Krypton Adsorption on Microporous Carbons and 5A Zeolite

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The sorption of Kr on three carbon molecular sieves, two activated carbons, and 5A Linde zeolite sieve has been studied at 77°, 195°, 273°, and 298°K. Except at 77°K, the carbon molecular sieve, exhibiting 5A molecular sieve properties, adsorbed more Kr than any other sample, at low relative vapor pressures at which the gas is released from nuclear reactors. With the exception of the zeolite sieve, sorption results for all samples could be satisfactorily represented by the Dubinin theory for adsorption in microporous solids. Heats of adsorption and structural parameters of the microporous adsorbents have been reported.

I. INTRODUCTION

Krypton is produced as a radioactive gaseous fission product in high-temperature gas-cooled nuclear reactors. Because of its obvious hazards, it cannot be released directly into the atmosphere. Various methods have been suggested to hold-up fission gases, such as complete containment in gas-storage tanks (1), absorption in kerosene-base solvents (2), and selective solvent absorption (3). Activated carbon is extensively used for removing Kr from various carrier gases associated with many nuclear operations (4) and has been shown to be more effective than such adsorbents as silica gel and alumina (5) and Linde 4A and 5A zeolite sieves (6). Recently, a variety of molecular sieve carbons have been produced in this laboratory (7–9). It is of interest to compare the adsorption of Kr on some of these selected materials with adsorption on commercially available active carbons and zeolites. Thus, adsorption of Kr has been studied on two activated carbons; three varieties of molecular sieve carbons exhibiting 4A, 5A, and 6A molecular sieve properties; and 5A Linde zeolite sieve at 195°, 273°, and 298°K.

II. EXPERIMENTAL

A. MATERIALS

1. Activated Carbons

Barneby-Cheney Co. low-activated and medium-activated coconut shell charcoals, having butane areas (273°K) of 1030 and 1420 m²/gm and neopentane areas (273°K) of 930 and 1430 m²/gm, were used.

2. Molecular Sieve Carbons

Results for three molecular sieve carbons have been reported in the paper. The first one was prepared from furfuryl alcohol polymerized with phosphoric acid (7). The polymer was carbonized in a stream of O_2-free N_2 at 700°C using a heating rate of 7.5°C/min and a soak time of 4 hr. The sieving properties of the sample compared favorably with that of the Linde 4A sieve (7). This carbon has been referred to as 4A-CMS (carbon molecular sieve) in the text.

The second carbon sieve was prepared from Saran 489 and a lignite pitch (8). The details of the process and of subsequent activation in CO_2 to open up the lignite binder carbon, which blocked accessibility to the Saran carbon filler, have been described elsewhere (9). This carbon has been shown to exhibit 5A molecular sieve properties; that is, it is effective in the separation of straight from branched chain hydrocarbons (8). It has, therefore, been designated as 5A-CMS in the present studies.

The third sample was prepared from PVDC in the manner described elsewhere (9). It has previously been shown to exhibit sieving for CO_2, *n*-butane, isobutane,

and neopentane (10). It has been termed 6A-CMS in the text.

3. Gas

Research grade Kr from the Matheson Co. was used. The gas had an as-received purity of >99.9% and was used as such without any further purification. It was dried by successive passage through columns of 13X Linde zeolite, Anhydron, and P_2O_5. The saturation vapor pressure of Kr at 195°K was taken as 35.93 atm (11).

B. SORPTION STUDIES

Sorption was followed gravimetrically using a Cahn RG Electrobalance. A sample weight of about 0.15–0.40 gm, depending on the adsorption temperature, was held in an aluminum foil bucket, which in turn was suspended from the balance arm by a platinum wire. Before adsorption runs, samples were outgassed to 10^{-6} torr at 450°C, except in the case of the zeolite sieve, where evacuation above 400°C is not recommended (12). The pressure range studied was ca. 2 millitorr to 500 torr. The extent of adsorption was measured after 30 min. Equilibrium was reached in all cases except for the 4A-CMS, as will be discussed. At 195°K, a thermal transpiration correction was applied for the thermomolecular flow between the adsorption tube and the remainder of the apparatus with the use of Liang's equation (13).

