TABLE 1. COMPARISON OF VALUES OF THE APPARENT VON KÁRMÁN CONSTANT K CALCULATED INDEPENDENTLY FROM THE GRADIENT AND INTERCEPT OF THE GRAPHICAL DATA OF VASELESKI AND METZNER (1974)

Additive fibre	Concentration, %	Apparent von Kármán constant K K from gradient	 K from intercept
Nylon	1.00	0.35	0.35
JM* Asbestos	0.01	0.34	0.36
	0.02	0.30	0.32
	0.08	0.28	0.29
	0.25	0.25	0.26
	0.50	0.11	0.11

* Johns-Manville, Asbestos, Quebec, Canada.

similar analysis to that outlined above for high bulk velocities:

$$\phi = \left[\delta - \frac{1}{K}\left(\frac{3}{2} - \ln\frac{D}{2}\right)\right]^{-2} \tag{10}$$

The salient feature of Equation (10) is the prediction that friction factor is independent of bulk velocity provided that the small increase in K with increased bulk velocity is compensated by a corresponding, small increase in δ. A regime of turbulent fiber suspension flow characterized by a value of friction factor approximately independent of bulk velocity has been observed in this and several previous investigations (for example, Mih and Parker, 1967; Seely, 1968). Good agreement has been obtained between values of ϕ calculated from Equation (10) by using average values of K and δ obtained from velocity profile measurements and values of ϕ calculated from flow resistance data by using Equation (7) (Lee and Duffy, 1976*a*).

ACKNOWLEDGMENT

The authors wish to gratefully acknowledge the financial support of N. Z. Forest Products Ltd., Tasman Pulp and Paper Co. Ltd., Caxton Paper Mills, and the Research Committee of the N. Z. University Grants Committee.

LITERATURE CITED

Kale, D. D., and A. B. Metzner, "Turbulent Drag Reduction in Fiber-Polymer Systems: Specificity Considerations," *AIChE J.*, **20**, 1218 (1974).

Kerekes, R. J. E., "Turbulent Drag Reduction in Pipe Flow of Ideal Fibre Suspensions," Ph.D. dissertation, McGill Univ., Canada (1970).

Lee, P. F. W., and G. G. Duffy, "An Analysis of the Drag Reducing Regime of Pulp Suspension Flow," accepted by *Tappi* (1976*a*).

——————, "Velocity Profiles in the Drag Reducing Regime of Pulp Suspension Flow," submitted to *Appita* (1976*b*).

Lee, W. K., R. C. Vaseleski, and A. B. Metzner, "Turbulent Drag Reduction in Polymeric Solutions Containing Suspended Fibers," *AIChE J.*, **20**, 128 (1974).

Mih, W., and J. Parker, "Velocity Profile Measurements and a Phenomenological Description of Turbulent Fiber Suspension Flow," *Tappi*, **50**, 237 (1967).

Radkin, I., J. L. Zakin, and G. K. Patterson, "Drag Reduction in Solid-Fluid Systems," *AIChE J.*, **21**, 358 (1975).

Seely, T., "Turbulent Tube Flow of Dilute Fiber Suspensions," Ph.D. dissertation, The Institute of Paper Chemistry, Appleton, Wisc. (1968).

Vaseleski, R. C., and A. B. Metzner, "Drag Reduction in Turbulent Flow of Fiber Suspensions," *AIChE J.*, **20**, 301 (1974).

Virk, P. S., "Drag Reduction Fundamentals," *ibid.*, **21**, 625 (1975).

Manuscript received March 15, 1976; revision received April 21 and accepted April 30, 1976.

Sorption of Oxygen, Nitrogen, Carbon Monoxide, Methane, and Binary Mixtures of these Gases in 5A Molecular Sieve

Equilibrium data for the sorption of oxygen, nitrogen, carbon monoxide, and methane in 5A molecular sieve are analyzed in terms of a simple theoretical model isotherm. The model provides an excellent correlation of the single-component isotherms over the entire concentration range, and it is shown that equilibrium data for sorption of binary mixtures of these gases are correctly predicted by the model using the parameters (Henry constants and molecular volumes) derived from analysis of the single-component isotherms. The model predicts that mixtures of two sorbates with equal molecular volumes should show approximately ideal solution behavior in the adsorbed phase. The experimental data of Lederman for the sorption of nitrogen-methane mixtures show the expected behavior over a wide range of pressures.

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SCOPE

Industrial adsorption separation processes generally involve the sorption of multicomponent mixtures, and a reliable predictive method of estimating mixture equilibria from single-component isotherm data is required for the proper design and modeling of such processes. Of the available methods which have so far been suggested, the method of Myers and Prausnitz (1965), which is based on the assumption of ideal behavior in the adsorbed phase,

is probably the most successful. To complement this generalized thermodynamic approach, a statistical thermodynamic model is required. A simplified model, applicable to sorption in the A type of sieves (and other similar zeolites), has been suggested (Ruthven, 1971) and extended to multicomponent sorption equilibria (Ruthven, Loughlin, and Holborow, 1973). The chief difficulty in using this model has been the accurate estimation of one of the model parameters (the effective molecular volume of the sorbate). In the present paper, a simple method of determining the molecular volumes directly from limited pure component isotherm data is suggested. It is shown that the model provides an excellent representation of the pure component isotherms for oxygen, nitrogen, carbon monoxide, and methane over wide ranges of concentration. From the model parameters (molecular volumes and Henry constants) obtained from the pure component data, the binary equilibrium data of Danner (1966) and Lederman (1961) are correctly predicted.

