HELIUM ADSORPTION ON ACTIVATED CARBONS AT TEMPERATURES BETWEEN 4 AND 76 K*

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ABSTRACT

Helium adsorption isotherms have been measured for two activated carbons in the 4-76 K temperature range for pressures from 0.1 to 3000 kPa. Such measurements have not been made previously in this temperature and pressure range, but they are needed for the design of an adsorption compressor for helium gas. This paper describes the measurement and analysis techniques for obtaining the adsorption isotherms. The isosteric heats of adsorption are derived from these isotherms. Adsorption isotherms on various charcoals are correlated using the effective adsorbed film thickness as a fundamental parameter.

INTRODUCTION

Activated carbon can adsorb and desorb large amounts of helium gas at high pressures and low temperatures, which makes this material useful for the design of adsorption compressors. An adsorption compressor could replace the mechanical compressor in refrigeration systems where temperatures as low as 4-15 K and high reliability are desired or required, such as satellite applications of the Joule-Thomson refrigerator. The data at low temperatures and high pressures are also useful for the design of regenerators utilizing adsorption of helium to provide a high effective heat capacity.

The design of adsorption compressors requires a knowledge of the mass adsorbed as a function of temperature and pressure. An extensive literature search has failed to discover data published within the range of pressures and temperatures of this study.

This paper presents measurements of helium adsorption isotherms on two different activated carbons for the temperature range from 4 to 76 K and pressures from 0.1 to 3000 kPa. It also presents the heat of adsorption derived from these isotherms.

EXPERIMENTAL TECHNIQUE

Figure 1 shows a schematic of the experimental adsorption apparatus. The calibrated volume was filled by passing helium gas through a charcoal trap, cooled by liquid nitrogen to remove any impurities. The pressure and temperature of the helium in the calibrated volume were measured using a 5 MPa capacitive pressure transducer and a platinum resistance thermometer, respectively.

Valve V_1 between the calibrated volume and the copper adsorption cell was then opened to allow an increment of the helium gas into the adsorption cell. The adsorption cell contains an internal copper grid structure to enhance thermal equilibrium within the activated carbon, a poor heat conductor. Valve V_1 was closed and the temperature and pressure of the calibrated volume and the adsorption cell were measured. Both the total amount of mass introduced into the adsorption cell from the calibrated volume and the amount of gas in the adsorption cell void space, which has not been adsorbed, were determined by using the density of the gas from the NBS equation of state for helium.[1]

The pressure and temperature of the helium gas in the adsorption cell were measured using another 5 MPa capacitive
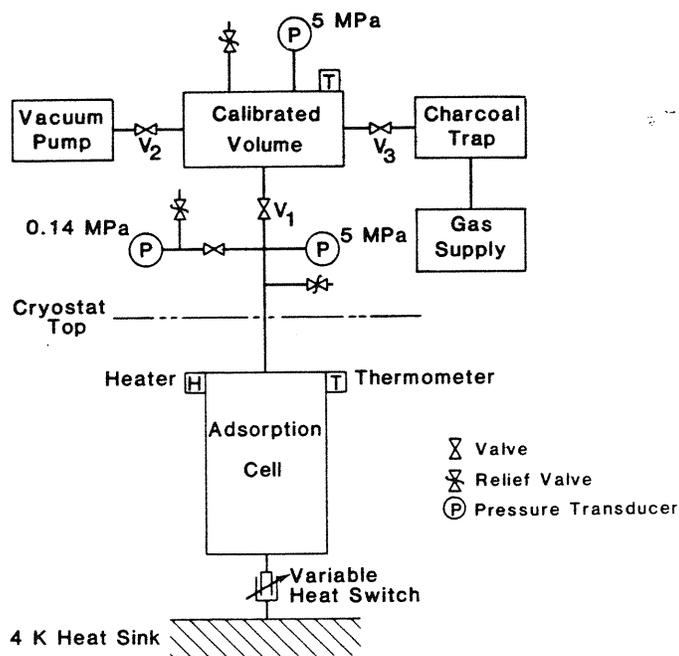

Fig. 1. Experimental apparatus

pressure transducer and a germanium resistance thermometer. The temperature of the adsorption cell was controlled using a resistance heater and a heat switch connected to a liquid helium bath maintained at 4 K.

