

# CARBON DIOXIDE SORPTION ON CARBON MOLECULAR SIEVES

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**Abstract**—The sorption of CO<sub>2</sub> on two carbon molecular sieves was studied at 273 and 298°K at pressures from about 2 millitorr to 250 torr. Over much of the pressure range, sorption was found to be reversible. The capacity of these carbons for CO<sub>2</sub> at a CO<sub>2</sub> pressure deemed physiologically safe in space vehicles for long missions was compared with the capacity of zeolitic sieves and other carbon adsorbents, reported in the literature. The capacity of the zeolite sieves for CO<sub>2</sub> is an order of magnitude higher than that of the carbon adsorbents.

## 1. INTRODUCTION

INTEREST in removal of CO<sub>2</sub> from atmospheres has increased recently concurrent with man's interest in short and long missions in space.<sup>(1)</sup> On short space missions (less than *ca* 30 days), the only concern about CO<sub>2</sub> is removing it from the atmosphere, where it would be harmful to the astronauts.† A regenerable system may be used, dumping the CO<sub>2</sub> overboard. On long space missions, a regenerable system is mandatory. Oxygen recovery from CO<sub>2</sub> is now of interest; methods that tie up CO<sub>2</sub> too strongly or dump it overboard are no longer practical. It is of interest to react CO<sub>2</sub> with H<sub>2</sub> to produce water, from which oxygen can be easily produced.

Synthetic zeolite molecular sieves are strong contenders for CO<sub>2</sub> recovery for both short and long space missions.<sup>(1)</sup> The zeolites have a large capacity for CO<sub>2</sub> (as we will see later) and can be regenerated. However, the zeolites have two distinct drawbacks. The first drawback is that the gas stream has to be dried to a dew point of *ca* -57°C before it goes through the zeolite sieves,<sup>(1)</sup> since the zeolites have a greater affinity for water than for CO<sub>2</sub>. A double adsorption system is

suggested, each consisting of a water adsorbent unit and a CO<sub>2</sub> adsorbent. Obviously the double adsorption system will result in carrying additional weight. The second drawback is that the zeolites hold CO<sub>2</sub> very tenaciously; and, consequently, to regenerate them, a temperature of *ca* 230°C is necessary.<sup>(1)</sup> This requires power and, again, additional equipment (weight).

Carbon molecular sieves are of possible utility for the uptake of CO<sub>2</sub> in space vehicles. First, carbon surfaces low in oxygen complex are known to be hydrophobic.<sup>(3)</sup> Carbon sieves low in oxygen complex can be made;<sup>(4)</sup> hence, the removal of sorption capacity for CO<sub>2</sub> by water uptake should be sharply reduced over that found for the zeolites. Second, the heat of adsorption of CO<sub>2</sub> on carbon molecular sieves is much less than on the zeolites.<sup>(5,6)</sup> Hence, regeneration of the carbon sieves should be easier than regeneration of the zeolites. In this paper, CO<sub>2</sub> sorption at 273 and 298°K on carbon molecular sieves prepared from Saran and polyvinylidene chloride (PVDC) has been studied.

## 2. EXPERIMENTAL

### Samples

Carbon sieve A was prepared from Saran 489 and a lignite pitch.<sup>(7)</sup> Saran 489 was obtained from the Dow Chemical Company; it is a copolymer consisting of *ca* 90 parts PVDC and 10 parts polyvinyl chloride. The Saran was carbonized by