III. THEORY

The Polanyi potential theory describes the temperature invariance of the characteristic curve of adsorption $A = f(av^*)$ for a given adsorbate-adsorbent system and can be expressed (14) as

$$\left(\frac{\partial A}{\partial T}\right)_{av^*} = 0, \qquad [1]$$

where

A = differential molar work of adsorption;
a = amount adsorbed; and
v^* = molar volume of the adsorbed substance.

Using the above postulate, Dubinin et al. (15, 16) and Radushkevich (17) have proposed the following equation to describe the

adsorption on microporous carbons:

$$W = W_0 \,[-\exp\,(\kappa A^2)]. \qquad [2]$$

Here

W = filled volume of the adsorption space.
W_0 = limiting volume of the adsorption space. It is a constant for a given microporous carbon provided the adsorbate size is not too close to the micropore size.
κ = a constant which indirectly characterizes the dimensions of the micropores most widely represented in the carbon.

Below the critical temperature, W equals av^* and A equals $RT \ln (p_s/p)$, where p is the equilibrium pressure and p_s is the saturation vapor pressure at adsorption temperature T. Nikolaev and Dubinin (18) have proposed that in not too wide a range above the critical temperature $W = ab$, where b = the constant of the van der Waals equation and $A = RT \ln [(p_{cr}/p)\tau^2]$, where p_{cr} = critical pressure and $\tau = T/T_{cr}$ = reduced temperature.

Dubinin (19) has expressed Eq. [2] in the following two forms to describe adsorption behavior below and above the critical temperature, respectively:

$$W = W_0 - \frac{0.434B}{\beta^2}\left(T \log \frac{p_s}{p}\right)^2; \qquad [3]$$

and

$$W = W_0 - \frac{0.434B}{\beta^2}\left(T \log \left(\frac{p_{cr}}{p}\,\tau^2\right)\right)^2. \qquad [4]$$

Here

B = a temperature-independent constant which is directly related to the constant κ of Eq. [2];
β = affinity coefficient of the characteristic curve for the given adsorbate relative to a standard adsorbate (benzene or N_2).