Two different procedures were used to take adsorption data. The first procedure consisted of filling the adsorption cell with a measured amount of helium gas and changing the conditions in the cell by cooling or heating it, taking adsorption or desorption data along constant mass lines. This process of cooling and heating provides a method to determine any hysteresis in the adsorption (desorption) process. Within the experimental uncertainty, no detectable difference was found between both processes. The second procedure consisted of keeping a constant temperature in the cell and adding known amounts of helium gas to the cell. The higher temperature isotherm data and the 4 K data were taken using this procedure. A detailed description of this experimental technique and apparatus is found elsewhere.[2]

SAMPLE CHARACTERIZATION

The two different activated carbons used in this study were Barnebey-Cheney, type 580-26 (also referred to as carbon A) and Saran A, 100% PVDC (also referred to as carbon B).** Carbon A is a coconut shell charcoal, -18+25 U. S. standard sieve. Carbon B is in the form of 0.5-0.8 mm diameter spheres. Table 1 shows the experimental parameters for each activated carbon. The surface areas of the carbons were estimated by using N_2 with the BET method.[3,4,5]

The apparent density is defined as the mass of adsorbent per unit cell volume. The total cell volume (69.3 cm^3) consisted of the volume occupied by the carbon solid, the macroscopic void volume (macropore volume and interparticle volume) and the micropore volume. Figure 2 shows scanning electron micrographs (SEM) of the carbon A and carbon B. The macropore and interparticle space can be clearly identified. The micropore volume has linear dimensions of the order of nanometers and cannot be identified in these pictures.

Table 1.   Sample parameters

Type	Carbon A	Carbon B
Mass, ±0.005 g	26.48	40.51
Specific surface area, ±10 m²/g	1474	1161
Apparent density, ±0.002 g/cm³	0.382	0.585
Micropore volume*, ±1.7%	26.6	24.7
Macroscopic void volume*, ±1.7%	58.0	47.0
Solid volume*, ±1.7%	15.4	28.3

* percent of the total cell volume

** Trade names are given here in order to fully characterize the samples, but it does not represent an endorsement by NBS. Other manufacturer's products may work as well or better.

Barnebey–Cheney 580-26   1 μm   Saran A, 100% PVDC   1 μm
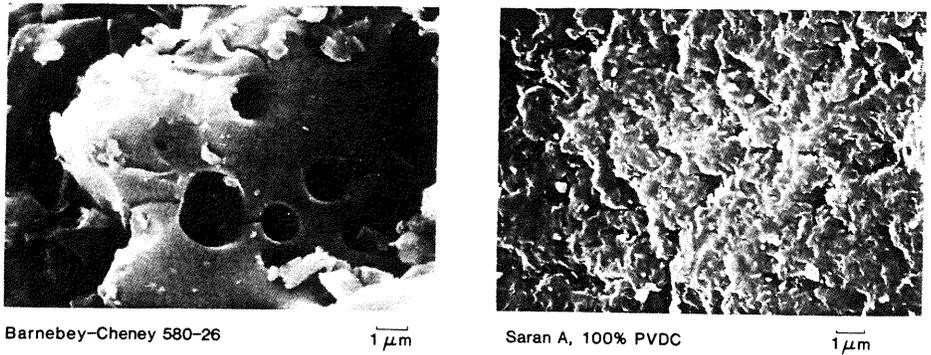
Fig. 2. Scanning electron micrographs for the Barnebey-Cheney 580-26 (carbon A) and the Saran A, 100% PVDC (carbon B).

     The total void volume in the cell was measured using helium gas at room temperature.[2] The micropore volume was calculated by dividing the mass of adsorbed nitrogen at saturation by the density of liquid nitrogen at saturation.