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†At CO<sub>2</sub> concentrations greater than about 1 per cent at a total pressure of 1 atm, CO<sub>2</sub> is considered harmful to man. For long space missions, it is felt desirable to keep the CO<sub>2</sub> concentration below 0.5 per cent.<sup>(2)</sup>

heating in a prepurified  $N_2$  atmosphere to  $900^\circ C$ , using a heating rate of  $6-7^\circ C/min$ . The sample was held at  $900^\circ C$  for 4 hr, cooled to room temperature in  $N_2$  and then ground to  $-100$  mesh. Analysis of the lignite pitch used is given in Table 1. Thirty parts by weight of  $-100$  mesh lignite pitch were intimately mixed at room temperature with 100 parts of carbonized Saran. The mix was pelletized at room temperature at 10,000 psi to yield cylindrical samples *ca* 5 mm in dia 5 mm long. The pellets were heated at  $5^\circ C/min$  to  $900^\circ C$  in  $N_2$  and held for 2 hr. Subsequently, the pellets were held in  $CO_2$  at  $800^\circ C$  until a weight loss of 1.3 per cent was obtained. This latter step was found necessary in order to slightly activate and open up the lignite binder carbon which blocked accessibility to the Saran carbon filler. This carbon sieve has been found to be suitable for the separation of straight from branched chain hydrocarbons.<sup>(4)</sup>

TABLE 1. PROPERTIES OF LIGNITE PITCH

%C	81.7
%H	7.3
%N	1.16
%S	0.77
%Ash	2.55
Specific gravity	1.174
Coking value, %	24.8
Softening point, $^\circ C$	103.0
Quinoline insoluble, %	8.6
Benzene insoluble	18.9

Carbon sieve B was prepared from PVDC, which in turn was prepared as described in detail by MARSH and WYNNE-JONES.<sup>(8)</sup> The PVDC carbon was prepared by heating in  $N_2$  up to  $1000^\circ C$  at a heating rate of  $7.5^\circ C/min$  and then heating to  $1500^\circ C$  at a heating rate of  $15-30^\circ C/min$ . The carbon was soaked 4 hr at  $1500^\circ C$ . The resulting carbon was ground to  $-100$  mesh for sorption studies. Carbon B has been previously shown to exhibit sieving for  $CO_2$ , *n*-butane, isobutane, and neopentane.<sup>(7)</sup>

#### Sorption studies

Sorption was followed gravimetrically using a Cahn RG Electrobalance. A sample weight of *ca.* 0.4g was held in an Al-foil bucket, which was in turn suspended from the balance arm by a Pt wire.

Before a sorption run, the sample was evacuated by a Vacion gettering pump to  $<10^{-6}$  torr at  $450^\circ C$ . The pressure range studied was from *ca* 2 millitorr to 250 torr. Equilibrium was attained within 30 min over the entire pressure range.

Coleman grade  $CO_2$  from the Matheson Co. was used. This gas, which had an as-received purity of  $>99.9$  per cent, was further purified by cryogenic pumping at  $78^\circ K$ .<sup>(9)</sup> The gas was dried by successive passage through columns of 13X Linde zeolite, Anhydron, and  $P_2O_5$ . In line with previous studies,<sup>(10)</sup> the gas is thought to have a water content of *ca* 0.026 volume ppm. The saturation vapor pressures of  $CO_2$  at 273 and  $298^\circ K$  were taken as 34.4 and 63.5 atm, respectively.<sup>(11)</sup>

### 3. RESULTS

Following the suggestion of DUBININ<sup>(12,13)</sup> and LAMOND and MARSH,<sup>(14)</sup> adsorption results have been plotted according to an equation derived from the Polanyi potential theory.<sup>(15)</sup> The equation is:

$$\log V = \log V_o - \frac{BT^2}{\beta} \log^2(P_o/P)$$

where

$V$  = amount adsorbed at equilibrium pressure  $P$ ;

$V_o$  = micropore capacity;

$P_o$  = saturation vapor pressure of adsorbate at adsorption temperatures;

$\beta$  = affinity coefficient of adsorbate relative to  $N_2$ ;

$B$  = constant.