CONCLUSIONS AND SIGNIFICANCE

In order to account for the equilibrium behavior of zeolitic systems, it is necessary to take account of interaction between sorbed molecules. The main effect of sorbate-sorbate interaction is a reduction in the free volume due to the finite size of the molecules. Attractive forces are relatively unimportant. A simple theoretical model in which sorbate-sorbent interaction is accounted for in terms of the Henry constant and sorbate-sorbate interaction is accounted for in terms of the effective molecular volumes of the sorbates is shown to give a satisfactory representation of both the single-component and binary mixture isotherms for sorption of oxygen, nitrogen, carbon monoxide, and methane in 5A zeolite. Henry constants and molecular volumes for these species are given for temperatures covering the range 145 to 298°K, and these parameters are sufficient to allow the computation of both single-component and mixture isotherm for any of these species over this range. Modest extrapolation outside the experimental range, on the basis of the model, is probably also justifiable. The model predicts that when the molecular volumes of the two components are similar, the adsorbed phase will show ideal behavior, as required by the generalized thermodynamic approach of Myers and Prausnitz. However, when the molecular volumes of the two components are substantially different, pronounced nonideality is to be expected. General conclusions are also drawn from the model concerning the variation of separation factors with pressure. Such considerations are an important factor in the choice of operating conditions for separation processes.

Industrial applications of molecular sieve adsorbents generally involve the sorption of multicomponent mixtures, and the problem of predicting mixture equilibria from single-component isotherm data has therefore attracted considerable attention. Three principal approaches have been followed: generalized extension of the Polanyi potential theory, the ideal adsorbed phase solution theory of Myers and Prausnitz (1965), and the use of simple models such as the extended Langmuir equations. The advantages and disadvantages of these approaches have been discussed by Bülow, Grossmann, and Schirmer (1972) and by Peinze, Bülow, and Schirmer (1974).

The general thermodynamic methods (the second and third) have the advantage of eliminating the requirement for a specific model, but this also limits the value of these approaches as a basis for extrapolation beyond the range of available experimental data. These methods also require the availability of isotherms for the pure components, at the relevant temperature, spanning the entire concentration range from zero to near saturation.

The simple Langmuir model is obviously inadequate since, for most zeolitic systems, the basic assumptions of the model (localized adsorption on a set of independent, identical sites with no interaction between adsorbed molecules) are not fulfilled, except under very restricted conditions. For those molecular sieve adsorbents (such as the type A zeolites) which consist of discrete cavities interconnected through relatively small windows, an alternative simple model isotherm (Ruthven, 1971) has been shown to provide a good correlation of single-component equilibrium data for a variety of systems over a wide range of conditions (Ruthven and Loughlin, 1972; Ruthven, Loughlin, and Derrah, 1973; Coughlin et al., 1975). The extension of this model to multicomponent systems is straightforward (Ruthven, Loughlin, and Holborow, 1973), but so far the predictions of the model for binary systems have been tested experimentally only for a few systems and then only over limited ranges of conditions.

The model involves two parameters for each component (the Henry's law constant K and the effective molecule volume β). The Henry's law constant may be determined directly from the limiting slope of the pure component isotherm in the low concentration region, and an approximate estimate of the molecular volume is provided by the van der Waals covolume. In order to apply the model at high sorbate concentrations, accurate values of the molecular volumes are required, and it is largely the difficulty of estimating the molecular volumes with sufficient accuracy which has hitherto prevented wider application of the theory.

In the present paper, a simple method of obtaining both the Henry constant and the molecular volume from a single pure component isotherm is suggested, and the model is shown to provide a satisfactory correlation of the equilibrium data for both single components and binary mixtures of oxygen, nitrogen, carbon monoxide, and methane in 5A molecular sieve over a wide range of conditions.

THE MODEL ISOTHERM

The model isotherm is based on the following simplified representation of the system:

1. It is assumed that the adsorbed molecules are confined within particular cavities of the zeolite lattice but not adsorbed at specific localized sites within a cavity. Evidence in favor of this assumption is provided by analysis of the entropies of sorption at low sorbate concentration (Ruthven, Loughlin, and Derrah, 1973).
2. When two or more molecules occupy the same cavity, the molecular interaction is represented simply as a reduction in free volume due to the finite size of the molecules. Attractive interactions between sorbate molecules and interaction between molecules in different cages are neglected.
3. The interaction between an adsorbed molecule and the sieve is characterized by the Henry's law constant (K

defined by $c = Kp$) which may be determined experimentally from the limiting slope of the single-component isotherm at low concentrations.

Subject to these assumptions, the expression for the single-component isotherm is obtained (Ruthven, 1971) as

$$c = \frac{Kp + (Kp)^2(1 - 2\beta/v)^2 + \ldots + \dfrac{(Kp)^m}{(m-1!)}(1 - m\beta/v)^m}{1 + Kp + \dfrac{1}{2!}(Kp)^2(1 - 2\beta/v)^2 + \ldots. + \dfrac{(Kp)^m}{m!}(1 - m\beta/v)^m} \tag{1}$$

where m is the saturation limit (an integer) determined by the condition $m \leqq v/\beta$. The corresponding expression for a binary mixture of A and B (Ruthven, Loughlin, and Holborow, 1973) is

$$c_A = \frac{K_A p_A + \sum_j \sum_i (K_A p_A)^i (K_B p_B)^j (1 - i\beta_A/v - j\beta_B/v)^{i+j}/(i-1)!\,j!}{1 + K_A p_A + K_B p_B + \sum_j \sum_i (K_A p_A)^i (K_B p_B)^j (1 - i\beta_A/v - i\beta_B/v)^{i+j}/i!j!} \tag{2}$$

with a corresponding expression for C_B. The summations are evaluated over all values of the indexes i and j satisfying the restrictions $i + j \geqq 2$; $i\beta_A + j\beta_B \leqq v$.