RESULTS

     Figures 3 and 4 show the helium adsorption isotherms for the carbon A and carbon B, respectively. The specific mass adsorbed (M_a) is plotted as a function of pressure where M_a is calculated by subtracting the mass of He in the void volume of the cell from
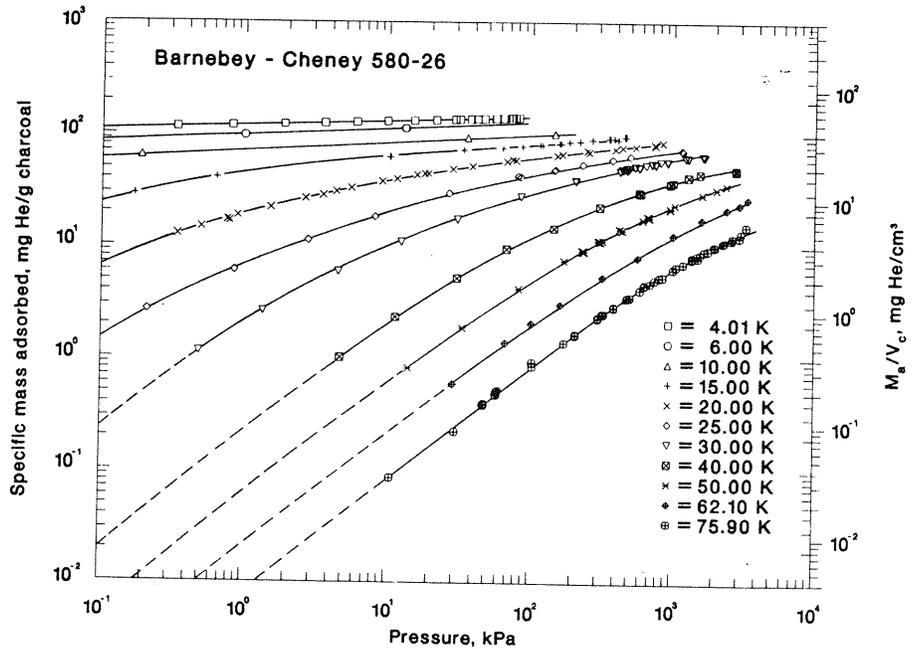

Fig. 3. Helium adsorption isotherms for the Barnebey-Cheney 580-26 (carbon A).
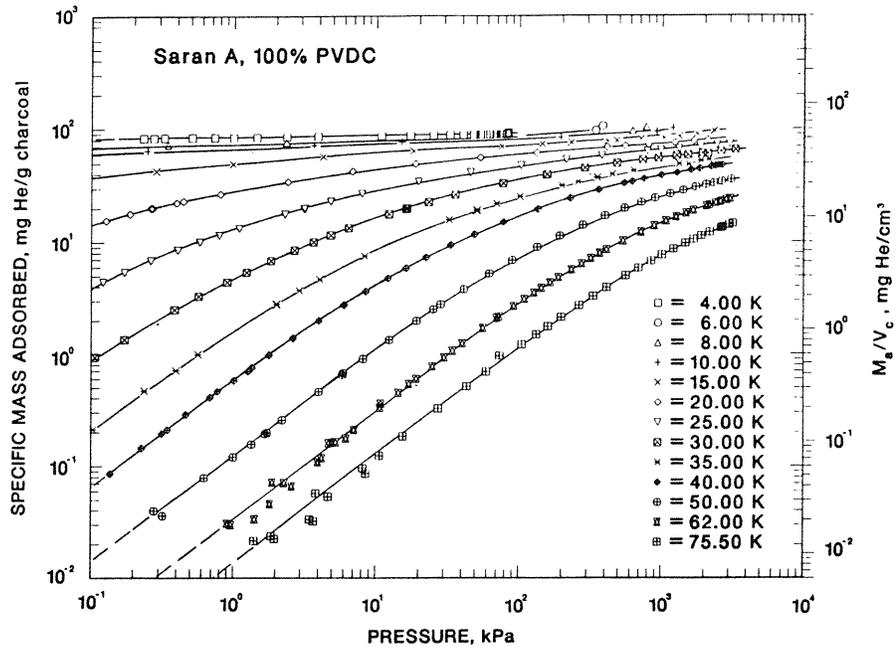
Fig. 4. Helium adsorption isotherms for the Saran A, 100% PVDC (carbon B).

the total amount of He mass in the cell, where the void volume of the cell does not include the volume occupied by the adsorbed film. Even though there are no known measurements of the specific volume of the adsorbed film for this pressure and temperature range, the Van der Waals volume b, (23.7 cm³/mol) should be a good representation of it[7] and was used here to obtain an approximate value of M_a. The value M_a is the mass equivalent of the STP volume (V_e), used by Chan, Tward and Boudaie[8] for H_2, Ne, and N_2 adsorption on activated carbon.

A linear behavior is observed in the 75.9 K isotherm at low coverage for carbon A and in the higher temperature isotherms for carbon B. Such behavior is theoretically predicted at low coverages by Henry's law and is the two dimensional analogue to the ideal gas law.[4] The dashed lines at low coverage for the carbon A represent Henry's law. At low coverage carbon A and B adsorb about the same amount per gram of carbon, but because of its higher density, carbon B adsorbs more per unit volume. Carbon B quickly saturates at a monolayer whereas carbon A continues to adsorb beyond the monolayer. At high coverage the mass adsorbed per unit volume is about the same for both carbons.

