

42. Prosad, S., *Brit. J. Appl. Phys.*, **3**, 58 (1952).
43. Rao, R. J., *J. Chem. Phys.*, **9**, 682 (1941).
44. Reamer, H. H., B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **41**, 482 (1949).
45. Reid, R. C., and T. K. Sherwood, "The Properties of Gases and Liquids," p. 237, McGraw-Hill, New York (1958).
46. Sakiadis, B. C., and Jesse Coates, *A.I.Ch.E. Journal*, **3**, 123 (1957).
47. Schaefer, C. A., and George Thodos, *Ind. Eng. Chem.*, **50**, 1585 (1958).
48. ———, *A.I.Ch.E. Journal*, **5**, 367 (1959).
49. Sellschopp, Wilhelm, *Forsch. Gebiete Ingenieurw.*, **5**, 162 (1934).
50. Sengers, J. V., and A. Michels, "Progress in International Research on Thermodynamic and Transport Properties," pp. 434-440, Academic Press, New York (1962).
51. Smith, J. F. D., *Ind. Eng. Chem.*, **22**, 1246 (1930).
52. ———, *Trans. Am. Soc. Mech. Engrs.*, **58**, 719 (1936).
53. Stiel, L. I., and George Thodos, *J. Chem. Eng. Data*, **7**, 234 (1962).
54. Stolyarov, E. A., *Zhur. Fiz. Khim.*, **24**, 279 (1950).
55. ———, V. V. Ipatiev, and V. P. Teodorovich, *ibid.*, 166 (1950).
56. Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Brussels, Belgium (1950).
57. Tsederberg, N. V., and D. L. Timrot, *Zhur. Tekh. Fiz.*, **26**, 849 (1956).
58. Uhler, Arthur, Jr., *J. Chem. Phys.*, **20**, 463 (1952).
59. Vargaftik, N. B., *Tech. Phys. (U.S.S.R.)*, **4**, 341 (1937).
60. York, Robert, Jr., and E. F. White, Jr., *Trans. Am. Inst. Chem. Engrs.*, **40**, 227 (1940).
61. Ziebland, Hans, and J. T. A. Burton, *Brit. J. Appl. Phys.*, **6**, 416 (1955).
62. *Ibid.*, **9**, 52 (1958).

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# The Adsorption of Nitrogen-Methane on Molecular Sieves

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Adsorption has been an important method of commercial and laboratory separations. Increasing use of lean natural gas recovery systems and chromatography suggests that adsorption can become a major tool for separations processes rather than a method used, in general, for removal of trace impurities.

The system methane-nitrogen-helium was originally chosen for this work because of the current interest in helium conservation. Equilibrium measurements were then made with the binary system methane-nitrogen. The first experiments showed the adsorption of helium to be virtually negligible.

## ADSORPTION THEORY

The customary method of correlating adsorption equilibria involves isothermal treatment of the data. Many adsorption isotherms for single-component systems have been proposed over the years. Among the first was the Freundlich isotherm

$$N = KP^{1/n} \quad (1)$$

In recent years this form has been derived on theoretical grounds (1, 24). The Langmuir isotherm (11) in its simplest form

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$$N = \frac{aP}{1 + bP} \quad (2)$$

has been widely used to fit isothermal adsorption data and was originally derived from thermodynamic principles assuming adsorption in a single molecular layer. It has been rederived from kinetic (12) and statistical (9) considerations as well. The equation has also been derived by Schay (22) without resorting to the limitation of no molecular interaction present in the original derivations. If the adsorption is multilayer, the more general isotherm of Brunauer, Emmet and Teller (6) is a good starting point. More sophisticated approaches seem necessary when dealing with systems where Knudsen flow and internal molecular adsorption exist. In this present study the Langmuir and Freundlich isotherms fitted the data satisfactorily.