In the original development of the theory, an exponential factor was also included to take account of sorbate-sorbate intermolecular attraction, but estimates of this term, based on available force constants, show that its effect is generally small. This factor has therefore been omitted in order to simplify the form of the isotherm equations. The pure component isotherm equation [Equation (1)] gives the sorbate concentration (in molecules per cavity) as a function of Kp and the parameter v/β (the ratio of cavity volume to molecular volume of the sorbate).

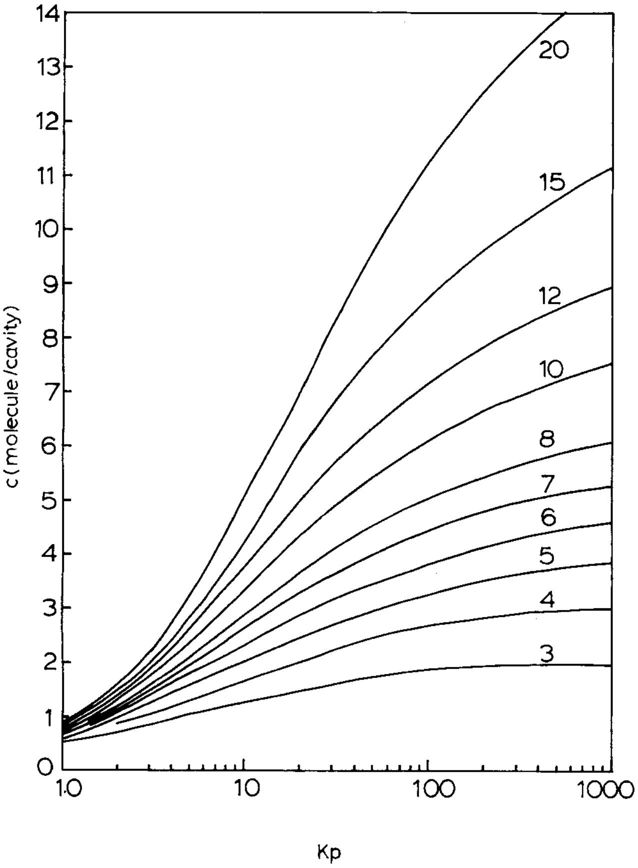

Fig. 1. Theoretical equilibrium curves calculated according to Equation (1) (parameter v/β).

A family of theoretical isotherm curves may therefore be calculated for a range of values of the parameter v/β. If this family of curves is plotted on log-linear coordinates, as in Figure 1, both the Henry constant and the appropriate value for the parameter (v/β) may be readily found by superimposing the experimental single-component isotherm, plotted on the same coordinates. This provides, in principle, a method of extracting both the Henry constant and the molecular volume from a single pure component isotherm, provided that the range of concentrations covered extends beyond the Henry's law region. However, for the systems investigated in this paper, the Henry constants may be obtained directly from the slopes of the low concentration isotherms, and the curve matching procedure is, in effect, used just to determine the molecular volume.

ANALYSIS OF SINGLE-COMPONENT ISOTHERM

Single-component isotherms for the sorption of nitrogen, oxygen, carbon monoxide, and methane are shown in Figures 2 and 3 together with the theoretical curves obtained by matching the experimental isotherms to the generalized theoretical curves of Figure 1. The origins of the experimental isotherms, which were obtained both in this laboratory and from previously published results, are indicated in Table 1 together with the Henry constants and molecular volumes obtained from the curve matching procedure. The Henry constants agree well with the values obtained

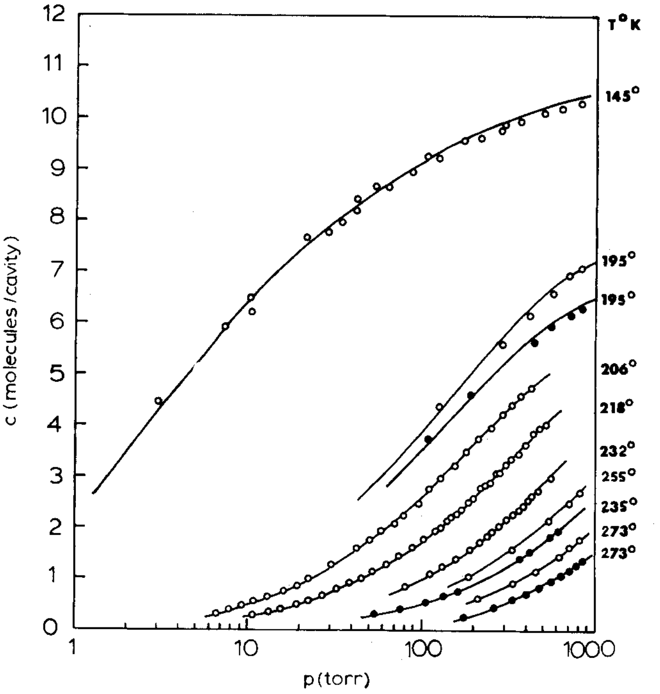

Fig. 2. Equilibrium isotherms for sorption of nitrogen in type A molecular sieves. Theoretical curves are calculated from Equation (1) with values of K and v/β listed in Table 1. Experimental points for 5A, ○; 4A, ●.

