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Statistical Thermodynamic Interpretation of Sorption/Dilation Behavior of Gases in Silicone Rubber

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ABSTRACT: The lattice–fluid equation of state is used to predict sorption isotherms for nitrogen, methane, carbon dioxide, and ethylene in silicone rubber at 308 K. In addition, partial molar volumes for each of these gases in the silicone rubber are predicted as a function of pressure and concentration. Model parameters are determined from pure component *PVT* values *without* the use of any mixing data. The sorption and partial molar volume predictions are then compared with experimental data. The predictions of the lattice–fluid model are in good agreement with the experimental data.

Introduction

A number of years ago, Sanchez and Lacombe proposed a lattice–fluid (LF) equation of state in order to establish a foundation for a general theory of mixed molecular fluids of arbitrary geometry and size.[1] In subsequent work, this theory was extended to describe polymer liquids and solutions[2] and polymer–gas systems.[3,4] The LF model allows zero-parameter predictions of gas sorption and partial molar volumes which have not previously been performed. In this paper, the predictions made by the LF model are compared with experimental sorption and dilation data for four separate gases (ethylene, carbon dioxide, methane, and nitrogen) in silicone rubber over pressures ranging from 0 to 65 atm in order to determine its applicability.

Theory

The lattice–fluid equation of state has been derived in detail previously[3] and is shown below:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln (1 - \tilde{\rho}) + (1 - 1/r)\tilde{\rho}] = 0 \qquad (1)$$

where $\tilde{\rho} = \rho/\rho^*$ is the reduced density, $\tilde{P} = P/P^*$ is the reduced pressure, $\tilde{T} = T/T^*$ is the reduced temperature, and r is the number of lattice sites occupied by the r-mer. The various parameters, P^*, T^*, ρ^*, and r, may be found by using pure component *PVT* data.[5-8] For the polymer, r is essentially infinite. The other polymer parameters are found from *PVT* data or by using a combination of an isothermal compressibility, a thermal expansion coefficient, and a density at a given temperature. A more detailed description is given in the Appendix.

The values of P^* and T^* for a binary mixture may be determined from a geometric mean of the pure component parameters by

$$P^* = \phi_1 P^*_1 + \phi_2 P^*_2 - \phi_1\phi_2[P^{*\,1/2}_1 - P^{*\,1/2}_2]^2 \qquad (2)$$

$$T^* = \frac{P^*}{\phi_1 P^*_1/T^*_1 + \phi_2 P^*_2/T^*_2} \qquad (3)$$

For a binary system such as that described in this work for a polymer–gas mixture, eq 1 may be solved in terms of $\tilde{\rho}$, where the subscripts 1 and 2 indicate the gas and polymer, respectively:

$$\tilde{\rho} = 1 - \exp[-\tilde{\rho}^2/\tilde{T} - \tilde{P}/\tilde{T} - (1 - \phi_1/r_1)\tilde{\rho}] \qquad (4)$$

where ϕ_1 represents the volume fraction of gas. (The term $\phi_2/r_2 \rightarrow 0$ as $r_2 \rightarrow \infty$ and is therefore ignored in eq 4.) In order to determine the sorption level of gas in the polymer, the chemical potential of the gas in the gas phase is set equal to the chemical potential of the gas in the polymer. For the binary system, the chemical potential is given, after simplification, by

$$\mu_1/RT = \ln \phi_1 + \phi_2 + \tilde{\rho}(M_1/\rho^*_1)\chi\phi_2^{\,2} + r_1\left[-\tilde{\rho}/\tilde{T}_1 + \tilde{P}_1\tilde{v}/\tilde{T}_1 + \frac{(1 - \tilde{\rho}) \ln (1 - \tilde{\rho})}{\tilde{\rho}} + \frac{\ln \tilde{\rho}}{r_1}\right] \qquad (5)$$

where M_1 is the gas molecular weight and χ may be represented by

$$\chi = (P^{*\,1/2}_1 - P^{*\,1/2}_2)^2/RT \qquad (6)$$

The chemical potentials are then equated:

$$\mu^\circ_1(\text{gas}) = \mu_1(\text{gas absorbed in polymer}) \qquad (7)$$

$$\left[-\tilde{\rho}_1/\tilde{T}_1 + \frac{\tilde{P}_1\tilde{v}_1}{\tilde{T}_1} + (\tilde{v}_1 - 1) \ln (1 - \tilde{\rho}_1) + \frac{\ln \tilde{\rho}_1}{r_1}\right]r_1 = \left[-\tilde{\rho}/\tilde{T}_1 + \frac{(1 - \tilde{\rho}) \ln (1 - \tilde{\rho})}{\tilde{\rho}} + \frac{\ln \tilde{\rho}}{r_1}\right]r_1 + \ln \phi_1 + \phi_2 + \tilde{\rho}\frac{M_1}{\rho^*_1}\chi\phi_2^{\,2} \qquad (8)$$

where $\tilde{\rho}_1$ is given by eq 1:

$$\tilde{\rho}_1 = 1 - \exp\{-\tilde{\rho}_1^{\,2}/\tilde{T}_1 - (1 - 1/r_1)\tilde{\rho}_1 - \tilde{P}_1/\tilde{T}_1\} \qquad (9)$$

Equations 4, 8, and 9 are solved simultaneously by a double trial and error procedure to determine ϕ_1 over a range of pressures. The sorption level, or weight fraction, of gas is then determined from the relation

$$\omega_1 = \frac{\phi_1}{\phi_1 + \phi_1(\rho^*_2/\rho^*_1)} \qquad (10)$$

A more detailed description of the calculations is given in the Appendix.

In the limit of low pressure, eq 8 reduces to Henry's law:

$$C_1 = k_H^{-1}P_1$$

where C_1 is the concentration of gas absorbed by the polymer at a partial pressure of P_1 and k_H is the Henry's law constant. (In keeping with customary practice, the Henry's law constant is defined in terms of volatility, $P_1 = k_H C_1$; i.e., if the concentration of the solute is C_1, then

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the partial pressure of the solute above the mixture is P_1.) If the units of C_1 are defined as the volume of gas at standard temperature (273.15 K) and standard pressure (1 atm) absorbed per unit volume of polymer, then k_H^{-1} with units of atm^{-1} is given by

$$k_{\mathrm{H}}^{-1} = \frac{M_1}{RT}\exp\left\{r_1\left[\tilde{\rho}_2/\tilde{T}_1 - 1 - \frac{(1-\tilde{\rho}_2)\ln(1-\tilde{\rho}_2)}{\tilde{\rho}_2}\right] - \tilde{\rho}_2 v^*{}_1\chi\right\} \tag{11}$$

The partial molar volume of a gas penetrant in a polymer provides insight on the type of environment in which the gas molecule resides. This value may be calculated with the lattice–fluid theory by using

$$\bar{v}_1 = \tilde{v}v^*{}_1[1 - \phi_2\beta g_{\tilde{v}\phi_1}] \tag{12}$$

where $\bar{v}_1$ is the partial molar volume in cm^3/mol, $\tilde{v}$ is the reduced volume given by $\tilde{v} = 1/\tilde{\rho}$, $v^*{}_1$ is the hard-core volume of the penetrant given by $v^*{}_1 = M_1/\rho^*{}_1$, β is the isothermal compressibility given by

$$\beta = (1/P^*)\frac{\tilde{v}^2}{\tilde{T}\tilde{v}[1/(\tilde{v}-1) + \phi_1/r_1] - 2} \tag{13}$$

and $g_{\tilde{v}\phi_1}$ is a mixed second derivative on the free energy 3 given by

$$g_{v\phi_1} = \tilde{\rho}^2(\phi_1 - \phi_2)[P^*{}_1{}^{1/2} - P^*{}_2{}^{1/2}]^2 + P^*{}_1\{\tilde{\rho}^2 + \tilde{T}_1[\ln(1 - \tilde{\rho}) + (1 - 1/r_1)\tilde{\rho}]\} - P^*{}_2\{\tilde{\rho}^2 + \tilde{T}_2[\ln(1-\tilde{\rho}) + \tilde{\rho}]\} \tag{14}$$

A trial and error procedure is again employed to determine the values of the partial molar volume over a range of concentrations.