Figure 1 represents sorption plots for  $CO_2$  on carbon A at 273 and  $298^\circ K$ . At  $273^\circ K$ , the plot is reversible and linear over the entire pressure range studied (31 millitorr to 254 torr). At  $298^\circ K$ , the plot is reversible and linear at pressures from 3.7 to 222 torr; at lower pressures,  $CO_2$  does not desorb reversibly. In the reversible region, the heat of adsorption of  $CO_2$ , as estimated from the Clausius-Clapeyron equation, is *ca* 5.5 kcal/mole. The slopes of the linear regions of the plots are  $10.8 \times 10^2$  and  $10.9 \times 10^2$  at 273 and  $298^\circ K$  respectively.

Figure 2 presents the sorption plots for  $CO_2$  on carbon B at  $298^\circ K$ . The adsorption plot is linear over the pressure range from about 3.7 to 240 torr, with a slope of  $13.3 \times 10^2$ . In the limited region studied, sorption was reversible.

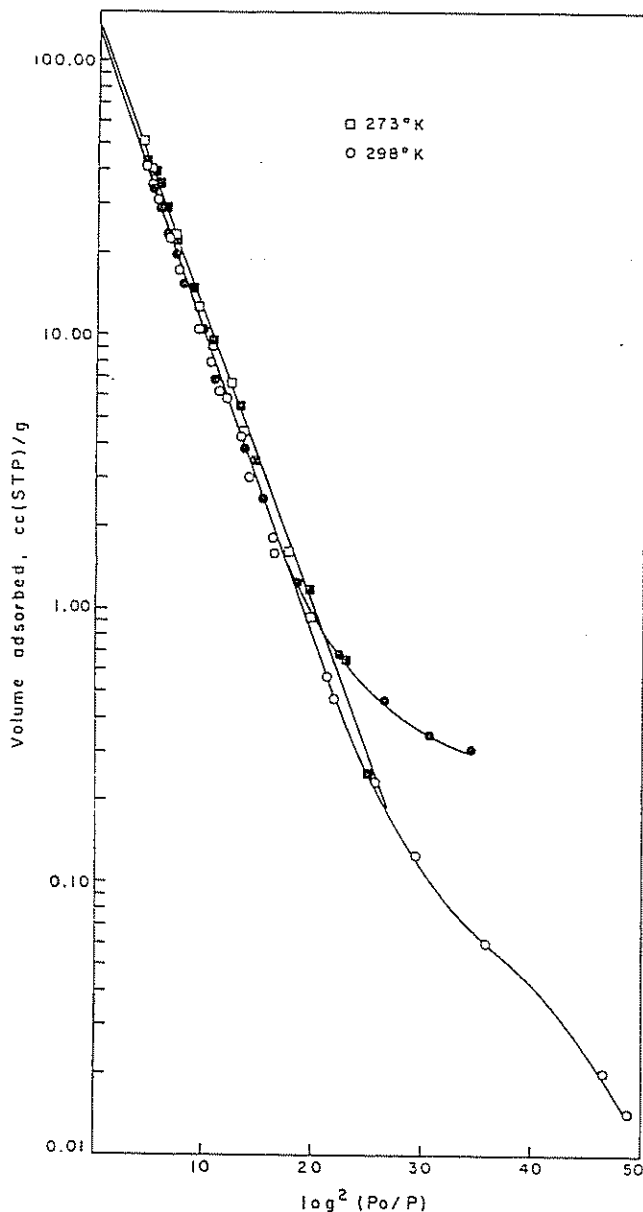


FIG. 1. Sorption plots of CO<sub>2</sub> on carbon sieve A. Solid points are desorption data.

