g P = z_A \gamma_A^s f_A^{0s}. \qquad [11]$$

FIG. 2. Activity coefficient of sorbate in the solid phase. (a) System 2 (H_2S on mordenite); (b) System 7 (isobutane on molecular sieve 13-X).

TABLE 3
Constants in Eq. [4] (VST Model) for Systems Listed in Table 1

System	Adsorbate gas	Adsorbent	Temperature (°C)	q_0	b_0	Λ_{12}	Λ_{21}
1	Carbon dioxide	Mordenite	10	13.776	3.1632	974.50	6.5280
			30	9.3720	1.0015	8.9340	5.0260
			50	8.8303	0.4038	1.2567	5.0993
2	Hydrogen sulfide	Mordenite	10	315.19	20.394	112.64	−22.761
			30	4.1865	12.701	7.2×10^5	2.9900
			65	3.6330	2.5913	4.3758	2.7584
			95	4.9053	1.1117	8.2521	3.6751
3	Propane	Mordenite	10	1.8187	12.038	89.031	3.1154
			30	1.7620	2.3860	22.353	2.3929
			51	1.6438	0.9386	16.716	2.1813
4	Ethane	Molecular sieve 13-X	0	6.2264	0.2400	1.1000	−0.8100
			25	8.9376	0.0842	0.7998	−1.3943
			50	8.7047	0.0372	13.816	−0.9857
			100	20.480	0.0098	19.646	2.0395
5	Ethylene	Molecular sieve 13-X	25	4.5865	2.0350	55.108	1.7398
			50	4.5520	0.4892	11.804	1.4734
			100	6.4540	0.0831	125.03	2.2210
6	Carbon dioxide	Molecular sieve 13-X	25	7.8640	2.3810	111.89	2.5828
			50	7.5230	0.5605	992.12	2.0120
7	Isobutane	Molecular sieve 13-X	25	2.3682	76.062	31.021	2.5540
			50	2.1004	36.829	31.493	2.3400
			100	1.9958	0.5358	100.08	0.3626
8	Carbon monoxide	Molecular sieve 5-A	−128	5.0905	75.658	5.4191	0.2595
9	Carbon monoxide	Molecular sieve 10-X	−128	7.3196	72.4074	5.6256	3.2598
10	Oxygen	Molecular sieve 5-A	−128	5.7181	58.6027	0.1458	6.9745
11	Propadiene	Activated carbon	5	9.8100	3504.90	7.7090	8.3030
			15	9.8100	1436.70	7.5210	7.9390
			20	9.8100	1078.30	9.7130	7.5910
			30	9.8100	127.670	8.7800	6.0240
12	Propylene	Activated carbon	5	7.2090	167.030	9.0100	5.2810
			15	7.2090	1289.90	7.5210	7.6790
			20	7.2090	1819.70	9.7130	8.0860
			30	7.2090	1237.10	8.7800	8.2911

The fugacity coefficient ϕ_A^g can be estimated through an equation of state such as a truncated virial equation. However, at low pressures we can assume ideal gas so that $\phi_A^g = 1$. For adsorption of a pure gas ($y_A = 1$), Eq. [11] becomes

$$P = z\gamma^s f^{0s}, \qquad [12]$$

in which, for simplicity in writing, subscript A has been omitted for a pure gas. Although the gas phase is pure, the solid phase is a binary mixture of the adsorbent and the adsorbing gas. Therefore, z is the weight fraction of sorbate (adsorbing gas) in the solid phase and $(1 - z)$ is the weight fraction of the adsorbent in the solid phase.

