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The Carbon Molecular Sieve Membranes. General Properties and the Permeability of CH_4/H_2 Mixture

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ABSTRACT

The properties, the advantages and drawbacks of hollow fiber carbon molecular sieving membranes as gas separators are discussed. Some mechanistic aspects are surveyed and permeability of methane-hydrogen mixture through the carbon membrane was studied. The presence of methane which is adsorbable and a poor permeant, does not impair the permeability of hydrogen even at temperatures as low as -80°C. This suggests that, because of the large difference in size of the two molecules, they occupy different positions in the membrane material prior to the jump through a critical constriction.

BACKGROUND

A few years ago, gas separations entered a new phase with the introduction of modules for industrial gas separations using organic, glassy polymer membranes (1,2). Today gas separation by the membrane process is of major importance and receives major interest among all gas separation processes. So far the major membrane candidates for gas separation have been the organic, glassy polymer films. These polymers stand between the crystalline polymers which are essentially impervious to gases (3) and the rubbery polymers which are about equally highly permeable for all permanent gases as well as for many organic vapours and are thus poor in selectivity (4,5).

Gas separation through nonporous membranes has recently become of interest in organic membrane science and technology which which previously was concerned primarily with liquid separation processes. The mechanism of gas permeation through the membrane material is closely related to the molecular structure and dynamics of the polymer materials (6). Glassy polymers exhibit, as a rule of the thumb, higher permeability to smaller molecules.

Porous solids are another class of media which are known to have gas separation capability via selective *adsorption*. These solids are studied as a branch of the physical chemistry of surfaces. The mechanism of gas permeation and uptake through porous solids is closely related to the internal surface area and dimensions of the pores and to the surface properties of the solid, rather than to its bulk properties of the solid as in the case with polymers.

Molecular sieves are porous alumino-silicates or carbon solids that contain pores of molecular dimensions which, in a similar manner to glassy polymers, exhibit selectivity according to the size of the gas molecule. The simply engineered, continuous and energy saving membrane process based on polymer membranes, invited research for similar processes based on molecular sieves. Membranes from molecular sieve solids have been made by compacting powders into a disk with or without an impervious filler which occupies the interstices between the particles and reduces the nonselective transport (7). The drawback to these membranes lies in our inability to fabricate them from continuous thin films.

After a few years of studying carbon molecular sieves as adsorbents (8-13) we applied the simple and basically well known process of pyrolytic carbonization to organic polymers in the form of a hollow fiber, to obtain hollow fiber carbon molecular sieve membranes (14). Obeying a basically different permeation mechanism than polymer membranes, the carbon membrane was expected to exhibit different permeability-selectivity properties. The carbon membrane exhibited similar or better selectivity for any pair of gaseous molecules. An unexpected result was that it exceeded the permeability figures of polymer membranes by one or two orders of magnitude (14). As compared to polymer membranes, the carbon molecular sieve membranes have the following advantages:

1) They have far superior permeability-selectivity combination than any known polymer membrane.
2) The same starting material can serve to develop membranes of different selectivity-permeability combinations for different gas mixtures. Frequently, different polymer membrane materials have to be employed for different separation purposes. The pore dimensions of carbons can be finely adjusted by simple thermochemical treatments so as to meet any separation objective optimally (4,11).
3) The carbon membrane is far more stable thermally than organic polymer membranes. They may therefore be well suited for separation processes at high temperatures. We have shown that at least a few days exposure to various gases and temperatures will not significantly alter their permeability characteristics, as shown in table 1.
4) The carbon membrane has superior stability in the presence of organic vapors at high temperatures, organic solvents, and nonoxidizing acidic or basic environments.
5) The carbon membrane is mechanically much stronger and will withstand higher pressure differences for a given wall thickness.

Table 1.
Thermal stability of the carbon membrane in presence of various gases

gas	He	H_2	CH_4	CO_2	O_2
temp.°C	700	>500	500	400	<200

This leads to a better specific active surface area-bore diameter combination, namely to a lower axial pressure drop for a given output rate.