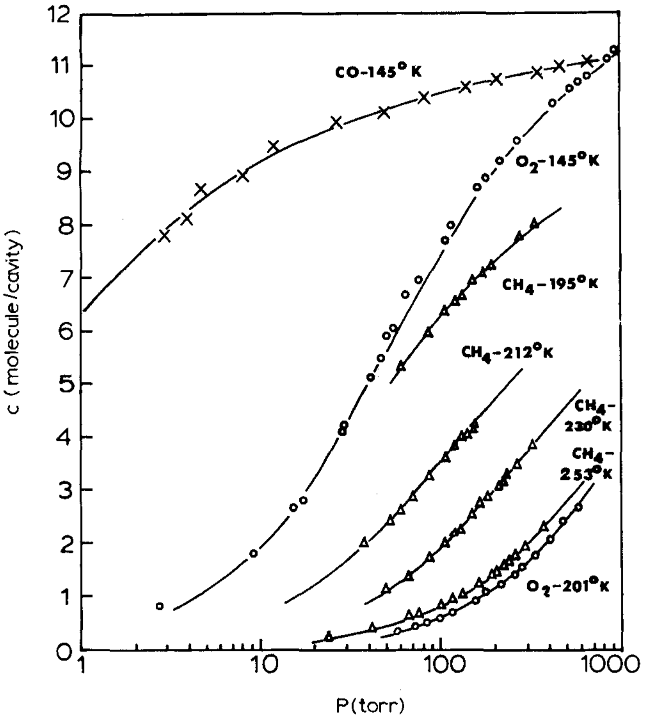

Fig. 3. Equilibrium isotherms for sorption of oxygen, carbon monoxide, and methane in 5A molecular sieve. Theoretical curves are calculated from Equation (1) with values of K and β given in Table 1. Experimental points for oxygen, ○; carbon monoxide, X; methane △.

TABLE 1. HENRY'S LAW CONSTANTS AND MOLECULAR VOLUMES CALCULATED FROM THE SINGLE-COMPONENT ISOTHERMS

System	T (°K)	K (molecule/cavity torr)	v/β	β, Å^3
N_2-5A	$T_c = 126$			$b = 65$
	145*	3.7	13.5	57.5
	195†	0.11	12	65
	205.5**	0.062	10	77
	218**	0.034	10	
	232**	0.015	10	
	252**	0.007	10	
	255†	0.008	10	
	273†	0 0037	10	
	298*	0.0016	10	
N_2-4A	195†	0.1	11	70
	235**	0.0063	10	77
	273†	0.0024	10	77
O_2-5A	$T_c = 155$			$b = 53$
	145*	0.31	17	46
	201**	0.007	17	46
	298**	0.00041	15	52
CO-5A	$T_c = 133$			$b = 66$
	145*	50	13	59
	298*	0.011	8	97
CH_4-5A	$T_c = 191$			$b = 71$
	190**	0.33	13.5	57.5
	212**	0.083	12	64.5
	230**	0.033	12	64.5
	253**	0.011	12	64.5
	273**	0.007	10	77

Volume of zeolite cavity = 776Å^3.
* Isotherm data of Danner (1966).
† Isotherm data of Springer (1964).
** Isotherm data from this laboratory.
A sorbate concentration of 1 molecule/cavity is equivalent to 0.45 mmole/g Linde pellet or 0.56 mmole/g anhydrous zeolite crystals.

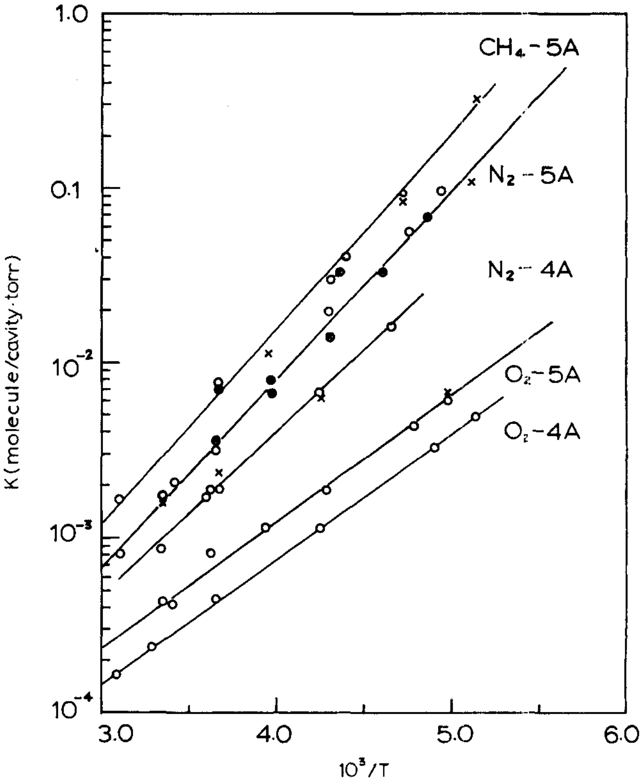

Fig. 4. vant Hoff plot showing temperature dependence of Henry's law constants for sorption 4A and 5A zeolites. [Experimental points calculated directly from slope of low concentration isotherms, ○; points derived by matching experimental isotherms to Equation (1), X].