The basic definition of the partial molar volume is given by[9]

$$\bar{v}_i = \left(\frac{\mathrm{d}v}{\mathrm{d}n_i}\right)_{T,P,n_j} \tag{15}$$

This definition may be altered to a more useful form for a binary system as shown by[9]

$$\bar{v}_1 = v + (1 - w_1)\left(\frac{\mathrm{d}v}{\mathrm{d}w_1}\right)_{T,P} \tag{16}$$

where w_1 represents the weight fraction of gas penetrant. The total specific volume of the gas–polymer system, v, is affected by two opposing forces: the sorption-induced dilation and the hydrostatic compression of the high-pressure gas. Therefore, the derivative in eq 16 must account for both of these effects:

$$\mathrm{d}v = \left(\frac{\partial v}{\partial w_1}\right)_{T,P}\mathrm{d}w_1 + \left(\frac{\partial v}{\partial P}\right)_{T,w_1}\mathrm{d}P \tag{17}$$

Thus

$$\left(\frac{\partial v}{\partial w_1}\right)_T = \left(\frac{\partial v}{\partial w_1}\right)_{T,P} + \left(\frac{\partial v}{\partial P}\right)_{T,w_1}\left(\frac{\partial P}{\partial w_1}\right)_T = \left(\frac{\partial v}{\partial w_1}\right)_{T,P} - v\beta\left(\frac{\partial P}{\partial w_1}\right)_T \tag{18}$$

Using the isothermal compressibility defined by eq 19, the working equation to determine the partial molar volume is obtained as shown by eq 20:

$$\beta = (-1/v)\left(\frac{\partial v}{\partial P}\right)_{T,w_i} \tag{19}$$

$$\bar{v}_1 = v + (1 - w_1)\left[\left(\frac{\partial v}{\partial w_1}\right)_T + v\beta\left(\frac{\partial P}{\partial w_1}\right)_T\right] \tag{20}$$

Complementary sorption and dilation data therefore provide the partial molar volume of the penetrant over the range of pressures studied.

Experimental Section

Materials. The polymer used in this study was silicon rubber [poly(dimethylsiloxane)] supplied by General Electric Co. The sample was a 30-mil-thick cross-linked film which had been "post-cured" for 4 min at 475 K. The density of the sample was measured at 303 K using an aqueous density gradient column and was determined to be 1.1003 g/cm^3, which agrees very well with the reported value of 1.10 ± 0.03 g/cm^3. To determine the effective cross-link density of the polymer sample, Flory's equation for network systems was employed along with a χ measured by Kuwahara et al.[10] for un-cross-linked dimethylsiloxane in cyclohexane. A dry sample of silicone rubber was weighed and then placed in reagent grade liquid cyclohexane. Sufficient time was allowed for the system to reach equilibrium, and the sample was reweighed. From these measurements, the effective cross-link density was determined to be $\nu_e/V_0 = 1.24 \times 10^{-4}$ mol/cm^3. The sample was also reported to contain no filler, and birefringence measurements showed no preferred molecular orientation.

The gases used in this study, carbon dioxide, ethylene, methane, and nitrogen, were obtained from Linde, Inc., with a purities of at least 99.99%, 99.5%, 99.97%, and 99.998%, respectively. The gas was used as received.

Equipment and Procedures. Sorption measurements were performed with a pressure decay cell as has been described by numerous authors.[11,12] The silicon rubber samples were evacuated for at least 24 h before initial exposure to a penetrant, and equilibrium sorption data were then obtained in increments of approximately 7 atm. Equilibrium was defined to occur when no appreciable change in sorption occurred over a period of 8–12 h.

Dilation measurements were performed with equipment which has also been described previously.[13] Samples for dilation were again evacuated for approximately 24 h before initial gas exposure. Equilibrium dilation data were then obtained by using the same criteria for equilibrium as were used in the sorption experiments.

All measurements were performed at 308 K.

Results and Discussion

Sorption Isotherms. Theoretical predictions were performed for four gases using the parameters shown in Table I. Figures 1–4 compare the theoretical sorption predictions with the experimental data for carbon dioxide, ethylene, methane, and nitrogen, respectively, where the theoretical predictions are given by the solid lines and the experimental data are given by the individual points. The comparisons show that the predicted values lie below the experimental data. However, for ethylene, methane, and nitrogen, the predictions were still within 15% of the experimental data over the entire pressure range studied. The carbon dioxide prediction is slightly less accurate but still falls within 30% of the experimental data and continues to show the correct trends.

