Adsorption of Gas Mixtures on Molecular Sieves

ALAN L. MYERS

School of Chemical Engineering
University of Pennsylvania, Philadelphia, Pennsylvania 19104

Danner and Wenzel (1969) obtained experimental data for adsorption of three binary gas mixtures ($N_2 + O_2$, $CO + O_2$, and $CO + N_2$) on 5-A and 10-X molecular sieves. These zeolites adsorb in the following order of increasing strength of adsorption: O_2, N_2, CO. Danner and Wenzel reported that the theory of ideal adsorbed solutions (Myers and Prausnitz, 1965) explained their data for the mixture $O_2 + N_2$ but failed for mixtures containing CO. Since the theory has been tested for adsorption of polar and nonpolar gases on microporous and nonmicroporous adsorbents, there is no expectation that it should break down for mixtures containing CO. The purpose of this note is to point out a serious mistake in the calculations of Danner and Wenzel and to show that the theory of ideal adsorbed solutions predicts selectivity for adsorption on molecular sieves with an accuracy comparable to that found for other adsorbents.

Predictions of adsorption from gas mixtures by the theory of ideal adsorbed solutions are based entirely upon pure gas isotherms and their spreading pressures (Π), which are computed by the equation

$$\frac{\Pi A}{RT} = \int_0^P \frac{n}{P} dP \qquad (1)$$

$n(P)$ is the adsorption isotherm of the pure gas. Experimental points at low coverage are needed to evaluate the integral in Equation (1).

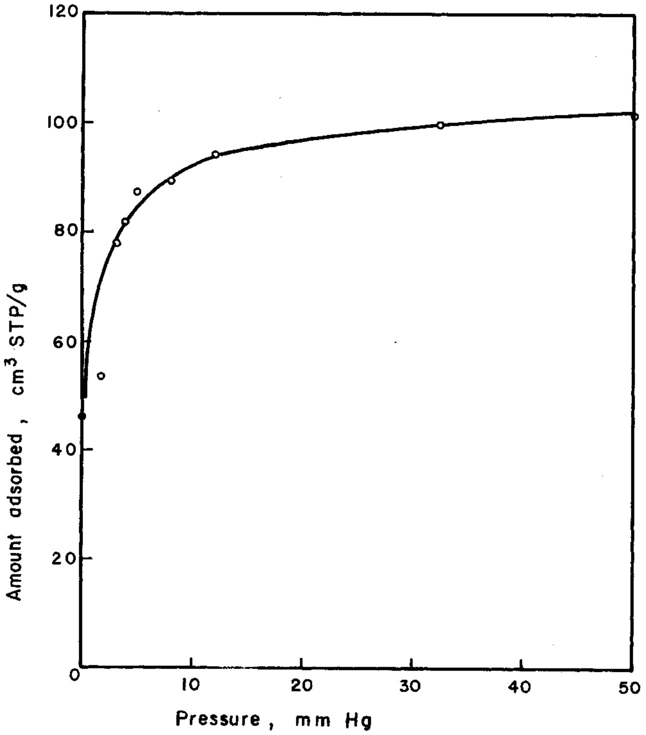

Fig. 1. Experimental data of Danner and Wenzel for adsorption of carbon monoxide on molecular sieve 5A at —200°F.

Figure 1 shows experimental data of Danner and Wenzel (1969) for adsorption of carbon monoxide on 5-A molecular sieve. The experimental point at the smallest loading of the adsorbent is about 50 cm³/g, or approximately one-half the capacity of the zeolite. The integral in Equation (1) cannot be evaluated at coverages below 50 cm³/g because there are no data, and therefore it is not possible to predict adsorption equilibria for mixtures containing carbon monoxide. The incorrect conclusions of Danner and Wenzel were based upon the unjustifiable procedure of extrapolating their isotherm for carbon monoxide to low coverage using the Langmuir equation.

There is another way to test the theory of ideal adsorbed solutions without actually measuring adsorption of carbon monoxide at low coverage. It can be shown (Van Ness, 1971) by applying the Gibbs adsorption isotherm to binary mixtures at constant pressure that

$$\frac{(\Pi_1 - \Pi_2)A}{RT} = \int_{y_1=0}^{1} \frac{n_1^e}{y_1 y_2} dy_1 \qquad (2)$$

where $n_1^e = n(x_1 - y_1)$ is the surface excess of component no. 1, n is the total amount adsorbed per unit mass of adsorbent, x_1 and y_1 are mole fractions in adsorbed and vapor phases respectively. Application of this equation to the experimental data of Danner and Wenzel for adsorption of CO (component no. 1) and N_2 (component no. 2) on 5-A molecular sieve at atmospheric pressure gives $A(\Pi_1 - \Pi_2)/RT = 324$ cm³/g. This difference supplies the missing integration constant for

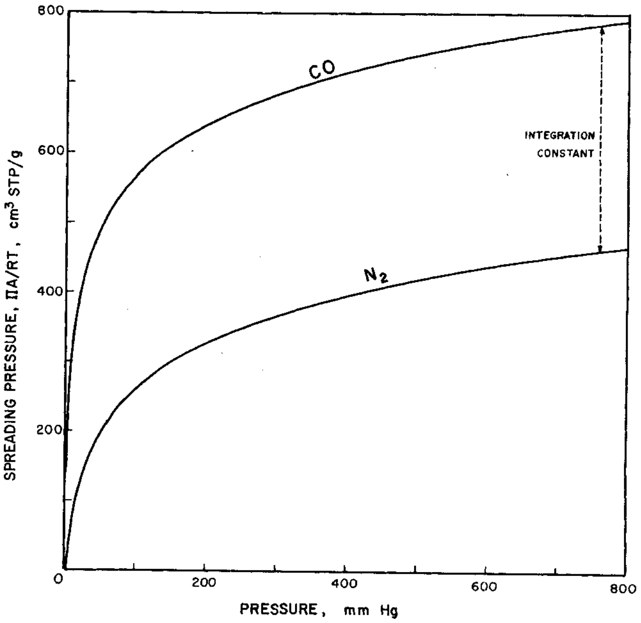

Fig. 2. Spreading pressures of carbon monoxide and nitrogen adsorbed on molecular sieve 5A at —200°F.