If the solid phase is ideal, then $\gamma^s = 1$. To derive a relation for the activity coefficient of nonideal solids, we treat the solid phase exactly as we would a liquid. Assuming that the excess Gibbs energy (G^E) for a binary solid can be represented by the Redlich–Kister expansion we have

$$\frac{G^E}{RT} = z(1 - z)(A + Bz + Cz^2 + Dz^3 + \ldots), \qquad [13]$$

where A, B, $\ldots$ are temperature-dependent parameters that must be determined from experimental data. From the above relation for G^E the expression for the activity coefficient in the solid phase is

$$\ln \gamma^s = (1 - z)^2(A' + B'z + C'z^2 + D'z^3 + \ldots), \qquad [14]$$

where A', B', $\ldots$ are temperature-dependent parameters related to A, B, $\ldots$ in Eq. [13]. The relations between these parameters are given by Prausnitz *et al.* (10). If the term z^2 and higher terms in Eq. [14] are neglected then it reduces to the three-suffix Margules equation. By substituting γ^s from Eq. [14] into Eq. [12] for an isotherm we can write

$$P = zf^{0s}\exp[(1 - z)^2(A' + B'z + C'z^2 + D'z^3 + \ldots)]. \qquad [15]$$

TABLE 4
Constants in Eqs. [5] and [6] (IAS and Khan's Models) for Systems Listed in Table 1

System	Adsorbate	Adsorbent	Temperature (°C)	IAS model (Eq. [5])			Khan's model (Eq. [6])		
				q_1	b_1	σ_1	q_2	b_2	σ_2
1	Carbon dioxide	Mordenite	10	2.260	0.256	1.352	0.356	7.484	0.687
			30	2.235	0.105	1.349	0.494	1.386	0.699
			50	2.267	0.042	1.241	0.240	1.846	0.626
2	Hydrogen sulfide	Mordenite	10	2.462	1.771	1.405	1.047	10.24	0.831
			30	2.273	0.949	1.298	1.188	3.348	0.857
			65	2.340	0.215	1.459	0.947	1.350	0.821
			95	2.394	0.067	1.393	0.487	1.589	0.724
3	Propane	Mordenite	10	1.105	1.536	1.679	0.457	11.512	0.856
			30	1.195	0.336	1.702	0.618	1.744	0.887
			51	1.085	0.210	1.418	0.555	0.886	0.871
4	Ethane	Molecular sieve 13-X	0	3.083	0.081	0.001	5.533	0.042	1.360
			25	3.130	0.028	0.004	6.166	0.014	1.540
			50	3.451	0.010	0.188	7.651	0.005	1.883
			100	3.966	0.002	0.116	5.841	0.002	1.432
5	Ethylene	Molecular sieve 13-X	25	2.766	0.293	1.229	1.047	1.763	0.803
			50	2.776	0.091	1.126	1.057	0.452	0.768
			100	2.231	0.024	0.827	0.728	0.109	0.647
6	Carbon dioxide	Molecular sieve 13-X	25	3.901	0.196	1.254	1.121	1.745	0.749
			50	3.651	0.075	1.143	0.682	1.047	0.654
7	Isobutane	Molecular sieve 13-X	25	1.747	3.805	1.391	1.200	8.566	0.935
			50	1.565	2.476	1.661	1.184	3.025	0.945
			100	1.268	4.260	3.626	1.652	0.195	1.063
8	Carbon monoxide	Molecular sieve 5-A	−128	4.852	5.014	0.002	4.614	5.651	0.990
9	Carbon monoxide	Molecular sieve 10-X	−128	5.383	1.019	1.731	1.776	15.473	0.839
10	Oxygen	Molecular sieve 5-A	−128	5.491	0.124	0.834	3.717	0.241	0.903
11	Propadiene	Activated carbon	5	6.661	0.196	1.649	3.037	1.362	0.869
			15	6.164	0.242	1.694	2.534	2.423	0.863
			20	5.980	0.324	1.919	2.248	5.418	0.866
			30	5.605	0.351	2.273	1.704	3.411	0.823
12	Propylene	Activated carbon	5	5.310	0.116	1.017	3.814	0.224	0.927
			15	5.278	0.108	1.548	3.112	0.344	0.902
			20	5.154	0.112	1.553	3.432	0.218	0.919
			30	5.116	0.448	1.143	3.593	0.093	0.926

