The Molecular Sieve 4-A Water Vapor Sorption Therm

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Over the years there has been a continued interest in the equilibrium sorption therms of the various adsorbents. In some instances sorption has been measured in the absence of air which from a practical standpoint is an important ingredient in the application of adsorbents in packed bed operations. In the case of the molecular sieves that are of particular concern here, the literature is not so extensive, for example, see Avgul et al. (1968), Breck et al. (1956), Bykov and Chcherbatyuk (1967), Dzhigit (1964), Langmuir (1918), Mirskig (1960), Nazarov et al. (1967), and Nutter and Burnet (1963, 1966).

Recently, we developed a digital computer program to analyze the progress of sorption in packed beds (Jury, 1971). Raw data and interpolation require too much high speed storage and execution is slow. This aspect represents the weakest link in the program. The heat of sorption can cause the temperature in packed beds to rise from ambient into the 339-367°K range and the concentration of the gas stream can vary from "bone dry" to saturated.

Because foregoing specifications are too broad for the data appearing in the literature, the present research was undertaken.

In the past we have reported on silica gel (Jury and Edwards, 1971), Florite (Jury and Edwards, 1972) and Drierite (Jury et al., 1972). In this report we are concerned with the Linde molecular sieve 4A.

EQUIPMENT AND PROCEDURE

The sorption isotherms were determined using a dynamic analyze the progress of sorption in packed beds (Jury, and Edwards, 1971). The same three humid air sources were used with laminar flow gauges to produce intermediate humidities by mixing.

The particulate mesh size was 10-14 or 12-16 U.S. mesh. Attempts to regenerate the 4A at 506°K for 2 to 4 hours in an oven were not completely successful and so the dynamic method of regeneration was used. Dry air was passed through the sample at about 367°K until the effluent air indicated regeneration was complete.

THE SORPTION THERM

The isotherms of water vapor on molecular sieve 4A were determined in the presence of air at a total pressure of one atmosphere and at 303°K, 311°K, 325°K, 339°K, 353°K, and 367°K with a range of absolute humidity from 50 to 15,600 ppm. All isothermal determinations were made with the same sample, and several key points were selected to be run in both the adsorption and desorption directions. Isotherms obtained are shown in Figure 1. From Figure 1 it can be seen that the adsorption of water vapor on molecular sieve 4A is characterized by a Langmuir type isotherm. It is also completely reversible, and no hysteresis was detected.

The Hey (1935) theory of sorption applies specifically to zeolites, and one would therefore suspect its applicability to the molecular sieve structures. According to this theory the sorption therm may be expressed thus

$$W = \frac{A_1 B_1 X_h}{1 + B_1 X_h} \tag{1}$$

where

$$X_h = \frac{e^{A/T}}{\sqrt{T}}\, p \tag{2}$$

By means of a cross plotting technique the best A was found to be $A = 7371$. This value reduces the data to a single sorption therm.

ANALYTICAL FIT OF THE SORPTION THERM

A curve fitting computer program was written for the IBM 360 digital computer. The least square fit of the Hey sorption therm to our data occurred when

$$A_1 = 0.1705, \qquad B_1 = 7.716 \cdot 10^{-9}$$

A plot revealed that even this fit is rather poor.

The Linde molecular sieve sorbent 4A actually comprises clay about 20% by weight that is used to cement together crystallites of the zeolite to form a mosaic structure. It is therefore reasonable to assume that Langmuir (1918) type sorption on the surfaces of pores in the clay may also contribute to the total sorption. Thus

$$W = \frac{A_h B_h X_h}{1 + B_h X_h} + \frac{A_L B_L X_L}{1 + B_L X_L} \tag{3}$$

where the subscripts h and L refer to Hey and Langmuir and each set of symbols otherwise retains the original definitions. In fact, X_L and X_h are equal if the latent heat of sorption in the clay binder is the same as in the zeolite. Because of the difficulty in distinguishing experimentally between X_h and X_L we have assumed

$$X_h = X_L$$

so that

$$W = \frac{A_h B_h X_h}{1 + B_h X_h} + \frac{A_L B_L X_h}{1 + B_L X_h} \tag{4}$$

The constants which fit best are $A_h = 0.1579$, $B_h = 6.371 \times 10^{-9}$, $A_L = 0.0479$, $B_L = 3.095 \times 10^{-11}$, and