IV. RESULTS AND DISCUSSION

A. ISOTHERMS

Sorption isotherms of Kr on different samples at 298°K are shown in Fig. 1. It is seen that the extent of adsorption follows the order: 5A-CMS > low-activated char-
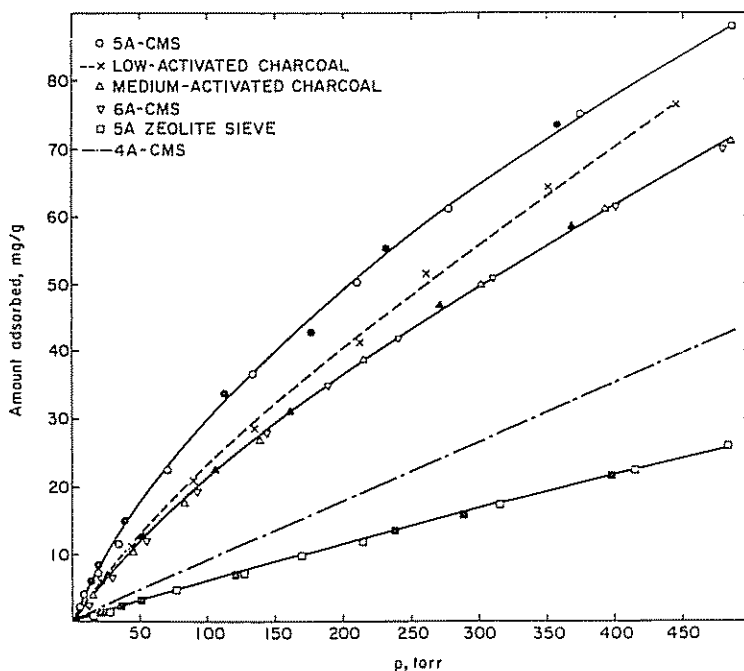
FIG. 1. Sorption isotherms of Kr on different materials at 298°K. Solid points are desorption data.
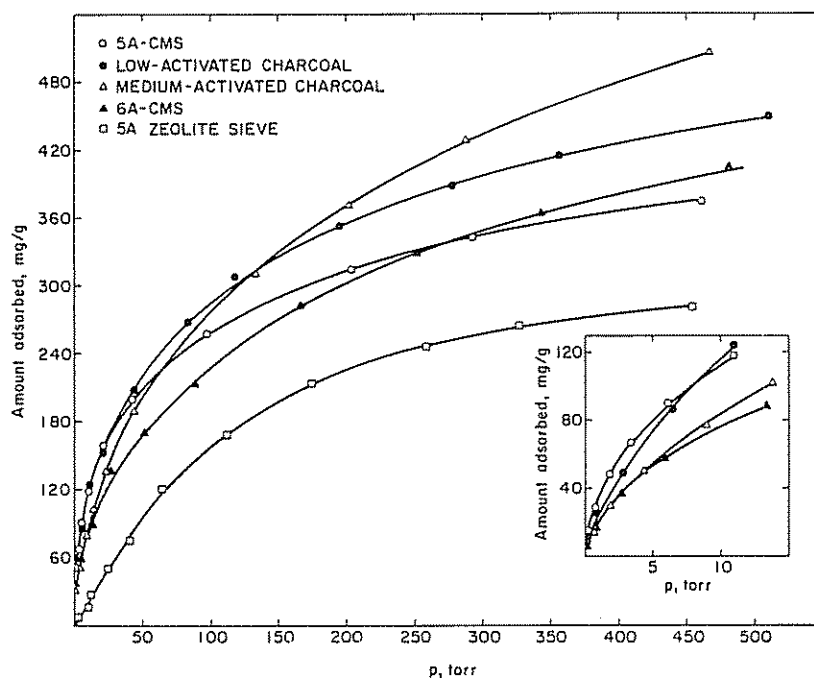
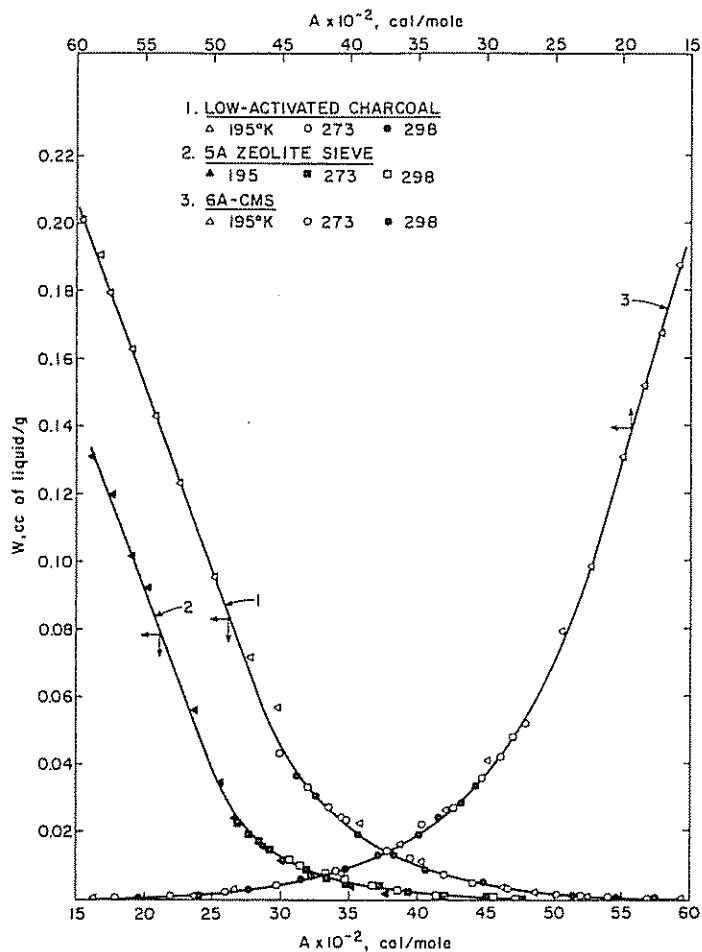FIG. 2. Sorption isotherms of Kr on different materials at 195°K.