Adsorption of multicomponent mixtures has received less attention than pure-component adsorption, although industrial applications commonly deal with mixtures. Markham and Benton (15) extended Langmuir's isotherm to mixtures by deriving results in two equations which assume no interaction between the adsorbed components. Schay (23) has developed a similar equation which considers interaction of the components and gives a better prediction of adsorption from mixtures especially at higher partial pressures. In the model these interaction coefficient

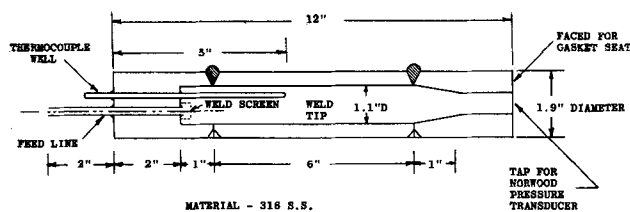


Fig. 1. Adsorption cell in cross section.

ents,  $\beta_i$ , are a complex function of the two-dimensional residual volumes of the components of the mixture, the maximum capacity of the adsorbent, and the adsorbent area. The resulting equation for multicomponent adsorption becomes

$$N_1 = \frac{A_1 P_1 / \beta_1}{1 + \sum_{j=1}^z (b_j P_j / \beta_j)} \quad (3)$$

No review, no matter how short, would be complete without mentioning the work of Polanyi (17, 18, 19, 20). The potential theory of adsorption was first advanced and developed by Polanyi and used by others such as Lewis (12, 13) and Dubinin (7, 18). The theory, based on thermodynamic principles, states that enough work must be supplied to compress the gaseous molecules into their adsorbed state such that

$$E_i = \int_{\rho_g}^{\rho_a} V dP \quad (4)$$

where  $E_i$  is the work required to compress molecules from the gas phase to adsorbate in the  $i^{\text{th}}$  layer. This work or adsorption potential varies from zero for the outer layer to some maximum at the solid-adsorbate interface. The adsorption potential  $E_i$  is a characteristic function of the amount of adsorbed material. A characteristic curve for a given adsorbate-adsorbent system may be established:

$$E = \varphi(v) \quad (5)$$

Once it has been determined for a temperature the curve will yield adsorption isotherms at any other temperature. This theory has been used to correlate adsorption data, but no critical test has been possible because the adsorbed phase density has never been evaluated or predicted successfully. In this work it has been assumed that the density of the adsorbate equals the density of liquid. The problem is acute at conditions above the critical point of the adsorbate. Dubinin has suggested several possible empirical approximations to the adsorbate density in the regions near the critical (7, 18), but none have proved satisfactory in the present work.

#### ADSORPTION APPARATUS

As with other forms of interphase equilibrium measurement, a choice exists between closed or flow apparatus. Adsorption cells used to obtain isotherms have historically been closed systems, which are ideal for pure components. In their more common forms, such as the McBain balance, they are not suited for multicomponent adsorption studies or for studies at high pressures. The large amount of gas that does not come into contact with the adsorbent in these cells precludes accurate measurement of the equilibrium adsorption compositions.

Flow systems are satisfactory for multicomponent adsorption, but do introduce some critical flow measurement and control problems. An added disadvantage is that relatively large amounts of gas are required.

For the ranges of pressure and temperature required by this study, the closed system was preferred because of lower consumption of materials, fewer operating problems and, possibly,

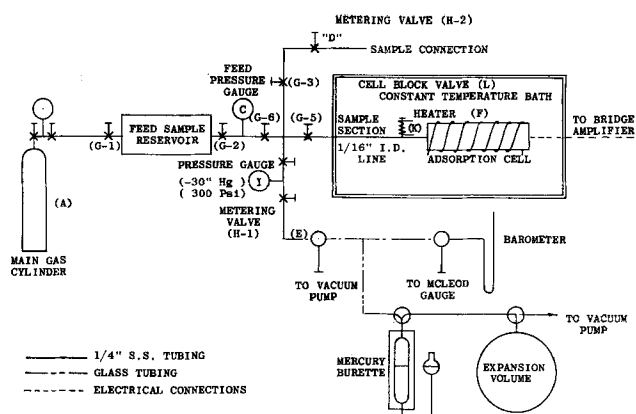


Fig. 2. Flow diagram of adsorption apparatus.