The carbon B isotherm data, at high coverages and temperatures from 6 to 15 K, shows a rapid increase in the amount of mass adsorbed with respect to pressure. This behavior is believed to be a consequence of a transition from a dense two-dimensional fluid to a two-dimensional solid.[9] Similar behavior probably exists with the carbon A but that region was not studied.

ISOSTERIC HEAT OF ADSORPTION

A thermodynamic analysis of an isosteric process[2], constant M_a, yields the equation

$$q_{st}/R \quad = \quad -Z \left(\frac{d\ln P}{d(1/T)} \right)_{M_a} , \qquad (1)$$

where q_{st} is the isosteric heat of adsorption, R the gas constant, Z the compressibility factor, P the pressure, and T the temperature. This equation has been derived from the Clausius-Clapeyron equation[2] where the specific volume of the adsorbed phase (high density gas) has been ignored. In this analysis Z=1 was used since in the region of this calculation $|Z-1| < 0.05$. The slope of the plot of ln P versus 1/T at constant M_a gives q_{st}/R. A value of $|Z-1| = 0.05$ would occur only for the highest pressures and represents, in the worst case, only one of about 4 or 5 data points used to determine the slope of ln P versus 1/T. The resultant error in q_{st}/R is about 1%, which is less than the 3-5% uncertainty of q_{st}/R.

Straight lines are obtained when each isostere is plotted as ln P versus 1/T, confirming the independence of q_{st}/R with respect to temperature over the studied range.[2] Figure 5 shows q_{st}/R versus the specific amount of mass adsorbed. A rapid change of q_{st} is observed at the monolayer completion at about 70 mg/g for both carbons.
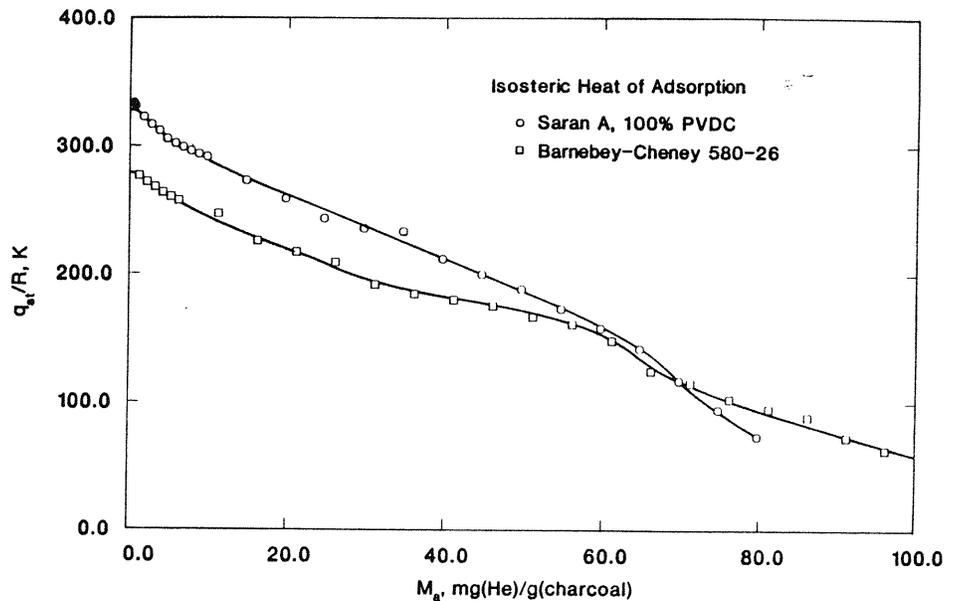

Fig. 5. Isosteric heat of adsorption for the Barnebey-Cheney 580-26 (carbon A) and the Saran A, 100% PVDC (carbon B).

GENERALIZED CORRELATIONS

Some analytic expressions for the mass adsorbed as a function of temperature and pressure have been developed by different investigators. The adsorption isotherm data studied here have been compared to some of these correlations.