Additionally, the Henry's law constants for the four gases in silicone rubber were calculated with eq 11. The results are listed in Table II along with the Henry's law constant values obtained from the experimental low-pressure sorption data. All of the calculated values are slightly low but still fall within approximately 25% of the experimentally determined values, indicating a good agreement with the theory.

Partial Molar Volumes. Theoretical predictions of the penetrant partial molar volume in silicon rubber over a range of gas concentrations were also made by using the equations presented earlier. The experimental sorption

Table I
List of Gases and Silicone Rubber with Corresponding Characteristic Parameters

component	r	T^*, K	P^*, atm	ρ^*, g/cm^3
CO_2	7.6	283	6510	1.62
C_2H_4	6.19	277.5	3357	0.6682
CH_4	5.05	199.2	2493	0.4846
N_2	5.41	129	1933	0.9452
silicone rubber[a]	∞	560	3500	1.2

[a] Determined at 308 K using $\beta = 8.3 \times 10^{-5}$ atm^{-1}, $\alpha = 8.2 \times 10^{-4}$ K^{-1}, and $\rho = 1.1$ g/cm^3 (measured by Dr. D. J. Walsh, Central Research Dept., E. I. du Pont de Nemours and Co., Wilmington, DE 19800-0356).

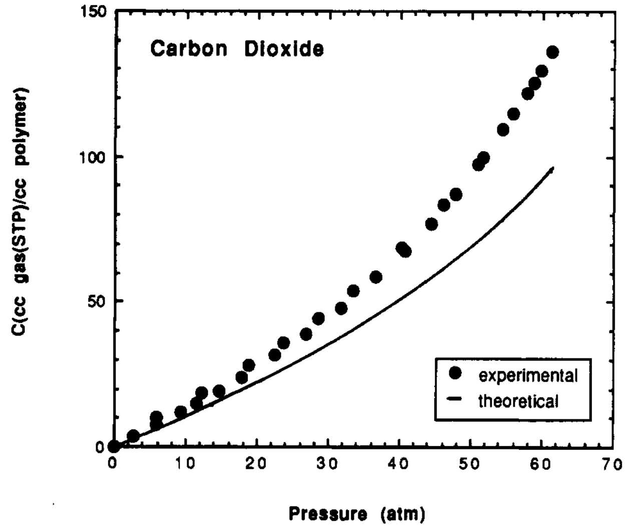

Figure 1. Comparison of theoretical predictions with experimental results for carbon dioxide sorption in silicone rubber.

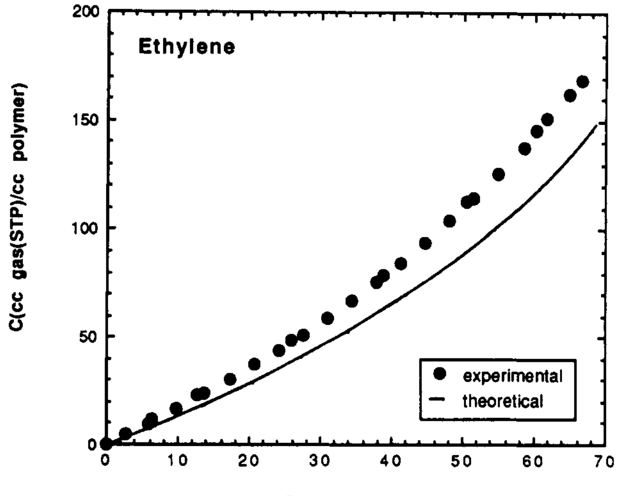

Figure 2. Comparison of theoretical predictions with experimental results for ethylene sorption in silicone rubber.

and dilation data were combined as described earlier to provide a basis for comparison with the theoretical predictions. Figures 5–8 compare the predicted partial molar volumes with the experimentally observed partial molar volumes for carbon dioxide, ethylene, methane, and nitrogen, respectively. Each of the concentration ranges corresponds to pressure ranges of approximately 0–65 atm. The range of concentration depended on the sorption levels of the penetrant in the polymer. The ethylene had the highest sorption level and was therefore compared over the largest range of concentration, whereas nitrogen, which had the lowest sorption level, was compared over the smallest concentration range.