slightly greater accuracy than exist in a flow system. The resulting design is shown in Figure 1. The cell was constructed of stainless steel for low temperature service. The entire volume was filled with adsorbent, and the open end was sealed with the pressure-sensing element. The assembly was then connected to the feed system and placed in a constant temperature bath. The adsorbate volume not in contact with the adsorbent is minimized, and in this case it amounts to less than 2% of the void space in the filled cell. The entire system is shown schematically in Figure 2.

The pressure-sensing element was a strain gauge which proved to be stable and sensitive. The signal from the transducer is balanced and amplified in a bridge amplifier. The amplified signal was read out on an oscilloscope, but a recording oscilloscope may also be used.

The system was tested with a helium leak detector and found free of leaks. The pressure in the adsorption cell increased only  $10\mu$  at the  $10\mu$  level in 24 hr. Temperature during test runs was controlled by a combination of dry ice and heaters. Supplementary liquid nitrogen at lower temperatures was supplied on demand from an on-off recorder-controller. This system controlled the temperature of adsorption within  $\pm 0.5^\circ\text{C}$ . Temperatures were measured with a copper-constantan thermocouple.

#### ADSORBENT AND ADSORBATES

The adsorbent was a calcium substituted alumina silicate (5, 21). This material has a large interior cavity formed by a framework of alumina and silica tetrahedra linked at the apexes. The opening into the cavity was about  $5\text{\AA}$  in diameter. The sieve used was in the form of  $1/16$  in. pellets and contained about 80% actual crystals. The surface area was measured in this work; the area of square meters per gram agreed with the data of Breck (5, 21). In order to assure that the sieve was free of water it was activated at  $175^\circ\text{C}$ . and  $10^{-2}$  mm of mercury for 12 hr. before use and for 4 hr. at the same conditions between each equilibrium measurement.

The gases were used as received. The methane was pure grade and analyzed 98.7% methane and 1% nitrogen. The nitrogen was the prepurified grade. It analyzed 99.9+ % nitrogen with no evidence of water or oxygen by mass spectrometer.

#### EXPERIMENTAL METHOD

The experimental technique needed to obtain an adsorption equilibrium point is quite straightforward. The two gaseous components were mixed thoroughly in a calibrated reservoir. A measured amount of gas was admitted to the evacuated adsorption cell which was in a constant temperature bath. The gas was allowed to equilibrate with the adsorbent. The adsorbate-adsorbent was found to be at equilibrium within measurable precision 4 hr. after the pressure in the cell stabilized.

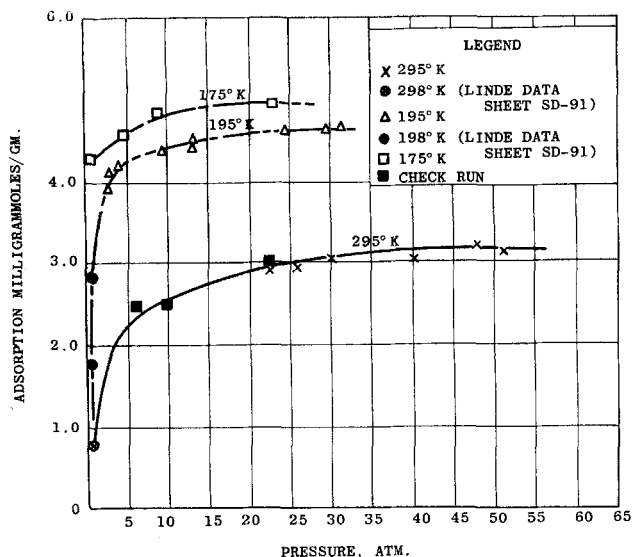


Fig. 3. Methane adsorption isotherms on molecular sieve.