At a constant temperature (an isotherm) the fugacity at standard state f^{0s} is a constant. One common standard state is to take f^{0s} as the fugacity of a pure solid. The other option is to set $f^{0s} = 1$ kPa. However, no matter what standard state is chosen for f^{0s} for an isotherm it is a constant. Analysis of data on various systems shows that this constant can be set equal to unity. Since even when f^{0s} is not unity, the constant can be combined with the constants of the activity coefficient model A', B', ... Through extensive analysis of gas adsorption isotherms for various gases and adsorbents we found that the most general form of Eq. [15] for a pure gas adsorption isotherm is

$$P = z \exp[(1 - z)^2(a + bz + cz^n)], \qquad [16]$$

where n is an integer number greater than 1. If $n = 2$, the expression for the solid activity coefficient is similar to the four-suffix Margules equation for liquid systems. For the 12 systems studied in this work we found that the exponent n is either 2 or 5. However, for a given sorbate–adsorbent system n is the same for all different isotherms. We found that n mainly depends on the type of adsorbent rather than the sorbate. For example for various gases adsorbing on activated carbon $n = 2$ for any gas, while if adsorbent is molecular sieve $n = 5$ for any kind of sorbate gas. This is mainly because various adsorbents may follow different activity coefficient models. Knowing the value of n for an adsorbent, the proposed method (Eq. [16]) becomes a three-parameter model. Constants a, b, and c in Eq. [16] can be easily determined from the experimental data. Equation [16] can be converted into a linear form in terms of z as

$$Y = a + bz + cz^n, \qquad [17]$$

TABLE 5
Constants in Eq. [7] (Martinez Model) for Systems Listed in Table 1

System	Adsorbate gas	Adsorbent	Temperature (°C)	q_0	m	r	s	W/k
1	Carbon dioxide	Mordenite	10	5.458	134.00	1.7955	2.329	49.980
			30	4.970	134.00	1.9718	1.978	60.472
			50	5.804	657.00	1.6884	2.068	28.150
2	Hydrogen sulfide	Mordenite	10	5.350	0.1881	1.8285	1.0	1404.3
			30	5.240	3.611	2.1810	1.0	1344.9
			65	5.879	2.6810	1.6679	1.0	1950.2
			95	10.71	15.820	0.9149	1.0	7595.3
3	Propane	Mordenite	10	2.186	0.2175	4.4833	1.0	336.34
			30	1.880	0.9730	5.2128	1.0	64.114
			51	2.360	1.7368	4.1522	1.0	493.57
4	Ethane	Molecular sieve 13-X	0	2.939	12.579	1.6161	1.0	−254.38
			25	2.789	40.240	1.7031	1.0	−335.71
			50	2.823	87.020	1.6826	1.0	−291.85
			100	3.837	413.53	1.2378	1.0	−67.970
5	Ethylene	Molecular sieve 13-X	25	3.103	2.2010	1.5300	1.0	111.63
			50	2.961	7.1400	1.6000	1.0	23.060
			100	3.808	48.980	1.2500	1.0	664.96
6	Carbon dioxide	Molecular sieve 13-X	25	4.570	3.6590	1.0400	1.0	499.40
			50	4.739	8.3370	1.0000	1.0	812.20
7	Isobutane	Molecular sieve 13-X	25	2.121	0.0220	2.2395	1.0	590.63
			50	1.904	0.0270	2.4947	1.0	557.60
			100	1.520	8.4100	3.1248	1.0	−551.3
8	Carbon monoxide	Molecular sieve 5-A	−128	5.402	0.0138	3.7212	1.0	−19.67
9	Carbon monoxide	Molecular sieve 10-X	−128	8.375	0.6644	5.5809	1.0	−30.478
10	Oxygen	Molecular sieve 5-A	−128	6.629	7.150	3.0321	1.0	−79.19
11	Propadiene	Activated carbon	5	11.59	0.888	4.4335	1.0	293.91
			15	11.54	0.779	4.4556	1.0	379.83
			20	10.74	0.343	4.7858	1.0	383.64
			30	11.20	2.231	4.5886	1.0	300.79
12	Propylene	Activated carbon	5	11.66	0.560	4.4082	1.0	649.34
			15	11.31	0.850	4.5463	1.0	610.02
			20	11.21	0.723	4.5836	1.0	629.85
			30	11.67	1.737	4.4045	1.0	749.38