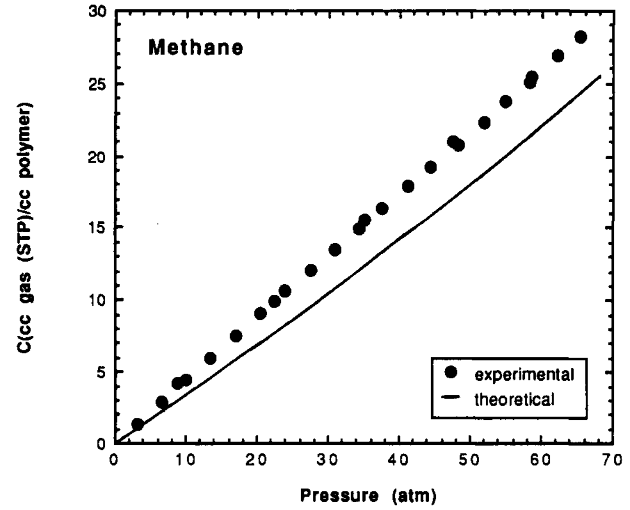

Figure 3. Comparison of theoretical predictions with experimental results for methane sorption in silicone rubber.

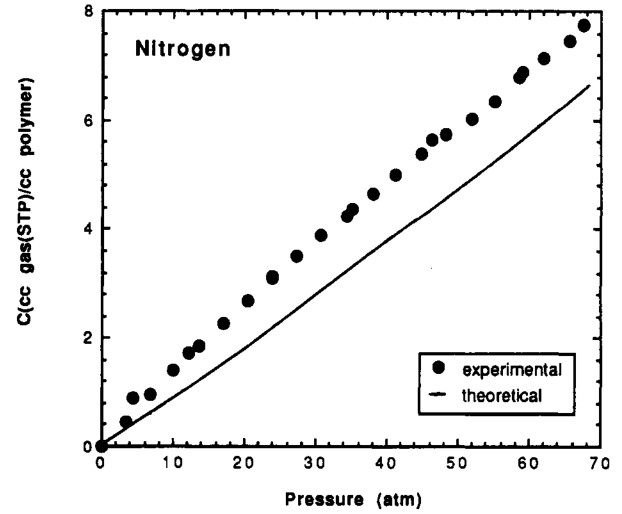

Figure 4. Comparison of theoretical predictions with experimental results for nitrogen sorption in silicone rubber.

Table II
Comparison of Calculated and Experimental Values of the Henry's Law Constants and Infinite Dilution Partial Molar Volumes

	k_H^{-1}, cm^2 (STP)/cm^3 polymer atm		$\bar{v}_1^\infty$, cm^3/mol	
	exptl (±0.01)	calcd	exptl (±0.1)	calcd
ethylene	1.66	1.26	58.3	58.9
carbon dioxide	1.28	0.98	46.1	45.9
methane	0.43	0.33	52.2	49.8
nitrogen	0.12	0.088	49.7	49.4

In Figure 5, the predicted carbon dioxide partial molar volume shown by the solid line corresponds very closely to the experimental values shown by the individual points up to a carbon dioxide weight fraction of approximately 0.12. Up to this point, the predicted curve follows the experimental trend of increasing partial molar volume with increasing concentration. However, above a weight fraction of 0.12, the experimental values begin a sharp upswing while the predicted values continue along the same path. Although the prediction is not as accurate in this case, the same trends are seen in Figure 6 for ethylene. The prediction shows a gradual increase in partial molar volume with concentration while the experimental data show a gradual increase up to a weight fraction of about 5% at which point the partial molar volume values begin to increase much more sharply.