TABLE 2. PARAMETER K_0 AND q_0 GIVING TEMPERATURE DEPENDENCE OF HENRY CONSTANTS ACCORDING TO $K = K_0 e^{q_0/RT}$

	K_0 (molecule/cavity torr)	q_0 (kcal/mole)
CH_4-5A	6.0×10^{-7}	5.1
N_2-5A	3.5×10^{-7}	5.0
N_2-4A	6.4×10^{-7}	4.35
O_2-5A	14.8×10^{-7}	3.30
O_2-4A	12.3×10^{-7}	3.20

directly from the slopes of the initial linear portions of the isotherms, as may be seen from Figure 4. The effective molecular volumes of the sorbates are of the same order as their van der Waals covolumes (see Table 1) and in most cases show the expected small increase with temperature. The molecular volume of nitrogen, however, approaches a constant value (~77Å^3) at the higher temperatures. It is evident that the model provides an excellent representation of the experimental isotherms for both 4A and 5A sieves. In particular, the shapes of the low temperature isotherms for oxygen, nitrogen, and carbon monoxide (data of Danner) are correctly predicted over a wide range of concentrations.

The vant Hoff plot showing the temperature dependence of the Henry's law constants ($K = K_0 e^{q_0/RT}$) is given in Figure 4, and the parameters K_0 and q_0 are given in Table 2. For both nitrogen and oxygen, the Henry constants for sorption in 4A sieve are slightly smaller than for 5A. The heat of adsorption of nitrogen is appreciably higher than that of oxygen, reflecting the effect of the quadrupole interaction energy (Barrer and Stuart, 1959). Heats of sorption of nitrogen and methane in the 5A sieve are essentially the same.

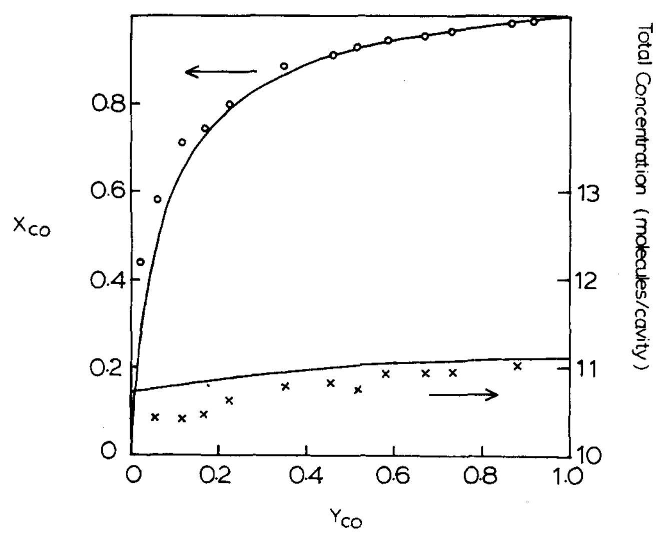

Fig. 5. Equilibrium diagram for sorption of carbon monoxide-nitrogen binary mixture on 5A sieves at 145°K, 1 atm (data of Danner ○, X). Theoretical curves are calculated from Equation (2) with $K_{CO} = 50$, $K_{N_2} = 3.7$ molecules/cavity · torr, and $\beta_{CO} = 59$, $\beta_{N_2} = 57Å^3$.

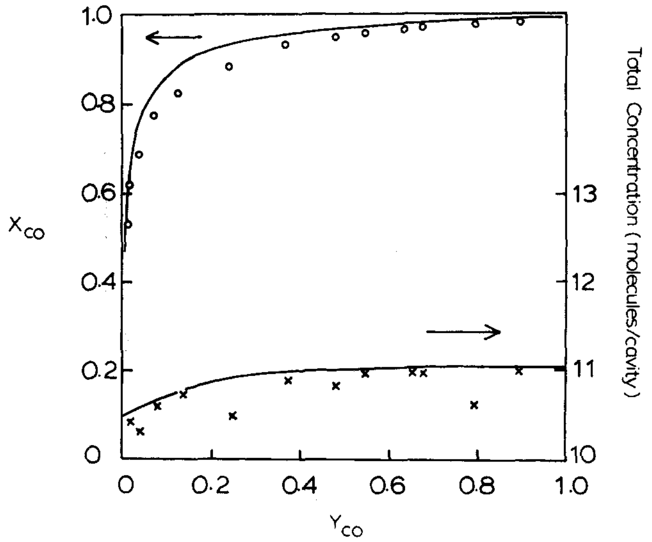

Fig. 6. Equilibrium diagram for sorption of carbon monoxide-oxygen binary mixture on 5A sieves at 145°K, 1 atm (data of Danner ○, X). Theoretical curves are calculated from Equation (2) with $K_{CO} = 50$, $K_{O_2} = 0.31$ molecule/cavity · torr and $\beta_{CO} = 59$, $\beta_{O_2} = 46Å^3$.

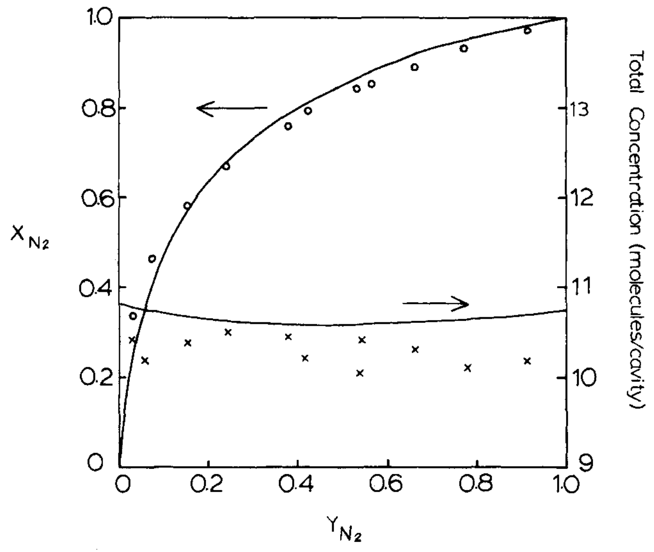

Fig. 7. Equilibrium diagram for sorption of nitrogen-oxygen binary mixture on 5A sieves at 145°K, 1 atm (data of Danner, ○, X). Theoretical curves are calculated from Equation (2) with $K_{N_2} = 3.7$, $K_{O_2} = 0.31$ molecules/cavity · torr, $\beta_{N_2} = 57$, $\beta_{O_2} = 46Å^3$).