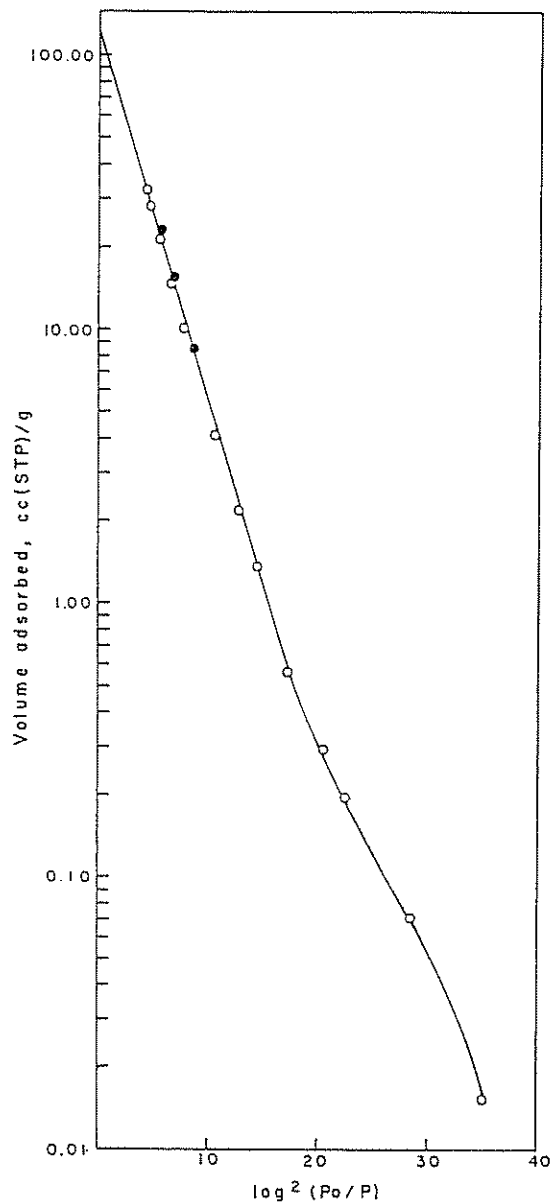


FIG. 2. Sorption plot of CO<sub>2</sub> on carbon sieve B at 298°K. Solid points are desorption data.

The  $V_0$  values, estimated from the intercepts of Figs. 1 and 2, are given in Table 2. As discussed,<sup>(14)</sup> these  $V_0$  values can be used to closely approximate surface areas for molecular sieve materials. Surface areas are listed in Table 2. The molecular area of CO<sub>2</sub> was taken as 17.0Å<sup>2</sup>, for this calculation.\*

\*Previously, a molecular area for CO<sub>2</sub> at 298°K of 25.3Å<sup>2</sup> was suggested by workers in this laboratory.<sup>(16)</sup> However, a value of 17.0Å<sup>2</sup> has been taken in this study so that the results can later be compared with those of LAMOND and MARSH.<sup>(14)</sup>

TABLE 2.  $V_0$  VALUES AND SURFACE AREAS OF CARBON SIEVES

Sample	Adsorption temp. (°K)	$V_0$ (cm <sup>3</sup> (STP)/g)	Area (m <sup>2</sup> /g)
A	273	142	649
A	298	124	566
B	298	115	525

## 4. DISCUSSION

Lamond and Marsh previously measured CO<sub>2</sub> sorption on charcoals, carbon blacks, polyvinylcyanide carbon, and polyfurfuryl alcohol carbon at 273 and 293°K.<sup>(14)</sup> For all these materials, they found the slopes (called *D*) of the potential energy plots to vary from  $9.0 \times 10^2$  to  $17.8 \times 10^2$ . The slopes found for our plots fall within these values. *D* is inversely proportional to  $\beta$ , an affinity coefficient. The heat of adsorption can be taken as a relative measure of  $\beta$ . Therefore, at constant temperature *D* will decrease as the heat of adsorption increases. Obviously for the uptake of gas to be high at low relative pressures, *D* should be low. For carbons, *D* should be lowest for molecular sieve materials. That is, for these materials, the adsorbate has a significant attractive interaction with more than one wall of the pore; and, therefore, the heat of adsorption will be higher than normal. LAMOND and MARSH<sup>(14)</sup> show this effect clearly for the molecular sieve material, polyfurfuryl alcohol carbon. For CO<sub>2</sub> adsorption at 273°K,  $D=9 \times 10^2$  for the original carbon; as the material is progressively activated in CO<sub>2</sub> at 850°C to a burn-off of 95 per cent, *D* monotonically increases to  $17.8 \times 10^2$ . Activation has enlarged the pore size; and with increasing burn-off, the extent of adsorbate interaction with more than one wall of the pore continuously decreases. Therefore, even though activation increases the surface area of the polyfurfuryl alcohol carbon from 440 to 870 m<sup>2</sup>/g, CO<sub>2</sub> uptake at low relative pressures decreases, as seen in Table 3. Table 3 summarizes the adsorption capacity of a number of adsorbents to CO<sub>2</sub> at 273°K and a pressure of 3.8 torr [ $\log^2(P_0/P)=14.7$ ]. This pressure represents closely the upper limit of CO<sub>2</sub> pressure thought to be tolerable to man in space vehicles for long missions.