The gas phase was sampled and analyzed. Replicate samples were taken on a number of runs after another 8 hr. to verify the equilibrium assumption. In all cases there was good agreement between the first and last samples. The cell was then evacuated and the off-gas recovered. The adsorbent was regenerated after each such manipulation.

The amount of gas admitted into the cell was determined from the pressure difference in the reservoir, and the quantity of each component adsorbed was obtained by the difference between the amount admitted to the cell and the amount remaining in the void space (as determined from free-space measurements using helium). Since samples taken to determine equilibrium gas phase compositions were less than 3% of the gas volume, the equilibrium was not appreciably disturbed. These samples were analyzed by mass spectrometer.

Adsorption isotherms were calculated from the experimental data for nitrogen, methane, and their mixtures as described by the material balance

$$N_j = [(V_{PI} - V_{FP}) Y_{I,j} - V_{SPFS} Y_{FS,j}] / G \quad (6)$$

where the density,  $\rho$ , is a function of temperature and pressure. The Benedict-Webb-Rubin (2, 3) equation as modified by Bloomer (4) and Ellington (8) was used to define the P-V-T relationship of the pure and mixed gases. The evaluation of the experimental data was made with the help of an IBM-704 computer. In general, a material balance was made around the process of adsorption and desorption which supported the validity of the technique.

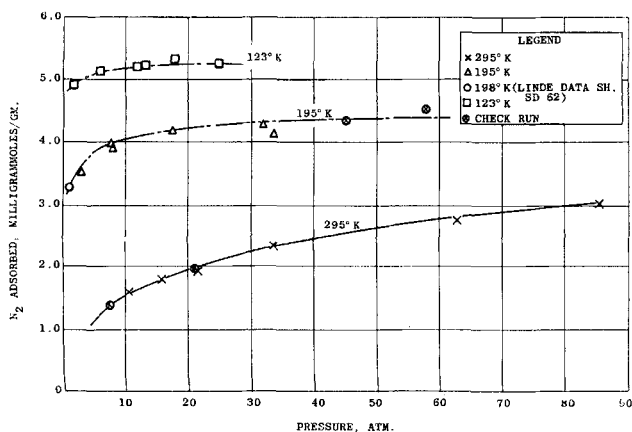


Fig. 4. Nitrogen adsorption isotherms on molecular sieve.

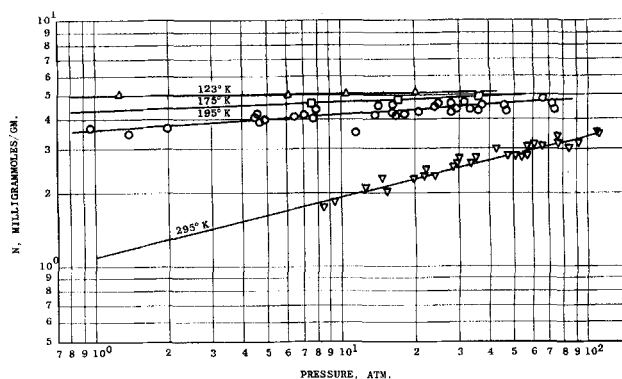


Fig. 5. Mixed-adsorption as a function of pressure and temperature

### EXPERIMENTAL RESULTS

The equilibrium loading of the molecular sieve with methane and with nitrogen<sup>\*</sup> is shown as a function of the equilibrium pressure in Figures 3 and 4.

The total amount adsorbed<sup>\*</sup> on loading for the mixed adsorbents is presented in Figure 5 which shows that the total loading is independent of composition. The results for the pure components are believed correct to  $\pm 5\%$  (at the 95% confidence level). The mixture data are good to only  $\pm 7\%$  at the same confidence level.