where $Y = (1 - z)^{-2}\ln(P/z)$. By simple linear regression of Y versus z, parameters a, b, and c for each isotherm can be determined. Although Eq. [16] is implicit in z, it can be solved by Newton's method to find z when P is known. For systems in which Eq. [16] cannot be applied we may develop a similar relation based on other activity coefficient models used for liquid systems (i.e., van Laar or Wilson models). In such cases the relation for P would be completely different from the form presented in Eq. [16].

In a limiting case where $z \rightarrow 0$, Eq. [16] reduces to

$$P = kz, \qquad [18]$$

where parameter k is a constant for each isotherm and for a given system it is only a function of temperature. Equation [18] is similar to Henry's law for the liquid systems and we found that at low adsorption ($z < 0.02$) most systems follow Eq. [18].

Usually data on the amount of gas adsorbed (q) are given in units of mol/kg, std cm^3/g, or mg/g. For such data z can be calculated from

$$z = \frac{Mq}{1000 + Mq}, \qquad [19]$$

where M is the molecular weight of sorbate and q in this relation is in mol/kg. If q is in mg/g, then M must be deleted in the above relation. If q is given in std cm^3/g and the standard conditions are 1 atm and 273 K, then q must be multiplied by 0.002067 before using Eq. [19]. Similarly when z is calculated using Eq. [16] at a given pressure, Eq. [19] can be used to estimate the amount of gas adsorbed (q) in standard units. Although z, as defined by Eq. [19], is not directly measurable, it is directly related to a measurable property of q. This does not cause any problem in the use of

TABLE 6
Evaluation and Comparison of the Proposed Thermodynamic Model with Other Models for Estimation
of the Equilibrium Pressure for Systems Listed in Table 1

System	Adsorbate gas	Adsorbent	Temperature (°C)	VST	IAS	Martinez	Khan	This work
						Average absolute deviation %		
1	Carbon dioxide	Mordenite	10	4.3	21.0	1.4	4.0	3.9
			30	5.9	25.5	2.8	7.8	5.9
			50	7.9	21.8	2.8	7.3	5.0
2	Hydrogen sulfide	Mordenite	10	2.8	6.7	2.7	2.3	2.3
			30	6.9	9.0	6.9	8.1	3.4
			65	8.5	18.8	3.9	7.8	5.7
			95	3.9	5.7	4.1	5.4	0.7
3	Propane	Mordenite	10	16.9	19.7	11.2	5.9	7.8
			30	18.4	15.9	22.6	11.3	11.0
			51	11.9	14.3	11.9	5.8	7.0
4	Ethane	Molecular sieve 13-X	0	5.1	17.4	5.5	12.2	3.8
			25	5.7	9.8	4.7	5.0	3.4
			50	5.0	6.1	2.9	3.5	1.7
			−100	5.3	15.5	1.8	2.1	1.8
5	Ethylene	Molecular sieve 13-X	25	12.7	16.1	13.8	18.7	5.5
			50	6.8	14.5	10.0	8.5	4.9
			100	4.0	10.2	3.9	3.9	2.9
6	Carbon dioxide	Molecular sieve 13-X	25	12.4	27.1	13.4	17.8	8.9
			50	5.8	29.6	6.9	13.0	4.3
7	Isobutane	Molecular sieve 13-X	25	24.8	37.0	22.8	22.9	16.5
			50	18.9	41.1	23.5	13.3	11.2
			100	17.2	19.5	16.0	16.8	7.1
8	Carbon monoxide	Molecular sieve 5-A	−128	21.8	37.4	16.7	26.6	8.8
9	Carbon monoxide	Molecular sieve 10-X	−128	8.3	27.4	13.2	25.5	4.9
10	Oxygen	Molecular sieve 5-A	−128	20.3	13.6	7.4	11.9	10.1
11	Propadiene	Activated carbon	5	9.6	20.8	9.2	5.2	6.2
			15	10.2	18.1	4.6	6.9	2.5
			20	29.4	23.3	14.2	10.2	6.6
			30	22.9	27.4	3.8	16.5	1.4
12	Propylene	Activated carbon	5	17.0	20.6	12.2	12.0	7.1
			15	20.0	22.5	13.3	9.4	10.1
			20	27.7	29.5	31.0	22.4	9.0
			30	12.4	20.7	12.0	12.0	6.0
Total			−128 to 100	11.7	19.5	9.9	10.5	5.3