Kidnay and Hiza[10] represent their He adsorption data using the Dubinin correlation[6] in which the volume of adsorbed helium, V_t, is a function only of the volumetric adsorption potential (ϵ), in which

$$\epsilon = (RT/V_\ell) \ln(P_s/P), \qquad (2)$$

where V_ℓ is the specific volume of the adsorbate in the liquid phase at the normal boiling point, R is the gas constant, T the temperature, P the pressure and $P_s = (T/T_c)^2 P_c$ is the equivalent saturation pressure above the critical temperature. V_t is analogous to the adsorbed mass, M_t, which is not the same as the previously discussed M_a. It represents the mass of the adsorbate within the micropore volume (total mass of helium in the cell minus the mass within the macroscopic void volume). This study's 76 K adsorption isotherm data for the carbon A agrees very well with the 76 K isotherm data of Kidnay and Hiza when comparing the mass adsorbed per unit surface area.[2]

For Ne, H_2 and N_2 Chan, Tward and Boudaie[8] used the Maslan correlation[11], which is similar to the Dubinin correlation except that the saturation pressure above the critical point was taken as

$$\ln P_s = A + B/T, \qquad (3)$$

where the A and B coefficients are obtained from a linear least squares approximation of the adsorbate saturation values below the critical temperature. They found that the log of mass adsorbed is linear with respect to the adsorption potential, ϵ.

Figure 6 shows that the carbon B isotherm data does not show linear behavior using the Maslan correlation when the log of the effective film thickness, t_a, is plotted versus ϵ. The t_a, analogous to M_a, is equal to M_a divided by the density of the adsorbed film and the adsorbent surface area. It is used instead of M_a with the purpose of later comparison between different adsorbates and adsorbents. Not only do the curves deviate from linear behavior, but there is a temperature dependence as well for temperatures above 20 K. The dashed lines in Figure 6 represent the 4 K and the 76 K isotherms for the carbon A. Again, deviation from linearity and a temperature dependence are observed. The Dubinin correlation also shows a temperature dependence above 20 K and a deviation from straight-line behavior for log t_a versus ϵ.[2]

SUMMARY AND CONCLUSIONS

Extensive data on the He adsorption isotherms of two activated carbons have been presented in the pressure-temperature range proposed for the operation of an adsorption compressor, a range which had not been studied previously. Henry's law is observed at low coverages in both carbons. The derived isosteric
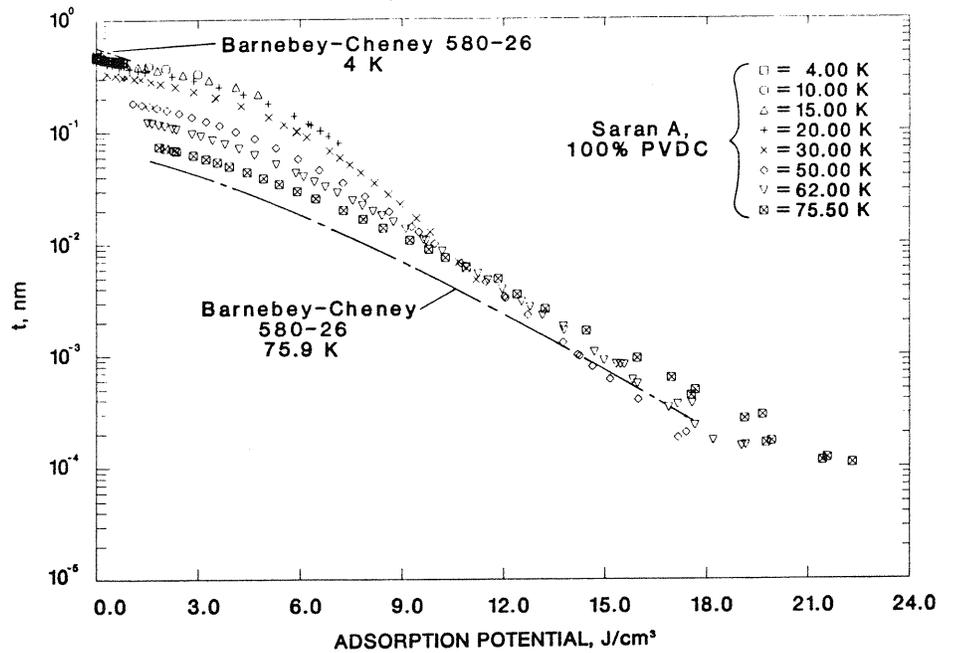
Fig. 6. Helium adsorption isotherms for the Saran (carbon B)
using Maslan correlation[11]. The dashed lines are the 4 K
and 76 K isotherms for Barnebey-Cheney.

heat of adsorption shows a rapid decrease at the expected
monolayer completion. The two carbons behave somewhat differently
when comparing the amount adsorbed per unit surface area. The two
commonly used correlations do not satisfactorily represent the
data over the wide range of pressure and mass adsorbed studied
here because of an additional temperature dependence not account-
ed for by the correlations. Further correlation studies are
needed.

ACKNOWLEDGEMENTS

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