The data may be correlated with good accuracy using either the Freundlich equation or the Langmuir equation. The constants in these equations which were determined by the method of least squares are shown in Figures 6 and 7 as functions of temperature. As seen, the data are fitted rather well. In the logarithmic form the correlation coefficients are 0.96 and 0.99 for the Freundlich and Langmuir relationships, respectively. In all cases the 95% confidence limit is less than  $\pm 0.16$  mg. moles adsorbed per gram adsorbent.

<sup>\*</sup> Tabular material has been deposited as document 7718 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for \$1.25 for photoprints or for 35-mm. microfilm.

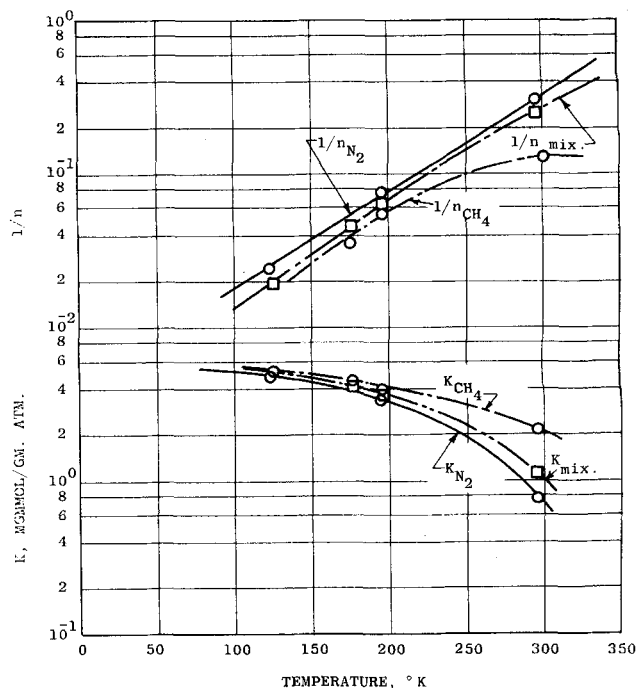


Fig. 6. Constants for the Freundlich equation for nitrogen and methane and their mixtures ( $P$  in atm.).

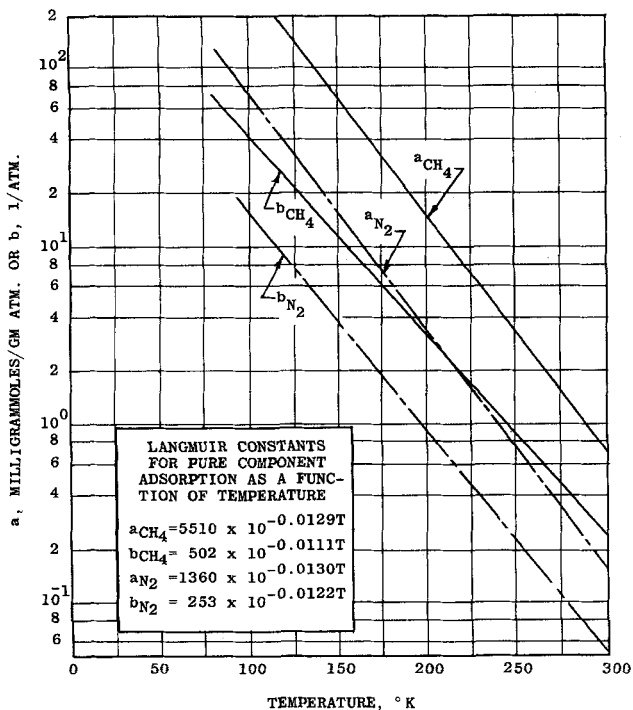


Fig. 7. Langmuir constants for pure component adsorption.

If the value of  $n$  in the Freundlich equation is near unity and if the value of  $bP$  is substantially less than unity in the Langmuir equation, the two become similar. Hence, it is not surprising that either the Freundlich or the Langmuir isotherms fit the data well with the proper choice of coefficients particularly in the middle-pressure range.