Fig. 3. Characteristic curve of Kr adsorption, according to Eq. [1], on low-activated charcoal, 6A-CMS, and 5A zeolite sieve.

coal > medium-activated charcoal ∼ 6A-CMS > 4A-CMS > 5A zeolite. The same trend is observed at 273°K. In a few cases where desorption was studied, sorption was found to be reversible as is seen in Fig. 1.

Isotherms at 195°K are shown in Fig. 2. The data at lower pressures have also been plotted on an extended scale (Figure 2, insert). At lower pressures the extent of adsorption follows the same trend as that at 273° and 298°K. However, at higher pressures, there is a reversal in the sorption capacities of the charcoals and carbon molecular sieves; the order now being: medium-activated charcoal > low-activated charcoal > 6A-CMS > 5A-CMS.

B. THEORETICAL PLOTS AND CALCULATIONS

Figure 3 satisfactorily represents the characteristic curve, according to Eq. [1], for the adsorption of Kr at 195°K (below the critical temperature) and 273° and 298°K (above the critical temperature) on three representative samples: low-activated charcoal, 6A-CMS, and 5A zeolite sieve. For calculating W at 195°K (which is above the normal boiling point but below the critical temperature) the density of the adsorbed phase was estimated with the use of the approach of Dubinin (19), with the density of liquid Kr at the normal boiling point taken as 2.413 gm/cc (20).