The carbon fiber membrane has two major drawbacks:
1) It is more brittle, therefore requiring more careful handling.
2) Because the transport is via a pore system rather than through the bulk, the carbon membrane gas separator may require a pre-purifier for removing traces of strongly adsorbing vapors which could clog up the pores. This is typical of many industrial adsorption separators. Cost effective solutions are known. This problem may be avoided by operating at sufficiently high temperatures.

A DESCRIPTION OF CARBON MOLECULAR SIEVES

Carbon molecular sieves are produced by thermal decomposition in a controlled chemical environment of organic compounds that do not melt or soften during carbonization. Without a melting stage, the intermediates that are essentially planar, polycondensed aromatic entities, they have insufficient freedom of motion to be alligned as in graphite. Moreover, since pyrolysis involves emanation of organic gases through the matrix, a pore system is formed within the solid matrix. Upon completion of the carbonization process, the resulting solid is a highly distorted, graphitic material with low specific gravity (1.2-1.6 g/cc as compared to 2.2 for nonporous crystalline graphite) and a pore system of molecular dimensions. Further evidence **(8,15)** has shown that the pore system consists of relatively wide openings with narrow constrictions. The openings contribute the major part of the pore volume and are thus responsible for the adsorption capacity, while the constrictions are responsible for the stereoselectivity of pore penetration by host molecules and for the kinetics of penetration.

MECHANISM OF GAS PENETRATION THROUGH THE CARBON MEMBRANE

The technique of activation or partial burnoff, which is used to enlarge the pore system in carbon **(8,16)**, together with annealing at high temperatures in an inert atmosphere which brings about pore closure **(8,17)**, has been employed recently to prove that the permeability of gases through the carbon membrane proceeds through a pore system of molecular dimensions **(8,18)**. We have shown that progressive activation causes progressively larger molecules to permeate through a carbon membrane, whereas the selectivity between the smaller molecules declines **(14)**.

Degassing carbon molecular sieves at temperatures up to 650-750°C, removes some surface oxygen functional groups as carbon oxides, and hence, enlarges the pore dimensions. Heating at still higher temperatures anneals the carbon and brings about pore closure (8). By applying the same treatment to a carbon membrane we have shown that the permeabilities for pure hydrogen and pure methane first increase upon heating, then decrease, indicating again that molecular sieving through a pore system is responsible for the molecular permeation process.

These features, together with the fact that the carbon matrix itself is impervious (14) suggests that permeation through carbon membranes can be attributed entirely to the pore system. In this sense, gas permeation through the molecular sieving carbon membrane, is simpler than that through the glassy polymer membranes. In the later case, gas permeation has been attributed to the *dual mode* model involving permeation through the matrix and the free volume system (19). The distinction between voids and matrix in glassy polymers is not as clear as is in the case of molecular sieve carbons since the void system in polymers gradually disappears upon approaching the glass transition temperature, Tg, (20) and gas permeation is very frequently carried out at temperatures not far below Tg. The dual mode model which seems to be commonly accepted is still receiving some objections (21) .

In this paper we present the first experimental results on pure component permeabilities at low temperatures and on gas mixture permeabilities at both high and low temperatures. Since the results were rather surprising, only a preliminary attempt will be made here to interpret them in terms of the molecular sieving effect of a microporous system. Further experimental data on various gas mixtures at low temperatures will be necessary for a more comprehensive picture of the carbon molecular sieve membrane behaviour.

EXPERIMENTAL

The vacuum-pressure system and the linear shell and tube cell for heat treating and measuring the permeability of gases in the carbon hollow fiber membrane have been described elsewhere (14). Permeability measurements were made by monitoring the pressure increase as gas flowed into a calibrated volume on the bore side of the hollow fiber. The Exeperimental system is shown in figure 1.

Besides the linear shell-and-tube cell, a U shaped cell also was used in order to allow the membrane to be insert in a cryostat bath for low temperature measurements. The lowtemperatre results are presented here for the first time for carbon membranes.