In Figures 8a and 8b the data have been correlated using the Polanyi adsorption potential as modified by Lewis. Instead of using pressures as suggested by Polanyi, the present correlating equation substitutes fugacities, thus

$$E_i = RT \rho_s \ln \frac{f}{f_s} \quad (7)$$

The density of saturated liquid at the temperature of saturation at the equilibrium pressure is used as the correlating density,  $\rho_s$ . A characteristic curve is obtained for a system such that

$$E_i = \varphi (N/\rho) \quad (8)$$

Actual liquid-density data obtained by Bloomer and co-workers (4) were used. This method of correlation seems to be quite successful above the critical temperature. For methane, the data just below the critical temperature fell on the same characteristic curve. A different correlation exists below the critical temperature of the adsorbate,

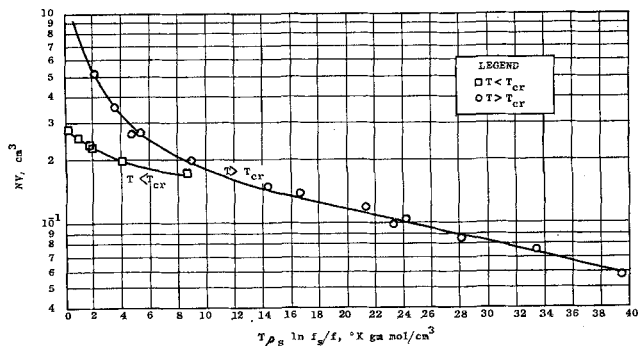


Fig. 8a. Volume of nitrogen adsorbed as a function of the adsorption driving force.

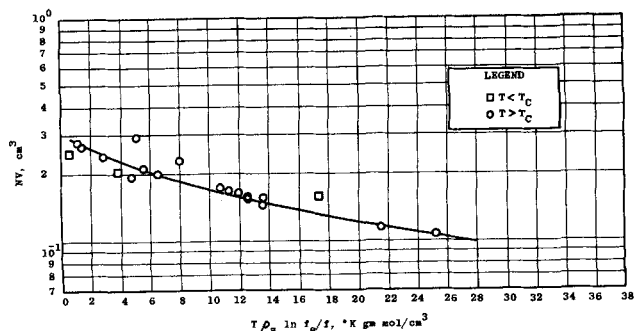


Fig. 8b. Volume of methane adsorbed as a function of the adsorption driving force.

nitrogen. This difference is probably attributable to the difficulty of estimating a density above the critical temperature to be used in the correlation. A similar correlation was attempted for the mixed nitrogen-methane adsorption. The results are shown in Figure 9. In this case the density of the adsorbate was taken as the weight average of the pure-component densities. A better understanding of the molecular packing and density of the adsorbed state would probably allow a correlation by this method.

The total adsorption or loading from a mixture of nitrogen and methane is independent of composition over the range of mixtures studied (15 to 80% methane in the gas phase). The Freundlich isotherm predicts the total mixed adsorption well. Constants for this equation are presented in Figure 6.

The adsorption of the individual components from the binary mixture may be predicted with the Langmuir isotherm as modified by Schay and simplified for binary systems

$$N_1 = \frac{a_1' P_1}{1 + b_1' P_1 + b_2'' P_2} \quad (9)$$

The constants for Equation (9) are plotted as a function of temperature in Figure 10. In the original extension of the Langmuir isotherm to binary adsorption, Markham and Benton found the coefficients,  $a'$ ,  $b'$  and  $b''$  to be equal to the respective coefficients for the pure isotherm. Schay in his extension of the theory found that the pure-component coefficients would be modified by interaction coefficients as discussed previously. The results of this study indicate that interactions do exist.