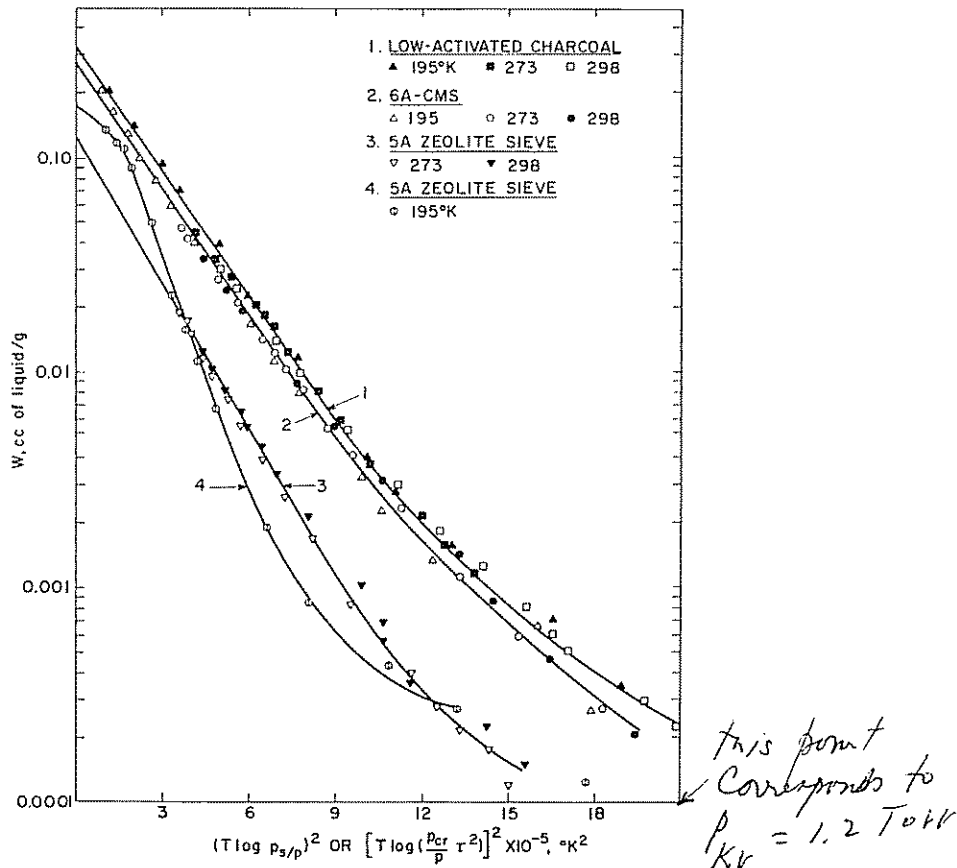When the data are plotted according to

Fig. 4. Characteristic curve of Kr adsorption, according to Eqs. [3] and [4], on low-activated charcoal, 6A-CMS, and 5A zeolite sieve.

Eq. [3] or [4] (Fig. 4), it is seen that in the case of the charcoal and carbon sieve, there is a fairly good straight-line relationship in the region above $W/W_0 = 0.02$, which is the lower limit of the applicability of the two equations (21). However, in the case of the zeolite sieve although the sorption data can be satisfactorily represented according to Eq. [1] (Fig. 3), the correlation suggested by Eqs. [3] and [4] is not observed. In fact, two distinct curves represent the data, one at 195°K and the other at 273° and 298°K. Dubinin and co-workers (22) have concluded it is not always essential that for the whole range of the applicability of Eq. [1], the characteristic curve must necessarily be represented by Eqs. [3] and [4]. Similar results to ours in the case of zeolites have previously been reported by Kadlec (23).

Recently the use of still lower adsorption temperatures have been suggested for the removal of Kr released from nuclear reactors. A few preliminary adsorption experiments were performed at 77°K on low-activated charcoal, 5A-CMS, and 5A zeolite sieve. The extent of adsorption, throughout the pressure range, varied in the order: low-activated charcoal > 5A-CMS > zeolite sieve. Reversal in the sorption characteristics of the charcoal and the 5A carbon sieve at low pressures and 77°K, as compared to 195°K, is thought to be due to activated diffusion of Kr in the 5A-CMS.

In sorption studies at 77°K, about 50% of total adsorption occurred at pressures less than 1 millitorr. The measurement of pressures below 1 millitorr with the conventional McLeod gauge is not reliable.

Further, at low pressures, the mean free path of the gas was large compared to the diameter of the hangdown tube of the balance, so that the gas molecules would collide more often with the walls of the tube than with one another. Thus, a true equilibrium pressure was not attained. Because of the two uncertainties involved in the accurate measurement of equilibrium pressure, sorption results at 77°K are of a qualitative rather than quantitative nature.

W_0 and B are structural parameters characteristic of the microporous carbons. The value of the affinity coefficient β has been shown to be independent of temperature and the nature of the carbon (14). With the value of β for Kr taken as 0.37, relative to benzene as the standard adsorbate (19), the values of the constants W_0 and B for different samples have been calculated from the intercept and gradient of the linear regions of the plots in Fig. 4 and are recorded in Table I. The values for 4A-CMS have not been included because, as will be shown, adsorption in this case involves activated diffusion. It is seen that further activation of the low-activated charcoal (to medium activated) has increased the pore size, as is evident from the higher value of B for the medium-activated charcoal.