Two arrangements for gas mixture preparation were employed. One was used for dynamic measurment in which the shell side of the cell was constantly flushed with the gas mixture, and a second arrangement was used for static experiments. For the dynamic measurments, the mixture was prepared using two flow control valves which preceeded the regular valves of the gas manifold. The mixture passed through valve 2 along the shell side of the hollow fiber and then exited to the atmosphere via another valve and through a gas bubbler (both not shown in figure 1). In this case the high pressure side of the membrane

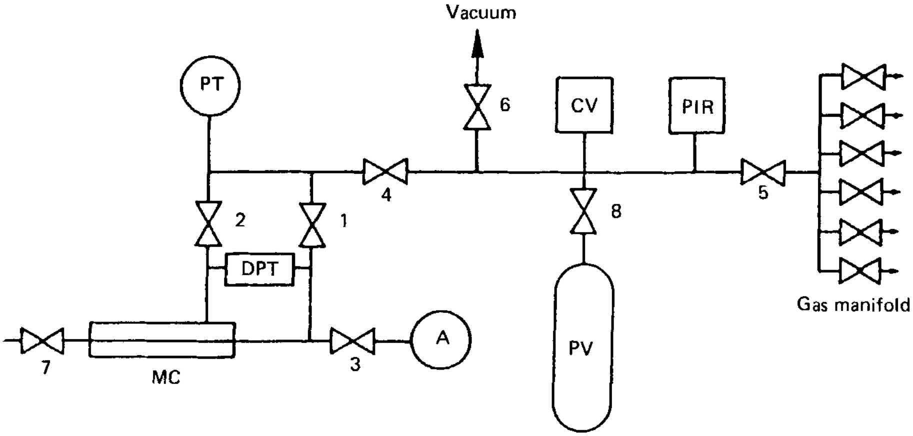

Figure 1. A schematic of the gas permeability system. PIR- Piranni vacuum gauge; CV- Check valve; PV- Pressurizing vessel; PT- absolute pressure transducer; DPT- differential pressure transducer; A- calibrated volume; MC- membrane cell

obviously was limited to 1 atmosphere. Samples from the gas mixture flowing out through valve 9 were analysed by a gas chromatograph, to verify the control valve calibrations.

For the static measusrments,the gas mixture was prepared in a stainless steel vessel, about 2 liters in volume, connected to the system through a short tube, 1/4" in o.d. and valve 8. The following procedure was employed: The system was first cleaned by thorough evacuation, then hydrogen was introduced into the bulb to an accurately measured pressure p_1. Valve 8 was then closed, and the system was evacuated. Methane was then admitted (while valve 8 was still closed) at a pressure considerably higher than the initial hydrogen pressure p_1. Admittance of methane was made through valve 5 which was partially open. While pressure was recorded vs. time through the pressure transducer PT, valve 8 was then opened carefully to full aperture, so that a stream of methane, throttled through valve 5, was constantly entering against the hydrogen pressure in the bulb. The main valve 5 was then closed so that the *total* constant pressure p_2 was recorded for a few seconds, then valve 8 was closed, and the line was pumped out. The mixture composition in % H_2 is calculated assuming ideal gas behaviour using the equation

$$\%_{H_2}=p_1/(p_2)x100 \qquad (1).$$

To ensure thorough mixing, a magnetic stirrer placed into the (nonmagnetic) stainless steel vessel was operated by an outside stirrer motor. The mixture was then left for at least half an hour prior to its use in the membrane cell. The same results were observed when the mixture was used immediately after preparation or after aging for 30 minutes to allow for diffusion mixing. However, mixing and aging were carried out to ensure confidence in the data. The mixture pressure in the vessel was of a pressure of about 2 atmospheres, and this was sufficient for several permeability experiments.

During a measurment the gas mixture at the high pressure side of the membrane was renewed by frequent flushing to ensure a constant feed side composition. No change in the rate of pressure increase was observed upon mixture renewal.

In both the dynamic and static methods, the low pressure (bore) side was initially below 1 torr and its overall pressure increase during a permeability measurment was never more than 20 torr. The low pressure could therefore be neglected in comparison to the upstream 1 atm. pressure.

PERMEABILITIES OF H_2-CH_4 MIXTURES AT HIGH AND LOW TEMPERATURES.