The maximum loading is equivalent to approximately 95% monolayer coverage. This might indicate that the B.-E.-T. equation is more applicable than the equations discussed above. This did not prove to be the case. It is interesting to note that the data for mixed adsorption, shown in Figure 11, show that the relative volatility is essentially constant over the range of pressure studied above the critical temperature. The data indicate that the relative

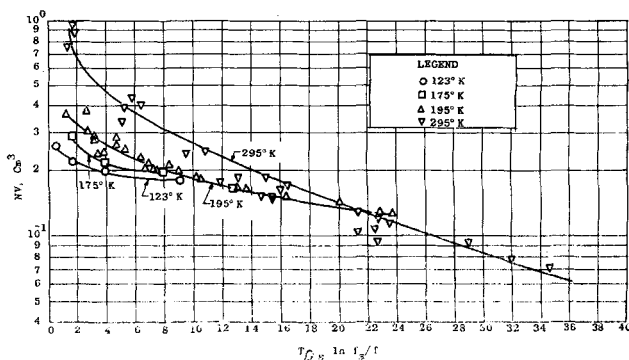


Fig. 9. Volume of nitrogen-methane mixtures adsorbed as a function of the adsorption driving force.

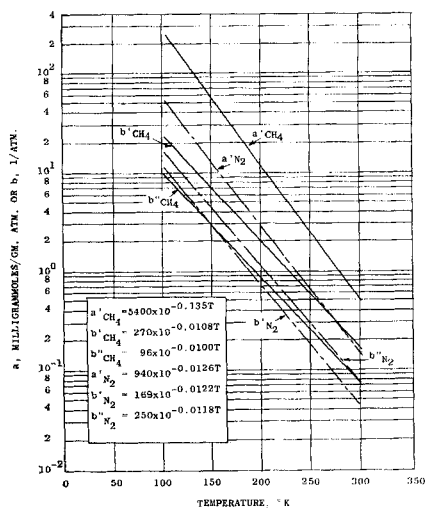


Fig. 10. Langmuir constants for adsorption from nitrogen-methane mixtures.

volatility of the gas-adsorbate state is of the same order of magnitude as the gas-liquid alpha.

### CONCLUSIONS

The equilibrium adsorption of nitrogen and methane on molecular sieves follows either the Langmuir or Freundlich isotherms. By a suitable choice of coefficients the adsorption of mixtures can be predicted by a Langmuir type of relationship. The Polanyi equation, which should be useful from a practical point of view does not give as good a correlation, probably because of the inability to predict the apparent density of the adsorbed phase especially at temperatures above the critical.

The adsorption of methane upon molecular sieves is somewhat greater than that reported for silica gel or activated carbon, while limited data from the literature indicate less adsorption on the sieves than upon carbon. In this study the maximum adsorption is equivalent to a monomolecular layer about 95% complete. The selectivity of the sieves in this study is based upon adsorption alone, since either component is small enough to pass through the pores into the interior structure.

The various models used for correlating the data cannot be critically evaluated in the pressure range considered. The potential theory is a fundamentally sound correlating technique. It should have the added advantage of showing the continuum between the adsorbed and liquid phases in equilibrium with the gas phase. The lack of data on the nature of the adsorbed state precludes drawing any conclusions at this time. A detailed study of the microscopic nature of the adsorbed phase is necessary in order that progress be made in this area. However, methods discussed here are useful in estimating mixed adsorption relationships from single-component adsorption data.

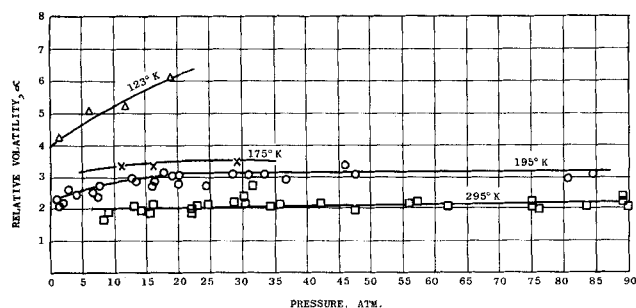


Fig. 11. Relative volatility as a function of pressure:  $[\alpha = (Y_{N_2}/X_{N_2})/(Y_{CH_4}/X_{CH_4})]$ .