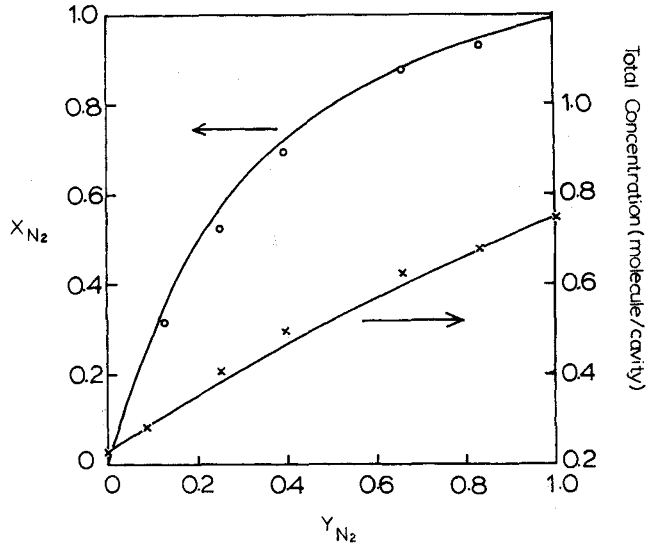

Fig. 8. Equilibrium diagram for sorption of nitrogen-oxygen binary mixture on 5A sieves at 298°K, 600 torr (data of Huang, ○, X). Theoretical curves are calculated from Equation (2) with $K_{N_2} = 0.0016$, $K_{O_2} = 0.00041$ molecule/cavity · torr, $\beta_{N_2} = 75$ Å^3, $\beta_{2O} = 52$ Å^3.

BINARY MIXTURE ISOTHERMS FOR OXYGEN-NITROGEN, CARBON MONOXIDE-NITROGEN, AND CARBON MONOXIDE-OXYGEN

Extensive binary mixture equilibrium data for the sorption of oxygen-nitrogen, carbon monoxide-nitrogen, and carbon monoxide-oxygen in 5A molecular sieves at 195°K, 1 atm total pressure, have been presented by Danner (Danner, 1966; Danner and Wenzel, 1969). Data for the oxygen-nitrogen system are also available at 298°K, 600 torr (Huang, 1970). In Figures 5 to 8 these data are compared with the theoretical curves calculated according to Equation (2) by using the values of the parameters (K and β) derived from the single-component isotherms. In all cases, both the X-Y diagram and the total quantity adsorbed are predicted approximately correctly by the theory.

SORPTION OF NITROGEN-METHANE MIXTURES AT HIGH PRESSURE

Lederman (1966) has presented experimental equilibrium data for sorption of nitrogen, methane, and the nitrogen-methane mixture in 5A sieves at 195° and 295°K over the pressure range 3 to 100 atm. These data, particularly at the lower temperature, extend well beyond the pressures at which the gas phase may be considered ideal. Fugacities were therefore calculated, with the aid of Lewis and Randall's rule, from the generalized fugacity chart. The total pressure was not maintained constant in Lederman's experiments, and this makes it difficult to plot the data in the conventional way. However, from the above analysis of the low-pressure, single-component isotherms for nitrogen and methane, it has been shown that the molecular volumes of these species are essentially the same. It follows from Equation (2) that, for such a system, the X-Y diagram should depend only on the ratio of the Henry constants for the two components and should be independent of the total pressure (Ruthven, Loughlin, and Holborow, 1973). The experimental X-Y curves, shown in Figure 9, exhibit the expected behavior. The points obtained at lower pressure (3 to 25 atm) and those obtained at higher pressures (25 to 100 atm) follow essentially the same curves. The theoretical curves cal-

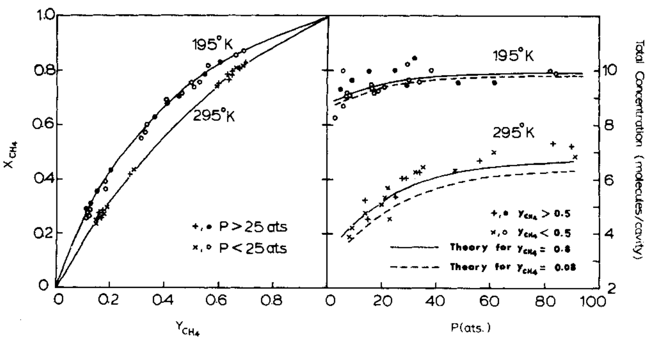

Fig. 9. Equilibrium diagram for sorption of methane-nitrogen binary mixture in 5A sieves (data of Lederman). 295°K; $P < 25$ atm, X; $P > 30$ atm, +; 195°K: $P < 25$ atm, ○; $P > 30$ atm, ●. Theoretical curves are calculated according to Equation (2) with $K_{CH_4} = 0.33$ (195°K) and 0.0027 (295°K), $K_{N_2} = 0.11$ (195°K) and 0.0017 (295°K) (molecule/cavity · torr), and $\beta CH_4 = \beta N_2 = 65$ Å^3 (195°K) and 75 Å^3 (296°K).