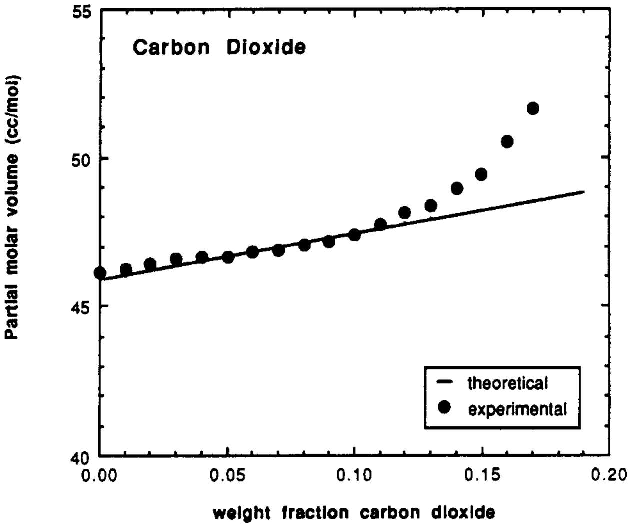

Figure 5. Comparison of theoretical predictions with experimental results for partial molar volume values of carbon dioxide in silicone rubber.

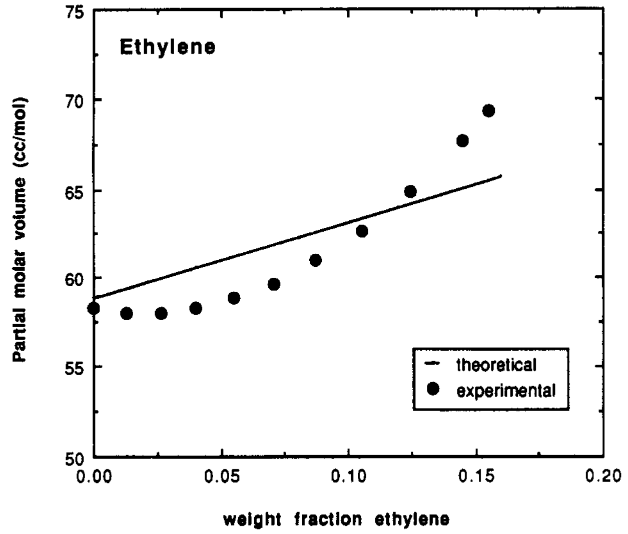

Figure 6. Comparison of theoretical predictions with experimental results for partial molar volume values of ethylene in silicone rubber.

Figures 7 and 8 compare the predicted partial molar volumes for methane and nitrogen in the silicone rubber with the experimental data. Since these are comparatively low-sorbing gases, a much smaller concentration range is studied. Again, for both gases, the trend of a gradual increase in partial molar volume with increasing concentration is seen as predicted by the lattice–fluid model. Very accurate predictions are made for both methane and nitrogen since the predictions fall within 5% and 2%, respectively, over the entire concentration range studied.

Table II also summarizes the calculated and experimental infinite dilution partial molar volumes. Excluding the calculated partial molar volume for methane, which falls within 5% of the experimental value, all of the calculated infinite dilution partial molar volumes are seen to fall within 1% of the experimental data, which again indicates a very good agreement with the theory.

Conclusions

The lattice–fluid model provides a good first-order estimate of gas sorption in silicon rubber *without* the use of any gas–polymer mixture data. Sorption values of carbon dioxide, ethylene, methane, and nitrogen were predicted to within 15% of the experimental data over pressures ranging from 0 to 65 atm.

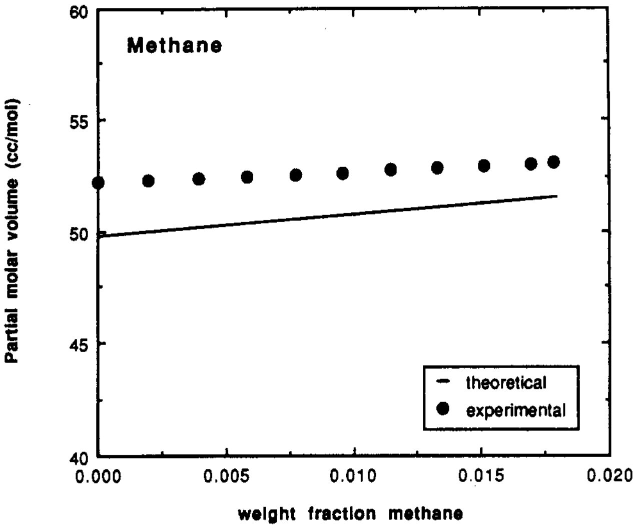

Figure 7. Comparison of theoretical predictions with experimental results for partial molar volume values of methane in silicone rubber.

