Effect of temperature on oxygen-argon separation on carbon molecular sieves

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Carbon molecular sieves (CMS) are used as adsorbents in the separation of O$_2$, N$_2$ and Ar from air by pressure swing adsorption (PSA). Due to its aperture-cavity type pore structure, a CMS for this application exhibits greater selectivity for O$_2$ uptake. The economics of this process or other competitive technologies, such as cryogenic and membrane separations, is largely impacted by the product recovery and purity profiles. There is great demand for ultra high purity Ar in many chemical, metallurgical, and electronic processes. High purity gases are also desired in numerous laboratory processes. Trace impurities such as O$_2$ and CO$_2$ are left behind during recovery of other gases. Such trace impurities can be efficiently removed by flowing the product gas of a traditional separation process through a column of CMS that selectively adsors the impurities.

In previous publications [1-3] we have described methods for preparation of CMS for separation of O$_2$ from N$_2$ or Ar. The performance of CMS was evaluated by following diffusion of these gases under ambient conditions. In this study we have investigated the adsorption of these gases at lower temperatures.

The carbons used in this study were CMS-A and modified CMS-B. CMS-A is a pelletized commercial molecular sieve adsorbent for separation of O$_2$ from N$_2$ or Ar; it is classified as a 0.3-0.4 nm CMS [1]. CMS-B is a granular carbon of pore size of about 0.5 nm [1]. The modified sample of CMS-B was prepared by depositing carbon from propylene cracking [3]. This treatment produced a CMS-B sample that exhibited properties similar to a 0.3-0.4 nm CMS. Physical properties of the carbons used are discussed elsewhere [1-3]. The rate of gas diffusion on these carbons and their adsorption capacities were measured volumetrically in a manner reported earlier [1].

Carbon was degassed at 383 K for 1 h prior to gas adsorption.

Physical data for O$_2$, N$_2$ and Ar, reported elsewhere [2], indicate that boiling and critical temperatures of these gases lie in a very close range. Therefore, their equilibrium capacity on a carbon should be essentially similar under specific adsorption conditions. As a CMS, separation of O$_2$ from Ar or N$_2$ occurs because the critical pore dimension (CPD) of CMS is below the minimum dimension of Ar or N$_2$, thus restricting the entry of these molecules. It can be seen that the diffusion of these gases becomes activated. Rao et al [4] have reported that there are two types of energy barriers for the adsorbing molecule, one at the entrance of the pore of critical dimension and the second for diffusion within the pore. However, the relative rate of diffusion of adsorbing species is dependent on the magnitude of the energy barrier at the pore entrance which is the largest of the two types of energy barrier. Using the Lennard-Jones [6-12] potential, Walker and co-workers [5] estimated that the diffusion of gases becomes activated when the pseudographitic basal planes are closer to each other than the sum of the kinetic diameter of the diffusing species and 0.16 nm.

![Figure 1](image-url) Uptake of O$_2$ and Ar on CMS-A.
uptake is enhanced. Selectivity of the carbon at 189 K is sharply increased to ~ 7.8.

The results show the desirability of reducing adsorption temperature to enhance the separation of O₂ from Ar. Since the activation energy for O₂ diffusion into a CMS is lower than that for Ar [6], a reduction in temperature will reduce the Ar diffusion parameter more drastically than the of O₂. This is desirable for greater separation. Also a reduction in temperature will enhance O₂ and Ar uptake at equilibrium. Enhancement at equilibrium will be about equal since their isosteric heats of adsorption on a CMS are very similar (~ 17-18 kJ/mole) [7-8]. However, because the diffusion parameter for Ar is much less than that of O₂ on the CMS, in a reasonable cycle time for pressure swing adsorption, Ar uptake will be much more removed from its equilibrium value than that for O₂. As a result, it is seen in Fig. 1 that O₂ uptake at 8 min at 189 K (~ 7.8 cc/g) is greater than O₂ uptake in 8 min at 298 K, whereas Ar uptake at 189 K is sharply reduced over that at 298 K. Or, for an 8 min cycle, thermodynamics dominates for O₂ uptake and kinetics dominates for Ar uptake.

Figure 2 shows plots of O₂ and Ar uptake at 298 and 189 K on a CMS sample prepared from CMS-B by deposition of carbon [3]. Again the advantage of operating below ambient temperature on the separation of O₂ from Ar is seen. At 298 K, the Ar uptake on this CMS is lower than that on CMS-A. Just like CMS-A, the uptake rate of Ar on this carbon is diminished upon reducing the adsorption temperature to 189 K. Over the first minute, this carbon shows no discernible uptake of Ar. By contrast, the O₂ uptake rate and amount adsorbed are increased 2-3 fold by operating at 189 K, thus causing a significant improvement in selectivity to ~ 19.

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REFERENCES