### NOTATION

- $a$  = Langmuir constant, mg. moles/atm. g.
- $A$  = constant, mg. moles/g. atm.
- $b$  = Langmuir constant, 1/atm.
- $E$  = work of compression, adsorption potential; calories/g. mole
- $F$  = fugacity
- $G$  = g. of adsorbent
- $K$  = Freundlich constant, mg. moles
- $n$  = Freundlich exponential constant
- $N$  = mg. moles adsorbed/g. adsorbent
- $P$  = pressure, atm.
- $R$  = gas constant
- $T$  = temperature, °K.
- $v$  = volume adsorbate, cc.
- $V$  = volume, cc.
- $Y$  = mole function in gas phase
- $\beta$  = Schay's interaction constant, dimensionless
- $\rho$  = density, mg. moles/cc.
- $\varphi$  = function of

### Subscripts

- $a$  = adsorbed state
- $F$  = final, load cell
- $FS$  = final in system
- $g$  = gaseous state
- $i$  =  $i$ th layer
- $I$  = initial, load cell
- $j$  =  $j$ th component
- $s$  = saturated
- $VS$  = free space in system
- 1, 2 = components

### LITERATURE CITED

1. Baly, E. C. C., *Proc. Roy. Soc.*, **A160**, 465 (1937).
2. Benedict, Mason, G. B. Webb, and L. C. Rubin, *J. Chem. Phys.*, **8**, 334 (1940).
3. *Ibid.*, **10**, 747 (1942).
4. Bloomer, O. T., J. D. Parent, *Institute of Gas Technology Bull. No. 17*, (1952).
5. Breck, D. W., W. G. Eversole, R. M. Milton, T. B. Reed, and T. L. Thomas, *J. Am. Chem. Soc.*, **78**, 5963 (1956).
6. Brunauer, Stephen, P. H. Emmet, and Edward Teller, *ibid.*, **60**, 309 (1938).
7. Dubinin, M. M., *Chem. Rev.*, **60**, 235 (1960).
8. Ellington, R. T., O. T. Bloomer, B. E. Eakin, and D. C. Gami, "Thermodynamic and Transport Properties of Gases, Liquids and Solids," p. 102, *Am. Soc. Mech. Engrs.*, New York (1959).
9. Fowler, R. H., and E. A. Guggenheim, "Statistical Thermodynamics," Macmillan, New York (1939).
10. Freundlich, H., "Colloid and Capillary Chemistry," Mathuen, London, England (1926).
11. Langmuir, Irving, *Phys. Rev.*, **8**, 149 (1916).
12. ———, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
13. Lewis, W. K., E. R. Gilliland, Bernard Chertow, and W. P. Cadogan, *Ind. Eng. Chem.*, **42**, 1319 (1950).
14. *Ibid.*, 1326 (1950).
15. Markham, E. D., and A. F. Benton, *J. Am. Chem. Soc.*, **53**, 497 (1931).
16. Nikoiaev, K. M., and M. N. Dubinin, *Izv. Akad. Nauk, USSR, Otdel. Khim. Nauk*, 1165 (1958).
17. Polanyi, M., *Ber. Deut. Physik. Ges.*, **16**, 1012 (1914).
18. ———, *Ver. Deut. Physik. Ges.*, **18**, 55 (1916).
19. ———, *Z. Electrochemie*, **26**, 370 (1920).
20. ———, *Z. Physik, Chem.*, **A138**, 459 (1928).
21. Reed, T. B., and D. W. Breck, *J. Am. Chem. Soc.*, **78**, 5972 (1956).
22. Schay, G., *J. Chem. Phys.*, (Hungary), **53**, 691 (1956).
23. ———, P. Fejes, and J. Szethmary, *Acta Chim. Acad. Sci. Hung.* **12**, 299 (1957).
24. Zeldowitch, J., *Acta Physiochim. USSR*, **1**, 961 (1934).

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