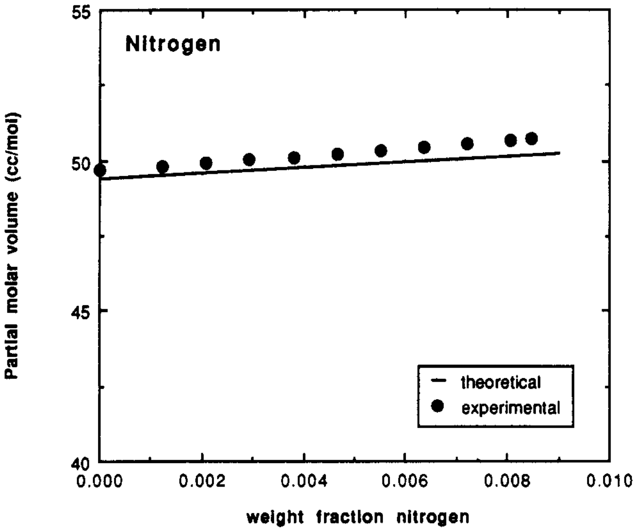

Figure 8. Comparison of theoretical predictions with experimental results for partial molar volume values of nitrogen in silicone rubber.

The lattice–fluid model also provides a very accurate infinite dilution prtial molar volume value for each of the four gases studied. In addition, for the low-sorbing gases, methane and nitrogen, the model gives a very accurate prediction over the entire concentration range. For the highly sorbing gases, CO_2 and C_2H_4, the model provides accurate predictions up to weight fractions of about 0.12 at which point the experimental data begin to deviate upward.

Overall, the lattice–fluid model has proved to be able to describe sorption and dilation in silicon rubber very well.

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Appendix

Calculation of Model Parameters. The parameters P^*, T^*, ρ^*, and r are found by using pure component PVT data. The reduced critical temperature is given by

$$\tilde{T}_c = \frac{2r}{(1 + r^{1/2})^2} \tag{21}$$

and the enthalpy of vaporization may be described by

$$\frac{\Delta H_v}{RT} - 1 = r\tilde{\rho}_{\text{liq}}\left(1 - \frac{\rho_{\text{vap}}}{\rho_{\text{liq}}}\right)/\tilde{T} \tag{22}$$

where ΔH_v is the enthalpy of vaporization of the penetrant, ρ_{liq} is the density of the penetrant in the liquid state, and ρ_{vap} is the density of the penetrant as a saturated vapor (all values are taken at the normal boiling point of the penetrant at 1 atm). Additionally, the three parameters are related through the equation

$$\frac{RT^*\rho^*}{P^*} = \frac{M}{r} \tag{23}$$

Equations 1, 21, 22, and 23 are solved simultaneously using the following procedure: (1) guess a value for the parameter r; (2) calculate $\tilde{T}_c$ using eq 21; (3) calculate $T^* = T_c/\tilde{T}_c$; (4) calculate $\tilde{\rho}_{\text{liq}}$ using eq 1; (5) calculate the right-hand side of eq 22 and compare with the right-hand side; (6) go back to step 1 until eq 22 is satisfied; (7) calculate ρ^* ($\tilde{\rho}_{\text{liq}} = \rho_{\text{liq}}/\rho^*$); (8) calculate P^* using eq 23.

Calculation of Sorption Isotherm Values. The following sequence of steps was used to calculate the penetrant sorption level in the silicone rubber at a given pressure: (1) select a pressure; (2) calculate $\tilde{P}_1$, $\tilde{P}_2$, and $\tilde{T}_1$; (3) determine $\tilde{\rho}_1$ from eq 9; (4) guess a value for ϕ_1; (5) calculate $\tilde{T}$; (6) determine $\tilde{\rho}$ from eq 4; (7) check value of ϕ_1 using eq 8; (8) return to step 4 until eq 8 is satisfied; (9) calculate ω_1 using eq 10.

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Registry No. CO_2, 124-38-9; $H_2C{=}CH_2$, 74-85-1; CH_4, 74-82-8; N_2, 7727-37-9.