Eq. [16]. At low values of q, one may find Mq is small with respect to 1000 and $z = Mq/1000$. In other words if q is in mg/g, $z = q/1000$ and we may replace z by $q/1000$ in Eq. [16].

It is interesting to note that at low values of q where $z \approx q \times 10^{-3}$, we can approximate $(1 - z)^2$ by unity and Eq. [16] will reduce to the truncated virial isotherm (11).

RESULTS AND DISCUSSION

An extensive data bank on gas adsorption data from various sources was collected. Sources for data and the types of systems studied in this work are given in Table 1. Constants a, b, and c in Eq. [16] for various systems are given in Table 2. As shown in this table for every system the value of n in Eq. [16] is the same for all isotherms. The exponent n in Eq. [16] mainly depends on the type of adsorbent, as can be seen from Table 2 for molecular sieve $n = 5$ and for activated carbon $n = 2$. For hydrogen sulfide and ethane the amount of gas adsorbed predicted from the proposed model (Eq. [16]) is compared with experimental data and is presented in Fig. 1. Weight fraction-based activity coefficients in the solid phase for hydrogen sulfide and isobutane are presented versus pressure in Fig. 2. Four other adsorption models discussed earlier were used for the purpose of evaluations and comparisons. These four models are VST (Eq. [4]), IAS (Eq. [5]), Khan *et al.* (Eq. [6]), and Martinez–Basmadjain (Eq. [7]). Constants obtained for these gas adsorption correlations for the data shown

in Table 1 are reported in Tables 3, 4, and 5, respectively. A nonlinear optimization procedure (modified Rosenbrock technique) as discussed by Rosenbrock (12) was used to obtain the constants for VST (Eq. [4]), IAS (Eq. [5]), and Martinez (Eq. [7]) correlations. The correlation parameters are very sensitive to the initial estimates. The objective function has been defined as the sum of squares of percentage errors to provide equal weightage to each point irrespective of its magnitude. Different models were evaluated based on the deviation between the predicted value of equilibrium pressure (P) and the experimental value. For each isotherm the average absolute deviation (AAD%) for the amount of gas adsorbed was estimated; the deviations are reported in Table 6. In general 12 different systems of sorbate–adsorbent with a total of 689 data points from various sources were studied. As shown in Table 6, the
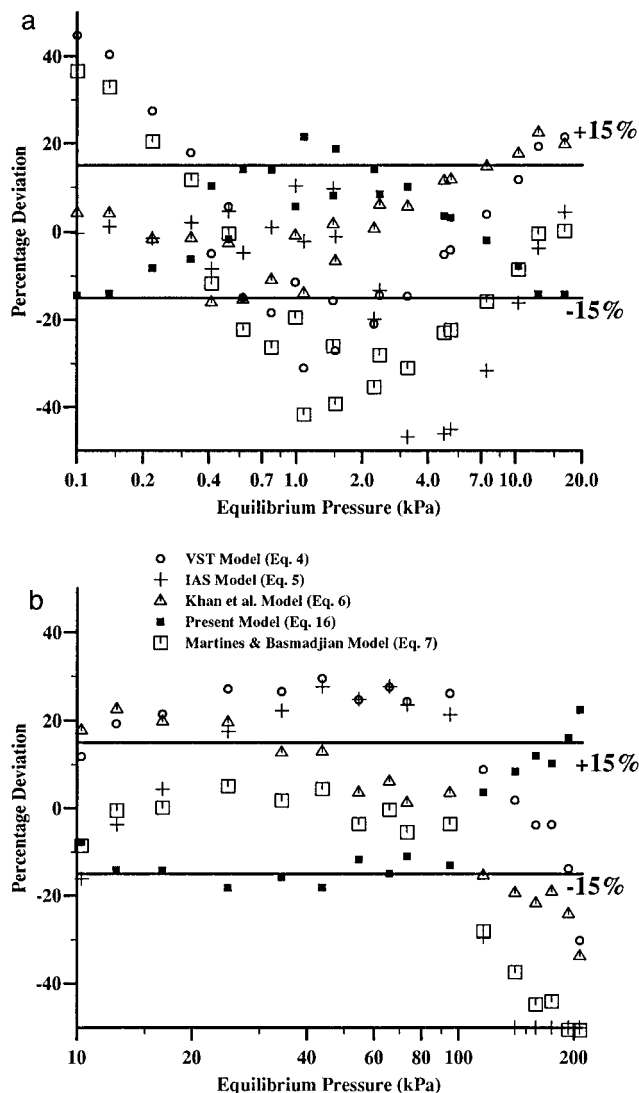
FIG. 4. Evaluation of various models for prediction of equilibrium pressure for System 3 (propane on mordenite at 30°C): (a) at low pressure, (b) at high pressure.