To make the first study of the gas mixture on the carbon membrane as simple as possible, the hydrogen-methane mixture was selected because of the weak adsorbability and nonpolarity of both molecules, and because of the great difference in their permeabilities. Also the separation of this mixture is of commercial importance. The much greater permeability of hydrogen allowed us to attribute, as a first approximation the entire permeate flux to it. This simplification saved, for the time being, the necessity of frequent permeate gas mixture analysis since only hydrogen was assumed to be present at the low pressure side of the membrane. The mechanistic importance of studying the gas mixture behaviour lies in the possibility that the less permeable molecule would impede the permeability of the faster permeant.

The results of the measured mixture permeability P_{exp} are presented below together with the permeabilities P_{cal} calculated from the pure gas data P_H and P_M of hydrogen and methane respectively, according to the equation

$$P_{cal}=P_HX_H+P_MX_M \qquad (2)$$

where X are the correspondidng molar fractions in the mixture.

Irrespective of the mixture permeability behaviour, the high temperature data and the high permeability values (thousands of Barrers) are noteworthy.

The main significance of Tables 2 and 3 is that the permeability of the main permeant is independent of the presence of a second gas over a considerable range of temperatures and mixture compositions. This is true at least at high temperatures where adsorption is negligible. The two gases behave independently, as free molecules in space, however, they are still sieved molecularly, as is evident from the much lower methane permeability.

To interpret this behaviour, the possibility of separate permeate paths in the pore system, larger pores for methane and narrower for hydrogen, have been considered. This option was rejected, however, since the wider passages should allow H_2 flow as well and should therefore be impaired by the presence of CH_4. This was not observed.

Table 2.
Intrinsic permeability in Barrers ($ccSTP-cm-cm^{-2}-sec^{-2}-cmHgx10^{-10}$) of different H_2/CH_4 mixtures at 500 C through a relatively narrow pore membrane (high selectivity).

P(cal)	P(exp)	% H_2
1024	1089	78
806	832	61
568	595	43
208	221	16

Table 3.
permeabilities P (in Barrers) and permselectivities S ($=P_{H_2}/P_{CH_4}$) of 45% H_2- 55% CH_4 mixture through a relatively wide pore membrane (higher H_2 permeability and lower selectivity) at different temperatures. Measurments were carried out by the flow method.

T(C)	S	P(CH_4)	P(H_2)	P(cal)	P(exp)
200	56.8	34	1920	678	698
300	43.4	45	1950	694	662
400	43.3	47	2030	722	686
500	34.8	60	2080	745	676

Recalling the abovementioned concept of wide pores and sieving constrictions, the following interpretation is suggested: The H_2/CH_4 ratio within the pores is the same as that of the outer gas mixture. This may be justified regarding the high experiment temperatures at which adsorption of the light H_2 and CH_4 molecules is negligible. The residence time of the molecules at the constrictions during the activated step of permeation is very short in the absence of adsorption so the constrictions are mostly unoccupied. Therefore no hinderance by the slow permeate is likely.

Surprisingly, H_2-CH_4 permeability measurments which have been extended to low temperatures, where considerable adsorption is very likely have still shown that H_2 permeabilities (which decrease consisdearably at lower temperatures) are still independent of the mixture composition.

These results become even more puzzling considering previous observations where the permeability of methane at 25°C decreases upon

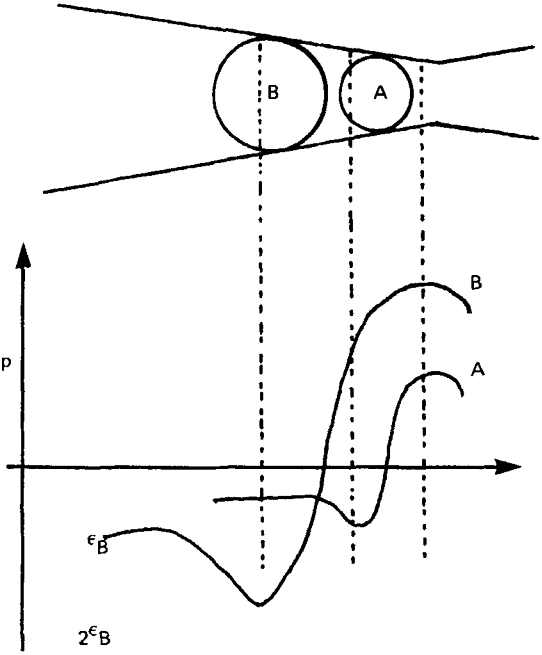

Figure 2. The potential energy along the permeation path of two molecules of different size representing hydrogen and methane.