Heats of adsorption were calculated from the 273° and 298°K adsorption isotherms; the values are included in Table I. The values represent the average heats of adsorption, calculated from individual heats, in turn, calculated for at least seven values of coverage from 5 mg/gm to maximum coverage. The heats showed a generally decreasing value with increasing coverage, with the extreme range of values also shown in Table I. Although the Clausius-Clapeyron equation does not apply for bulk phases above their critical temperature, Grant and Manes (24) attempted to justify the assumptions of liquid-like properties for the adsorbate, as well as the applicability of the Clausius-Clapeyron equation for calculating the saturation vapor pressure of the adsorbate. According to these workers, the critical temperature of the adsorbed liquid is greater than that of the bulk phase. The

TABLE I

STRUCTURAL CONSTANTS OF VARIOUS MATERIALS AND HEATS OF ADSORPTION

Material	W_0 (cc/gm)	$B \times 10^6$	Heat of adsorption (kcal/mole)
Low-activated charcoal	0.33	0.61	5.3 ± 0.4
Medium-activated charcoal	0.38	0.70	4.5 ± 0.2
4A-CMS	—	—	1.9 ± 0.3
5A-CMS	0.27	0.55	5.4 ± 0.6
6A-CMS	0.28	0.63	4.8 ± 0.6
5A zeolite sieve	—	...	4.1 ± 0.2

heat of adsorption on 4A-CMS is less than the heat of liquefaction of Kr (2.3 kcal/mole). This is indicative of activated diffusion. This conclusion is further supported by the fact that the sorption data at 273° and 298°K could not be correlated by the characteristic curves according to Eqs. [1] and [4]. In each case, the curve at 273°K fell below that at 298°K.

It is seen from Table I that the heat of adsorption varies inversely as the value of the constant B, as expected; that is, as the pore size decreases, the probability of interaction of the adsorbate molecule with more than one pore wall increases.

It is perhaps pertinent at this stage to explain why, at 195°K, the trend of adsorptive capacities of the charcoals and carbon sieves at lower pressures is different from that at higher pressures (cf. Fig. 2). It has just been shown that as the pore size decreases, the heat of adsorption increases. Consequently, the extent of adsorption will increase. Since the value of the constant B, which is a measure of the micropore size, is the smallest for 5A-CMS (Table I), this could explain its higher adsorptive capacity at lower relative vapor pressures. In this context, Lamond and Marsh (25) have shown that on increasing activation of a given carbon (which results in enlarging the pore size, i.e., increases the value of B) the extent of adsorption at lower pressures progressively decreases, although the surface area of the sample increases. This is because the probability of interaction of the adsorbate molecule with more than one
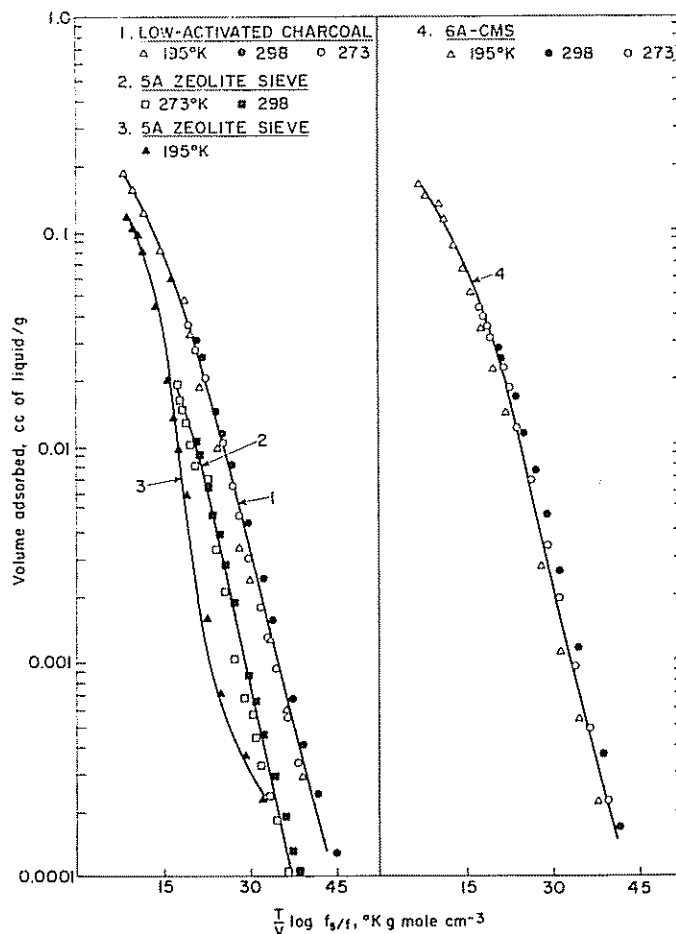
FIG. 5. Krypton adsorption plots on low-activated charcoal, 6A-CMS, and 5A zeolite sieve, as suggested by Grant and Manes (24).