AAD% for the proposed model is 5.3%, for the VST model is 11.3%, for the IAS model is 19.5%, for Khan *et al.* model is 10.5%, and for the Martinez–Basmadjain model is 9.9%. If evaluations were made on estimation of amount of gas adsorbed (q) from known pressure, then similar results were observed. Comparison of various models are also presented in Figs. 3, 4, and 5 for Systems 11, 3, and 5, respectively. Figures 4 and 5 clearly show that the proposed model performs much better than other models at low or high pressures.

For System 12 the pressures exceed the ideal gas conditions where ϕ^g in Eq. [11] cannot be considered as unity. However, we found that when the gas fugacity is considered, the improvement in Eq. [16] is so minor that for simplicity we did not include gas fugacity corrections for such systems. This in fact
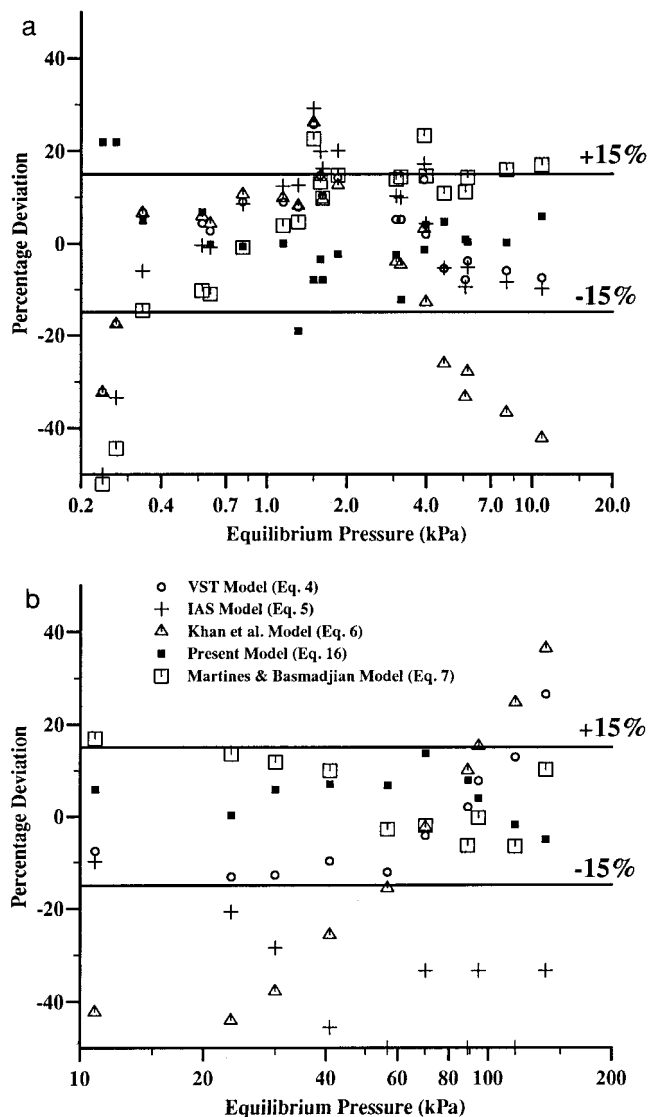
FIG. 3. Evaluation of various models for prediction of equilibrium pressure for System 11 (propadiene on activated carbon): (a) at 20°C, (b) at 30°C.