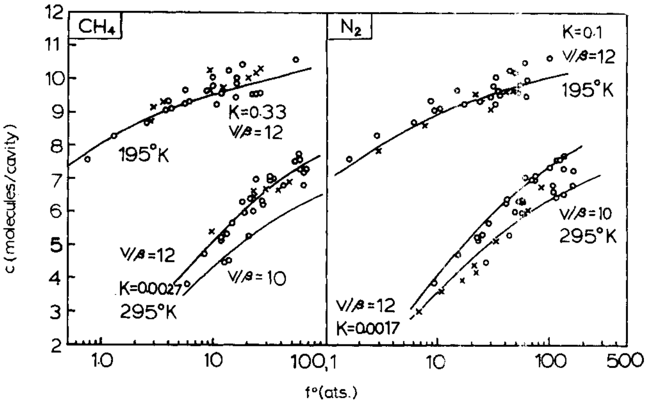

Fig. 10. Equilibrium isotherms for sorption of nitrogen and methane in 5A sieves. Points calculated from mixture isotherms, ○; points calculated from single component isotherms, X; theoretical curves are calculated from Equation (2) with the indicated values of the parameters.

culated according to Equation (2) using the values of K and β derived from the low-pressure, single-component isotherms (Table 1) correctly predict both the X-Y curves and the total concentration isotherms.

It follows also from Equations (1) and (2) that for a binary system in which the two components have equal molecular volumes, the adsorbed phase should show ideal behavior:*

$$f_A(i,j) = X_A \cdot f_A{}^\circ(i+j); \quad f_B(i,j) = X_B f_B{}^\circ(i+j) \quad (3)$$

where $f_A(i,j)$ denotes the fugacity of component A in equilibrium with an adsorbed phase containing i molecules of A and j molecules of B per cavity, and $f_A{}^\circ$ represents the fugacity in equilibrium with an adsorbed phase containing only component A at a concentration of $(i + j)$ molecules per cavity. Figure 10 shows plots of sorbate concentration vs. $f^\circ{}_{CH_4}$ and $f^\circ{}_{N_2}$, with these fugacities calculated from the mixed gas equilibrium data according to Equation (3). Also shown are the fugacities obtained directly from the high pressure isotherms for the pure components. There is considerable experimental scatter, but it is evident that the points calculated from the mixture data are in satisfactory agreement with the pure component values. At 195°K, the data agree well with the theoretical isotherm curve calculated from Equation (1) using the values of K and β given in Table 1. However, at 295°K the experimental data are better represented by the theoretical curve for a smaller molecular volume ($v/\beta \sim 12$ instead of 10). While the scatter of the data is too great to allow definite conclusions to be drawn, it is possible that this effect arises from a slight dependence of the effective molecular volume on pressure (a simple compressibility effect) which may be more pronounced at the higher temperature because of the correspondingly higher pressure range.

CONCLUSION

In spite of the severe approximations from which it is derived, the simple model provides a very satisfactory representation of both the single-component and binary mixture isotherms over a wide range of conditions. In the original development of this model, molecular volumes were estimated a priori from the van der Waals covolumes. This approximation limited the utility of the model to concentrations less than about half of saturation. However, with the more accurate values for the effective molecular volumes which can be obtained from the pure component isotherms, the model provides a satisfactory representation even up to 90% of saturation. Although the form of the isotherm equation is more complex than the simple Langmuir expression, it is still sufficiently simple to permit rapid calculation of the mixture isotherms. The model should therefore be useful in studies of the optimization and modeling of adsorption processes.

Even without detailed analysis, some simple general conclusions concerning the choice of operating conditions may be drawn. For systems in which the molecular volume of the more strongly adsorbed component (A) is smaller than that of the less strongly adsorbed species (B), the separation factor (X_AY_B/X_BY_A) will increase with increasing total pressure. Under these circumstances, a basic advantage is therefore to be gained from increasing the operating pressure of the process. Conversely, the lowest feasible pressure of operation is desirable for systems in which the more strongly adsorbed species has the larger molecular volume. In practice, this is the more common situation. When there is little difference in molecular volumes, as is the case for the nitrogen-carbon monoxide and nitrogen-methane systems, the separation factor will be essentially independent of total pressure.

For systems in which the molecular volumes of the components are similar, the theory predicts ideal adsorbed phase solution behavior as postulated by Myers and Prausnitz (1965). Such behavior is shown clearly by the methane-nitrogen system. Indeed, for all the binary mixtures examined in this study, the difference in molecular volumes between the components is quite small, and deviations from ideal behavior are therefore expected to be slight. However, the theory predicts that ideal adsorbed phase behavior will not always be observed, and that pronounced nonideality is to be expected whenever there is a large difference in the effective molecular volumes of the components.

