

EFFECT OF PRESSURE ON THE HEATS OF SORPTION AND DESORPTION OF O₂, NO AND N₂, ON AN ACTIVE CARBON AND A CARBON MOLECULAR SIEVE

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Introduction

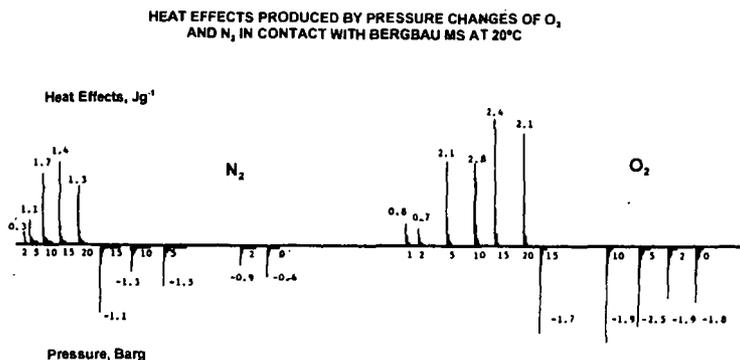
Pressure swing adsorption techniques with the use of carbon molecular sieves (CMS) are now all established for the separation of individual components of gas mixtures. One important example of such a separation is the isolation of pure oxygen and nitrogen from air. Recently K.M. Thomas, M.L. Sykes and H. Chagger have shown that the heat evolution which accompanies the adsorption of O₂ and N₂ on various CMS's from a stream of helium, takes place at rates which are closely similar to the heats of adsorption, with nitrogen adsorbing much more slowly than oxygen (1). The work was carried out at room temperature and at atmospheric pressures. Pressure swing separation processes which are used industrially, employ adsorption pressures that can vary from atmospheric pressure to 20 barg. The application of pressure increases the adsorption of individual components of gas mixtures and generates heat evolution due not only to adsorption of the first layer of molecules, but also to the pore filling phenomena which densify the gas contained in micropores. The heats evolved or absorbed during pressure swing operations are important parameters which affect the efficiency of gas separation operations as indicated recently by Sircar (2). But so far experimental determination of the heats of pore filling and gas adsorption on molecular sieves have not received much attention. This work was carried out, therefore, to determine experimentally the effect of pressure on heat evolution during adsorption of O₂ and N₂ on a commercial molecular sieve and an active carbon using a Microscal Flow Microcalorimeter (FMC) modified for use at high pressures under static conditions.

The pressures of oxygen and nitrogen in contact with the adsorbent were increased in steps from 1 to 20 barg and decreased back to atmospheric pressures and the resulting heats of sorption determined together with the duration of each heat effect. A limited amount of work was also carried out on nitric oxide.

Experimental

A schematic diagram of Microscal's Flow Microcalorimeter (FMC) which can be used under static conditions at pressures up to 50 barg is shown in Figure 1. In the procedure used, the calorimetric cell which had a volume of 0.17 cc was filled with accurately weighed adsorbent, with outlet tube in position, and the cell closed by a tightly fitting stainless steel inlet tube. The inlet tube is connected to a gas cylinder via a Druck pressure regulator capable of increasing or decreasing the gas pressure inside the cell in steps determined by the operator. The heat effects produced by the increasing or decreasing pressures are measured by the thermistors and calibration is effected by generating heat effects inside the cell electrically, as described previously for a Flow Microcalorimeter (3). The cell in the high pressure instrument is made from MACOR (glass reinforced with mica flakes) giving high temperature and pressure capability and very low time constant. With the inlet open and the outlet tube closed, the pressure was changed in a stepwise fashion resulting in the generation of heat effects. A typical record of one such measurement series is shown in Figure 2 for O₂ and N₂ adsorbed sequentially on a 0.095 g sample of Bergbau molecular sieve. The carbon adsorbents used in this study were Chemviron BPL active carbon and a commercial sample of a Bergbau molecular sieve. Gases were Aldrich materials with purities exceeding 99%. All the work was carried out at 20°C ± 1°C.

Figure 2



Results and discussions

A plot of differential heat effects represented in Figure 2 for the adsorption of O₂ and N₂ on the carbon molecular sieve is shown in Figure 3. There is a clear difference between the two gases with the ratio of the heats for O₂ and N₂ diminishing as the pressure increases. This suggests that the efficiency of gas separation would be somewhat higher for pressure swings of 0 - 2 barg than it would be for the swings of 18 - 20 barg, notwithstanding the greater amounts of gas throughput at the higher pressures. The heat effects plotted in Figure 3 do not take into account the rates of heat evolution which are very different for O₂ and N₂, as illustrated by the heat evolution peaks shown in Figure 4. It appears, however, that the differences in the rates of heat evolution under a pressure swing regime are smaller than those reported by K.M. Thomas et al for the adsorption at atmospheric pressure (1).