Lamond and Marsh find that the differential heat of adsorption of CO<sub>2</sub> on PVDC carbon (carbonized at 1000°C) varies from *ca* 6.0 to 6.5 kcal/mole.<sup>(5)</sup> As previously discussed, we find a heat of adsorption on carbon A of *ca* 5.5 kcal/mole. In contrast, KINGTON and MACLEOD<sup>(6)</sup> find the heat of adsorption of CO<sub>2</sub> on the natural zeolite, chabazite, to range from *ca.* 10 to 14 kcal/mole. This high heat of adsorption is consistent with the conclusion of Bertsch and Habgood, from infrared studies on Linde X zeolites, that the uptake of

TABLE 3. AREAS OF SELECTED ADSORBENTS AND THEIR CAPACITY FOR CO<sub>2</sub> AT 273°K AND 3.8 TORR

Material	Area* (m <sup>2</sup> /g)	Amt. adsorbed* (cm <sup>3</sup> (STP)/g)
AC charcoal 689	910	4.0
AC charcoal 691	290	4.0
Cellulose, 400°C	365	4.0
Carbolac 1	460	1.5
Polyfurfuryl alcohol		
Burn-off, 0%	440	4.7
23%	860	3.6
42%	800	1.6
67%	770	1.4
95%	870	<1.0
Carbon sieve A	566	3.7
Carbon sieve B	—	1.7†
Linde sieve, 5A powder	600	65
5A pellets	530	47
13X pellets	580	40
4A powder	480	54

\*With the exception of carbon sieves A and B, all data are taken from Reference 14.

†Calculated at 273°K assuming a heat of adsorption of 5.5 kcal/mole.

CO<sub>2</sub> in the low coverage region appears to involve chemisorption.<sup>(17)</sup> Thus, the slope of the potential energy plots for CO<sub>2</sub> on zeolites should be significantly lower than the slopes for carbons. LAMOND and MARSH<sup>(14)</sup> report slopes for the Linde zeolitic sieves at 273°K ranging from  $1.7 \times 10^2$  to  $2.2 \times 10^2$ —values much lower than those for the carbons. As a consequence of the low values of *D*, the uptake of CO<sub>2</sub> on the zeolitic sieves at 273°K and a pressure of 3.8 torr is an order of magnitude higher than for any of the carbon adsorbents, as seen in Table 3. This much higher uptake of CO<sub>2</sub> at this low relative pressure is observed for the zeolitic sieves in spite of the fact that they have lower surface areas than some of the carbon adsorbents studied.

## 5. CONCLUSION

Despite the facts that some of the capacity of zeolitic sieves for the adsorption of CO<sub>2</sub> is lost because of water uptake and that regeneration of the sieves following CO<sub>2</sub> adsorption requires heating to an elevated temperature, the large capacity of zeolitic sieves for CO<sub>2</sub> at low relative pressures (compared to the carbon sieves and other carbon adsorbents) suggest that the zeolitic sieves will continue to be the preferred adsorbent for CO<sub>2</sub> in space vehicles.

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