on activated carbon) at 5°C the resulting parameters are $a = 4.69789$, $b = 50867.1$, $c = -8.31 \times 10^7$, $n_1 = 5$, and $n_2 = 10$. Using these parameters, Eq. [20] can reproduce the experimental data within an average deviation of 3.5%, while using Eq. [16] with the parameters given in Table 2 produces an AAD of 7.0%. For System 12 at 15°C the parameters for Eq. [20] are $a = 4.92652$, $b = 58325.5$, $c = -1.082 \times 10^8$, $n_1 = 5$, and $n_2 = 10$. Using these parameters Eq. [20] reproduces experimental data with an AAD of 3%, while Eq. [16] gives an AAD of 10%. For Eq. [20], same as Eq. [16], the exponents n_1 and n_2 only depend on the adsorbent and they are the same for all sorbate gases and other respective isotherms. Similar improvements may be obtained for other systems. However, for all systems studied in this work Eq. [16] is quite satisfactory. The deviation is within the limits of experimental accuracy and there is no justification for applying Eq. [20] with four constants.

Results presented in this work indicate that the thermodynamically based proposed method, while it is simpler, outperforms other models for gas adsorption isotherms especially those based on modified forms of the Langmuir isotherm. Parameters a, b, and c in Eq. [16] are temperature dependent. The proposed model is based purely on the principle of phase equilibrium while the Langmuir isotherm or its modified versions are based on chemical equilibrium. Other models are just empirical modifications of the Langmuir isotherm. In fact in this model we have assumed that gas molecules are absorbed into the bulk of a porous solid phase. This is the main difference between the proposed model and other models available in the literature. A more comprehensive model would be to relate the parameters in Eq. [16] to temperature and to develop activity coefficient models for multicomponent gas mixtures.

Equation [16] shows significant improvement for prediction of gas adsorption isotherms. One major and direct application of the proposed model is to estimate equilibrium isotherms for selective adsorption of one compound in a gas mixture. Selective adsorption is important in environmental sciences and pollution control processes.

FIG. 5. Evaluation of various models for prediction of equilibrium pressure for System 5 (ethylene on molecular sieve 13-X at 25°C): (a) at low pressure, (b) at high pressure.

is due to adjustment of the parameters a, b, and c for any irregularity in Eq. [16].

The model presented here may be even further improved for some systems by choosing other forms of the activity coefficient expressed by Eq. [14]. For example, Eq. [16] can be written in a more general form as

$$P = z \exp[(1 - z)^2(a + bz^{n_1} + cz^{n_2})], \qquad [20]$$

where n_1 and n_2 are positive integers. However, for every system we analyzed, Eq. [16] was quite appropriate. But in the case where Eq. [16] fails to suit the data, Eq. [20] can be used. When Eq. [20] is applied to System 12 in Table 1 (propylene

CONCLUSIONS

In this paper, based on the principle of phase equilibria and the definition of a weight fraction-based activity coefficient model for the solid phase, a simple relation is proposed for adsorption of pure gases. The model has three parameters that can be easily determined from experimental data. The proposed model was evaluated with nearly 700 data points and compared with four other models commonly used in the literature. The proposed model gives an average error of about 5%. The VST, IAS, Khan *et al.,* and Martinez *et al.* models generate errors of about 12, 20, 10, and 11%, respectively. The model developed in this paper clearly outperforms other mod-

els and it can be used to predict adsorption isotherms for selective gas adsorption processes.

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