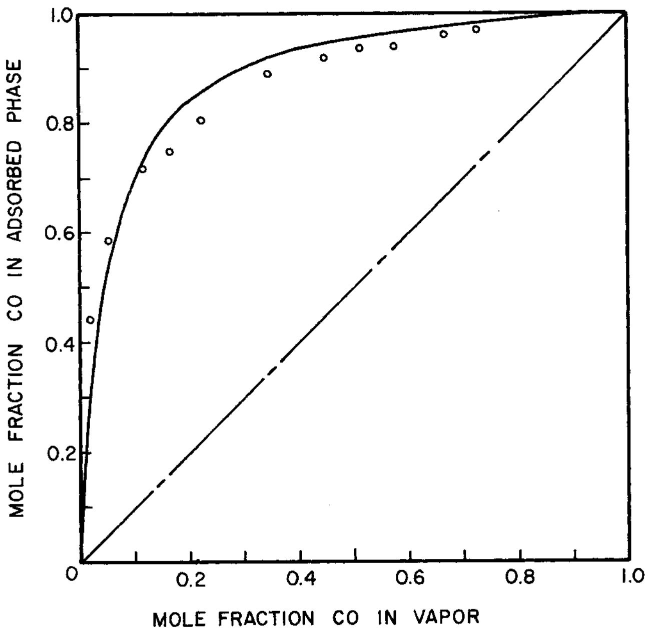

Fig. 3. Phase diagram for adsorption of carbon monoxide and nitrogen on molecular sieve 5A at —200°F. Circles: experimental data. Solid line: theory of ideal adsorbed solutions.

spreading pressure of carbon monoxide. Spreading pressures of carbon monoxide and nitrogen calculated by Equation (1) and the integration constant at one atmosphere are shown as a function of pressure on Figure 2.

Calculation of phase equilibria for adsorption at a particular pressure requires adsorption data on the more volatile adsorbate (here, nitrogen) at higher pressure. Unfortunately Danner and Wenzel failed to measure the adsorption of nitrogen at pressures greater than atmospheric. However, the selectivity may be calculated at lower pressure. On Figure 3, adsorbed and gas compositions predicted by the theory of ideal adsorbed solutions at 100 mm Hg are compared with experimental points of Danner and Wenzel at atmospheric pressure. It is known that selectivity decreases weakly with increasing pressure (Myers, 1968). The theoretical curve should shift somewhat closer to the 45° line, and therefore closer to the experimental points, at atmospheric pressure. Even if differences in pressure are ignored, these data can be explained quantitatively by activity coefficients in the adsorbed phase no larger than 1.5 at infinite dilution. We picked the CO—N_2—zeolite 5A system for discussion because the discrepancy between theory and experiment is greatest. For other mixtures (CO + O_2, N_2 + O_2) adsorbed on zeolites 5A and 10X the theory of ideal adsorbed solutions predicts the observed selectivity (x_1y_2/x_2y_1) within ± 10%.

LITERAURE CITED

Danner, R. P., and L. A. Wenzel, "Adsorption of Carbon Monoxide—Nitrogen, Carbon Monoxide—Oxygen, and Oxygen—Nitrogen Mixtures on Synthetic Zeolites," *AIChE J.*, **15**, 515 (1969).

Myers, A. L., "Adsorption of Gas Mixtures," *Ind. Eng. Chem.*, **60**, 45 (1968).

———, and J. M. Prausnitz, "Thermodynamics of Mixed-Gas Adsorption," *AIChE J.*, **11**, 121 (1965).

Van Ness, H. C., "Adsorption of Gases on Solids," in *Chemistry and Physics of Interfaces*," p. 121, Am. Chem. Soc., Washington, D.C. (1971).

Manuscript received and accepted December 13, 1972.

The Diffusivity of Carbon Dioxide in Some Organic Liquids at 25° and 50°C

W. J. McMANAMEY and J. M. WOOLLEN

Department of Chemical Engineering
University of Birmingham, Birmingham B15 2TT, England

The influence of diffusivity on the mass transfer of gases into both nonturbulent and turbulent liquids is now well established (Davies, 1972) so accurate diffusivity values are needed for the interpretation and calculation of mass transfer rates. Recently Akgerman and Gainer (1972a,b) showed that previously developed diffusivity correlations did not entirely satisfactorily predict the diffusivities of gases in liquids and proposed an improved equation based on significant liquid structure and absolute rate theory. However, only 41 of the 268 data points used to test their equation were for gases in organic liquids and the majority of these values were at temperatures between 20° and 30°C (Akgerman and Gainer, 1972a); this shows the need for diffusivity data for gases in organic liquids over a range of temperatures. As part of a study of mass transfer into turbulent liquids (Davies, 1972, Chapter 4) the diffusivity of carbon dioxide was determined in the following organic liquids at the temperatures in parentheses: toluene (25°, 50°C), decahydronaphthalene (25°, 50°C), tetradecane (25°, 50°C), 4-methyl-2-pentanone (25°, 50°C), fluorocarbon FC 75 (fully fluorinated C_8 compound) (25°C), and octyl alcohol (25°C). The diffusivity of carbon dioxide has previously been determined in water (6.5° to 75°C) (Unver

---

J. M. Woollen is with Amoco, Chicago, Illinois.