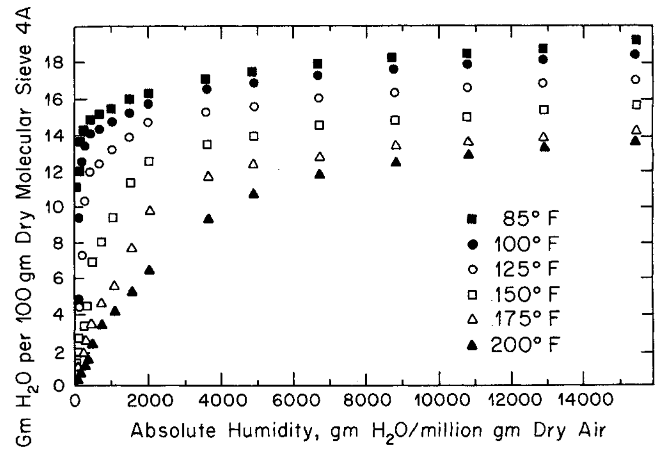

Fig. 1. Molecular sieve 4A data.

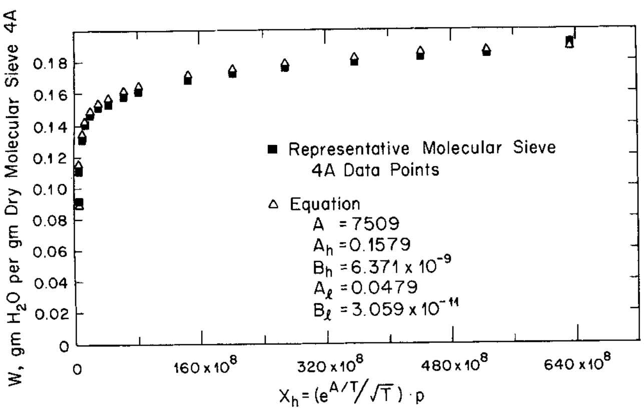

Fig. 2. Fit of molecular sieve 4A sorption therm using Equation (4).

$A = 7509.$

The values calculated from Equation (4) using these constants are compared to representative molecular sieve 4A datum points in Figures 2.

DISCUSSION

A comparison of our data with those previously described in the review of the literature shows that our data cover a broader temperature-concentration range and are therefore better suited for fitting and subsequent application. The sorption values also compare favorably with those of the manufacturer, suggesting that there is probably nothing unique about the way in which we regenerated our material.

Equation (4) describes the data quite well. The largest error of about 5% occurs in the low range of W where $W < 0.014$ and $X_h \simeq (4.2)\cdot(10^8)$. This error is not serious because this is also the range in which experimental error is greatest.

The constant A has theoretical meaning for the interpretation of the molecular sieve 4A-H_2O system. As was mentioned previously, A is equal to the ratio of the heat of adsorption to gas constant R. From this product of A and R (7509×1.987), the heat of adsorption for the system concerned was determined to be 14,920 cal/g-mole of water which gives good agreement with the value, 15,000 cal/g-mole of water found in literature (Avgul et al., 1968; Dzhigit et al., 1964).

The quantities

$$A_h = 0.1579, \qquad A_L = 0.0479$$

also have theoretical significance in that they are the sorption asymptotes as $X_h \rightarrow \infty$. This is about what one should expect because p is so large and T is so small.

The real differences in sorption efficiency of the zeolitic material and the clay are noted when one compares two other quantities that also have theoretical significance, that is,

$$A_hB_h = (1.006)\cdot(10^{-9}), \qquad A_LB_L = (1.483)\cdot(10^{-12})$$

These are the initial slopes of the two terms on the right-hand side of the sorption therm, Equation (4). On an equal weight basis A_hB_h should be about four times larger which means that the sorption efficiency (initial slopes) is about 2,700 times greater for the zeolitic crystallites than for the clay binder.

Finally, it should be remembered that the form of Equation (4) is not really new. It was suggested by Rabinowitch and Wood (1936). Based on a search of the literature it seems that no one has previously followed through with the suggestion.

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NOTATION

A_1, B_1, A_h, B_h, A_L, B_L = constants (The B_iX_j and W/A_i are dimensionless)
A = E/R, K
E = latent heat of sorption, cal/g-mole
p = partial pressure, mm Hg
R = gas constant, cal/g-mole K
T = absolute temperature, K
W = amount sorbed, g/g of dry sorbent
X_h = $\dfrac{e^{A/T}}{\sqrt{T}}p$
X_L = same form as X_h but A can have a different value

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