NOTATION

b = van der Waals covolume
c = sorbate concentration expressed in molecules per cavity
f_A, f_B = fugacity of component A or B in a mixture
$f_A{}^\circ, f_B{}^\circ$ = fugacity of component A or B in a single-component system
K = Henry's law constant expressed in molecules/cavity torr

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* Myers and Prausnitz (1965) define an ideal adsorbed solution as one in which Equation (3) is satisfied with f_A, f_B, and $f^\circ{}_A$, $f^\circ{}_B$ referred to conditions of equal spreading pressure. For a system which obeys the model isotherm [Equations (1) and (2)], the spreading pressure Φ is given by $\Phi = kT\ln\xi$, where ξ is the denominator of Equation (1) or Equation (2). If $\beta_A = \beta_B$, the condition of equal spreading pressures will therefore be fulfilled when the total sorbate concentrations in the mixture and in the single-component systems are the same. A more detailed discussion is given in the appendix to the paper by Ruthven, Loughlin, and Holborow (1973).

m = integral saturation limit defined by $m \leq v/\beta$
p_A, p_B = partial pressure of component A or B
q_o = limiting heat of sorption
v = volume of cavity of 5A sieve (776Å^3)
X_A, X_B = mole fraction of A (or B) in adsorbed phase
Y_A, Y_B = mole fraction of A (or B) in vapor phase
β = effective molecular volume of sorbate (Å^3/molecule)

LITERATURE CITED

Barrer, R. M., and W. I. Stuart, "Ion Exchange and Thermodynamics of Intracrystalline Sorption," *Proc. Royal Soc.*, *A254*, 464 (1959).

Bülow, M., A. Grossmann, and W. Schirmer, "Zur Adsorption von binaren Gasgemischen au festen Oberflachen; Moglichkeiten der Bestimmung von Gleichgewichts parametern der Gemische auf der Grundlag der entsprechenden Einzelgasadsorptions gleichgewichte," *Zeits. Chemie* (*Leipzig*), **12**, 161 (1972).

Coughlan, B., and S. Kilmartin, "Sorption of CO_2 and NH_3 in Zeolites X, Y and A enriched with Trivalent Cations," *J. Chem. Soc. Faraday Trans.*, **171**, 1809 (1975).

————, J. McEntee, and R. G. Shaw, "Interpretation of Zeolitic CO_2 Equilibria using a Theoretical Iostherm Equation," *J. Colloid Sci.*, **52**, 386 (1975).

Danner, K. P., "Adsorption of Binary Gas Mixtures on Molecular Sieves," Ph.D. thesis, Lehigh Univ., Pa. (1966).

————, and L. A. Wenzel, "Adsorption of CO-N_2, CO-O_2 and O_2-N_2 Mixtures in Synthetic Zeolites," *AIChE J.*, **15**, 515 (1969).

Huang, J. T., "Adsorption of N_2 and O_2 Binary Mixture on 5A Molecular Sieve," M.Sc. thesis, Worcester Polytechnic Inst., Mass. (1970).

Lederman, P. B., "Adsorption of N_2-CH_4 on Linde Sieve 5A," Ph.D. thesis, Univ. Mich., Ann Arbor (1961).

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

Peinze, T., M. Bülow, and W. Schirmer, "Eire Methode zur Berechnüng partieller Gemischadsorptionswerte aus den Daten der Einzel componentenadsorption," *Z. Phys. Chem.* (*Leipzig*), **255**, 765 (1974).

Ruthven, D. M., "A Simple Theoretical Isotherm for Zeolites," *Nature Phys. Sci.*, **232**, No. 29, 70 (1971).

————, and K. F. Loughlin, "Sorption of Light Paraffins in Type A Zeolites," *J. Chem. Soc. Faraday Trans.*, **68**, 696 (1972).

————, and R. I. Derrah, "Sorption and Diffusion of Light Hydrocarbons and Other Simple Non-polar Molecules in Type A Zeolites," *Advan. Chem.*, **121**, 330 (1973).

Ruthven, D. M., K. F. Loughlin, and K. A. Holborow, "Multicomponent Sorption Equilibrium in Molecular Sieves," *Chem. Eng. Sci.*, **28**, 701 (1973).

Springer, C., "Adsorption of He and other Gases on Microporous Solids," Ph.D. thesis, Iowa State Univ., Ames (1964).

Manuscript received February 23, 1976; revision received and accepted May 5, 1976.

Correlation of Liquid Heat Capacities with a Four-Parameter Corresponding States Method

A four-parameter corresponding states method with the critical temperature, the critical pressure, the radius of gyration, and a fourth parameter developed from the Frost-Kalkwarf vapor pressure equation has been applied to the correlation of liquid heat capacities. An equation has been developed to predict the temperature dependence of the saturated liquid heat capacities of both normal and polar fluids over the liquid range from a reduced temperature of 0.35 to 0.96. The accuracy of the predictions obtained is superior to that of the presently available generalized correlation for polar liquids. The new correlation may be easily adopted for computer use.

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SCOPE

Liquid heat capacity is an important property in design calculations. Although experimental data are available for many compounds, frequently these data are restricted to a small temperature region, and in numerous other cases no data can be found. Therefore one must often rely on some predictive method to estimate the liquid heat capacity. Furthermore, in many computer applications generalized analytical methods of predicting physical properties are needed, since it is not practical to store specific data for all properties of all the compounds that may be of interest.

Although a number of methods have been published for the estimation of liquid heat capacities, most of them are not general enough in terms of the compounds to which they apply, or are not in an analytical form, or have a limited temperature range. In fact only one other truly generalized correlation that is applicable to polar compounds has been found. The purpose of the work described in this paper was to provide a completely generalized correlation for heat capacity covering as wide a liquid range as possible.

The most valuable generalized methods of predicting properties are based on the theorem of corresponding states. In its simplest, two-parameter form, this approach is applicable only to small, unassociated molecules. In order for polar molecules to be incorporated into this type of approach, four parameters are generally required. Passut and Danner (1974) have published a new four-parameter corresponding states method. This generalized approach has been applied to vapor pressure prediction (Passut and Danner, 1974) and to second virial coefficients (Passut, 1973). In this paper the heat capacity of polar and nonpolar liquids have been so correlated.

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