pore wall decreases as the pore size increases. However, a smaller value of B is responsible only for the steeper rise of the isotherm at the lower pressures. The ultimate capacity of a given microporous material is determined by the value of the constant W_0.

The adsorption correlation of Lewis and co-workers (26), a modification of the Polanyi-Dubinin theory (27), although applicable below the critical temperature, breaks down above it (24, 26). Grant and Manes (24) have shown that sorption data both below and above the critical temperature can be correlated, if the variable volume in the abscissa in the Lewis correlation is replaced by the molar volume of the

adsorbate (V) at its normal boiling point. It was thought of interest to see if our data could be fitted according to this correlation. For calculating the saturation vapor pressure above the critical temperature, log vapor pressure was extrapolated as a linear function of reciprocal absolute temperature (28, 29), with the use of vapor pressure data of Michels et al. (11). Pressures were converted to fugacities (f) by means of standard fugacity coefficient charts (30, 31). Relevant data for the low-activated charcoal, 6A-CMS, and zeolite sieve have been plotted in Fig. 5. A fairly good correlation, throughout the pressure range studied, exists for the charcoal and carbon sieve; but two distinct curves, as in the Dubinin plots (Fig.

4), are obtained for the zeolite sieve. The breakdown of the Dubinin theory and the present correlation in the case of the zeolite sieve suggests that the sieve has adsorption characteristics different from those of the activated carbons and the molecular sieve carbons.

Although our experimental adsorption data on the carbons can be correlated by the relationship suggested by Grant and Manes, some of the assumptions envisaged in the correlation are questionable. No doubt, the density of the adsorbed phase should be more than that of the bulk phase at the same temperature; but, as correctly pointed out by Maslan et al. (29), there is no theoretical justification for assuming that the molar volume of the adsorbed liquid is equal to that of the bulk liquid at a temperature where the adsorption pressure equals the vapor pressure of the liquid. Moreover, the new correlation requires the evaluation of both density and vapor pressure of the liquid adsorbate, even much below its normal triple point. The observation of Walker and Kini (32) that in the case of microporous coals, the true state of adsorbed CO_2 at 195°K is intermediate between that of the perfect bulk liquid and perfect bulk solid strongly suggests that in the case of microporous adsorbents the assumption that the adsorbate exists as a supercooled liquid at temperatures considerably below its normal triple point is questionable. It may incidentally be pointed out that a fairly good correlation has been reported by Potter and Sussman (33), and verified in our studies, even when the molar volumes of the adsorbate at its normal boiling point are used both in the abscissa and the ordinate of Fig. 5.

CONCLUSIONS

The results of the present investigation show that 5A-CMS is slightly more efficient than activated carbons for the removal of Kr at temperatures of 195°, 273°, and 298°K, at least at the lower pressures at which it is released from nuclear reactors. In our judgment, activated carbon will, however, continue to be the preferred adsorbent because of its ready availability and much lower cost of production. Adsorp-

tion of Kr in microporous carbons, both below and above the critical temperature, is satisfactorily correlated by the Dubinin theory.

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