increasing the pressure, a behavior which would be expected for an adsorbing gas (18). At temperatures as low as -80°C, adsorption of methane is significant, but it still does not impair the hydrogen permeability. This behaviour leads to the conclusion that the small hydrogen molecules and the large methane molecules reside at different minimum energy positions prior to the activated jump through a constriction.

Figure 2 describes some of the potential energy positions of two guest molecules of different sizes on the potential energy-penetration coordinates (This is similar to figure 9 in reference 10 which was drawn for one molecule).

The circles show the positions of molecules of different sizes at their minimum potential energy prior to the jump through a constriction. It is evident from the figure that, due to the unparallel walls of the amorphous porous solid, a larger molecule will occupy a more distant position with respect to the center of the constriction and may thus not disturb the position of the smaller molecule.

In a sense, this very qualitative model resembles the well known immunity of ultrafilteration membranes to fouling by large suspended

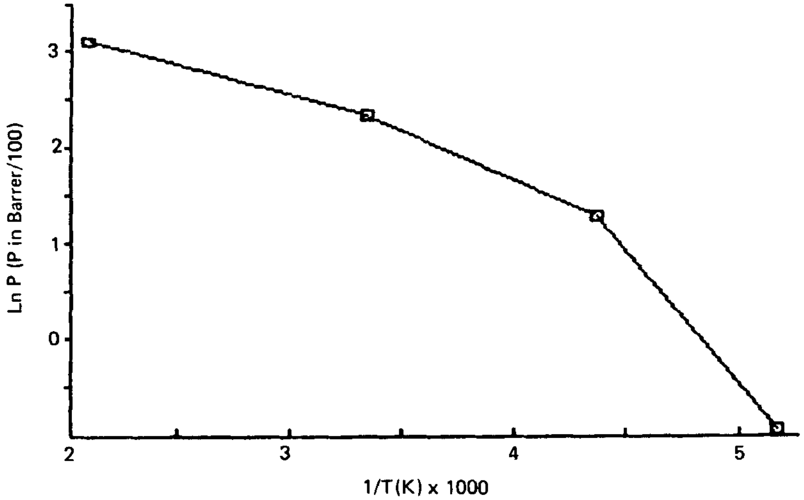

Figure 3. The dependence of log(permeability) of hydrogen on the inversed temperature 1/T(K). The carbon molecular sieve membrane had an open pore structure, namely large permeability and a relatively

Table 4.
Directly measured and calculated (equation 2) permeabilities of a 1:1 H_2-CH_4 mixture through a wide pore molecular sieving carbon membrane. Measurments carried on by the static method. Permeabilities in Barrers.

T°C	S	$P(CH_4)$	$P(H_2)$	P_m(exp)	p_m(cal)
200	32	98	3220	1590	1610
25	35	42	1460	650	753
-45	>35	<15	504	260	252
-80	>4	<10	55	24	27

particles. Stretching this analogy a step further, we may deduce that the narrow and strongly interacting CO_2 molecule in its mixture with hydrogen will interfere in the permeability of the later, since they may both occupy the same critical position at the constriction entrance. On the other hand and for the same reason CO_2 may not interfere with the penetration of methane at conditions where there is significant adsorption of CO_2, namely high pressures.

The pore constriction model has been adequate for qualitatively understanding the experimental results on single gas permeabilities presented in previous papers and for the H_2-CH_4 mixture in this paper. The low temperature permeability data on light gases which we have recently obtained (table 4) indicate the mechanistic complexities that will be encountered when adsorption takes place within the sieving pores. As an example, an Arrhenius plot of permeability of hydrogen at low temperatures is not a straight line (figure 3), although the permeability changes are very large.

It is hoped that future data will provide a more complete picture of the process of permeation through the molecular sieving membrane.

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