Figure 3

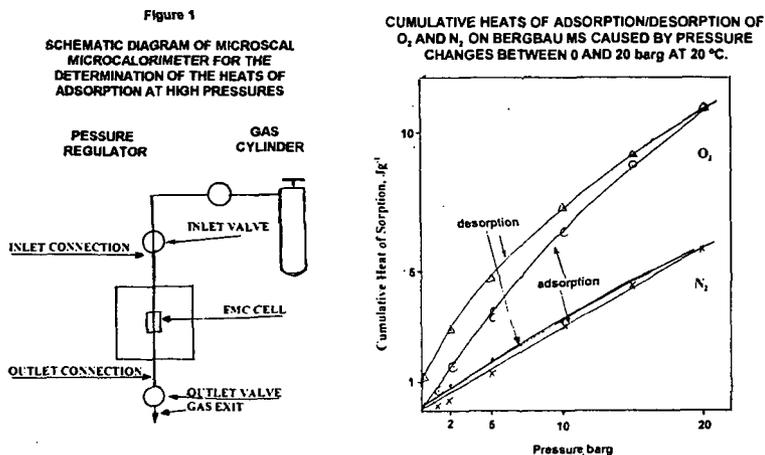
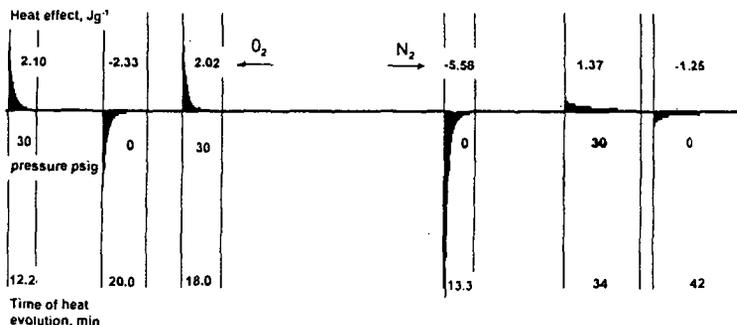


Figure 4

EVOLUTION AND ABSORPTION OF HEAT DURING A
PRESSURE SWING OPERATION WITH O₂ AND N₂
ON BERGBAU CARBON MOLECULAR SIEVE



The differences between the heats adsorptions of O₂ and N₂ on CMS and active carbon BPL are shown in Figure 5 for pressure changes between 0 and 2 barg. As can be seen, the active carbon, as expected, shows very different behaviour from the CMS and gives slightly higher heats of adsorption for O₂ than for N₂. The active carbon does not show any significant difference between the rates of heat evolution. However, for CMS it is evident that the periods of heat evolution for N₂ are longer than they are for O₂. If it is assumed that the rates of heat evolution are directly related to the rates of adsorption, the differences between the rates can be used to optimise the gas separation efficiency over the whole range of the pressures investigated.

A brief investigation of the effect of pressure on the heat of adsorption of NO shows that this gas is very strongly adsorbed on both carbons and that the adsorption that occurs initially at low pressures is to a large extent irreversible. However, after saturation of the surface sites on the carbon with the chemisorbed NO, the additional more weakly adsorbed gas gives much higher increases in the heats of adsorption to those shown by nitrogen or oxygen. This is shown in Figure 6 in which the heats of adsorption after the initial contact of NO with the carbon molecular sieve are monitored during pressure changes between 0 and 2 barg. The first adsorption cycle gives a higher heat of adsorption than the following two cycles for which the heats of adsorption continue to be higher than the heats of desorption. The rates of heat evolution for NO are even slower than those shown by N₂, indicating that even the weaker more reversible adsorption of NO is still much stronger than that of N₂ and O₂. The rates of heat evolution are also relatively low for NO indicating a difficulty that the molecule has in entering and leaving the micropores modified by chemisorption after several cycles of NO adsorption. The subsequent adsorption cycles of O₂ give much higher heats of adsorption and are of longer duration than those obtained on CMS before contact with NO. Clearly the interaction of CMS surface within the pores with NO changes fundamentally the nature of the interaction between the O₂ molecules and the micropores in the CMS.

Figure 5

EFFECT OF PRESSURE ON THE HEAT OF ADSORPTION OF O₂ AND N₂ ON CHEMIVRON BPL AND BERGBAU MS

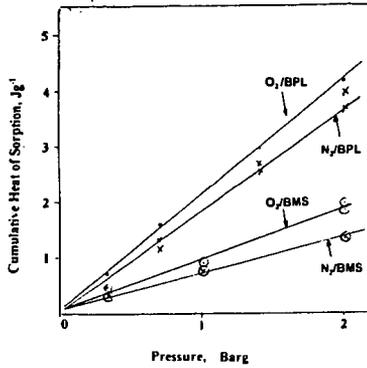
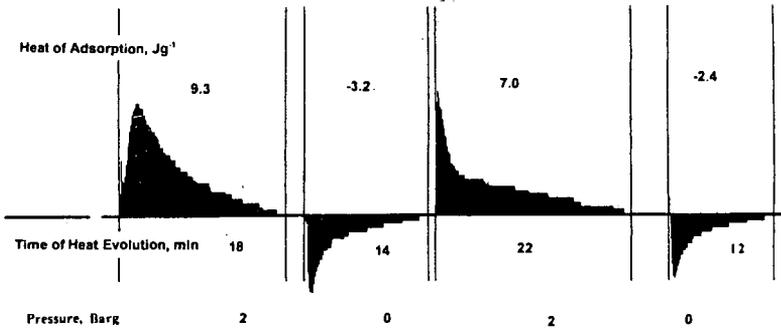


Figure 6

EFFECT OF PRESSURE CHANGES ON THE HEAT EVOLUTION OF NO IN CONTACT WITH BERGBAU MOLECULAR SIEVE AFTER INITIAL IRREVERSIBLE ADSORPTION



Conclusions

The heats of adsorption and desorption of O₂ and N₂ change significantly when the pressure is varied between 0 and 20 barg at room temperature. The changes are much greater for O₂ than for N₂ on carbon molecular sieve, but this effect is not observed for a typical active carbon which adsorbs both O₂ and N₂ with similar intensity and similar rates of adsorption. The work indicates that apart from the sieving action the pore filling mechanism may play an important role in the separation of gases on carbon molecular sieves. The adsorption of NO on microporous carbons is very intense and is partly irreversible. NO modifies the nature of the adsorbing sites in the carbon molecular sieve investigated and makes the adsorption of O₂ on such a modified adsorbent much stronger and apparently more extensive.

References

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