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Adsorption of NO and N_2O on Charcoal between 195 and 300 K[1]

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The adsorption–desorption isotherms of nitric and nitrous oxide have been measured on activated charcoal in the temperature range of 195 to 300 K. Also, argon isotherms at 77.3 and 77.7 K and nitrogen isotherms at 77.7, 90, and 215 K were measured. The equivalent surface area was measured yielding a value of 1082 m^2/g. Apparent adsorption energies were calculated, as a function of temperature, from the isotherms, using BET and Langmuir–Fowler equations. The ratio of the amount of gas not released during desorption to the total amount which should have been released is also given as a function of temperature. From the nitrogen desorption isotherm at 77.7 K a distribution of the average pore size was determined.

INTRODUCTION

In this work we measured isotherms for nitric oxide and nitrous oxide in the region between 195 and 300 K on charcoal using the volumetric method. A search of the literature showed that very few investigations had been made for nitric oxide (*1*) and nitrous oxide (*2*, *3*) on carbon surfaces at the temperatures studied.

Hysteresis was found in the isotherms measured, even the nitrogen (77.7 K), showing that pores are probably *the main* factors responsible for the hysteresis and not chemisorption as claimed by Smith *et al.* (*1*). The substrate surface area was determined from the argon isotherm using the monolayer volume obtained by the Point B method. From the nitrogen desorption isotherm at 77.7 K a distribution of the average pore size was determined. Since hysteresis was found in most cases and because the charcoal has pores with different shapes and sizes, all the quantities determined from the measurements are called apparent since it is very difficult to separate the several phenomena which might contribute to these quantities. The apparent adsorption energies were determined as a function of temperature as was the ratio of the amount of gas not released to the total amount which should have been released during the desorption measurements.

EXPERIMENTAL

The cryostat used for these measurements consisted of the sample cell, containing 0.50 g of charcoal, connected to the top of the cryostat by a Cu–Ni tubing 0.318 cm in o.d., 0.216 cm in i.d., and 16.0 cm in length. From the top of the cryostat the sample cell was connected to the gas handling system and to a Texas Instruments precision pressure gauge (Model 145-02), by 0.318-cm-o.d. copper tubing with a total volume of 32.5 cm^3. In order to vary the sample temperature

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a heater (110 Ω) made of Evanohm No. 36 wire was, wound bifilarly around the cell. A platinum resistance thermometer, with a resistance of 420 Ω at room temperature, served as sensor and was connected along with the heater to an Artronix Model 5301 temperature regulator, capable of regulating the temperature to within ±0.05 K. Temperatures were measured by a copper–constantan thermocouple properly calibrated and maintained during all experiments at a fixed and identical reference. Surrounding the sample cell was a 3.18-cm-i.d., 16.50-cm-long vacuum jacket of connected to an oil diffusion pump system isolated from the cryostat by a liquid nitrogen trap. This high-vacuum system was also used to pump out the sample cell after each run.

The charcoal used was activated cocoanut charcoal, 6.14 mesh on the average, supplied by Fisher Scientific Co., and the gases used were NO with a purity of 98.5%, supplied by Union Carbide, and N_2O with a purity 98.0%, supplied by Matheson Gas Products. The vacuum jacket containing the sample cell was placed in a mixture of dry ice and acetone for all measurements except those at 300 and 77 K. The adsorbed volumes are given at STP and void volume corrections were made for all isotherms. Thermomolecular corrections were not necessary because in all cases they were less than about 1% for pressures above 1 Torr. Void volume was measured at room temperature using He^4 gas which was passed through a charcoal trap at 77 K and the final equilibrium pressure was measured with the Texas Instruments precision pressure gauge. Before each isotherm was taken the sample was heated up to 65°C, being pumped with the high-vacuum system for 12 hr. The argon gas from Matheson Gas Products had a purity of 99.998%, and the nitrogen, 99.5% pure, from White Martins S.A., was further purified by passage through a charcoal trap at 195 K.

RESULTS

The apparent surface area of the adsorbent was determined from the adsorption isotherm of argon at 77.3 K. In the literature one finds many discussions about the validity of the surface area determination using several other inert gases. The argon isotherm was used following the arguments given by one of us (*4*) and the apparent surface area Σ was calculated from the equation $\Sigma = 0.296\,\sigma V_m$, where σ is the molecular area of the argon gas in its solid state, $\sigma = 11.5$ Å^2 and V_m is the monolayer volume which was determined from the Point B method [see Young and Crowell (*5*)]. Two argon isotherms were measured during the present work, one at the start of the experiments and the other at the very end. According to the first, $V_m = 318.0$ cm^3/g, and from the second, $V_m = 338.0$ cm^3/g, both by the Point B method. As can be seen there was a difference of about 6% between the two isotherms in a space of almost 1.5 years. This might indicate that no major changes occurred in the adsorbent due to possible reactions with the adsorbates. Figure 1 shows the last argon isotherm which also shows a possible hysteresis to be discussed later in this paper.

The apparent surface area of the adsorbent was calculated to be 1082 m^2/g for an apparent total area of 541 m^2. Figures 2 and 3 show the isotherms for NO and N_2O in the temperature interval of 195 to 300 K. The data are reproducible within an experimental uncertainty of 6% and all isotherms showed hysteresis. Figures 4 and 5 give typical isotherms showing adsorption and desorption for the lowest and highest temperatures measured for NO and N_2O. Nitrogen isotherms were measured at 77.7, 90, and 215 K; the first shows hysteresis as can be seen in Fig. 6. From the nitrogen desorption isotherm at 77.7 K using Kelvin's equation (*6*) a distribution of the average pore size of the

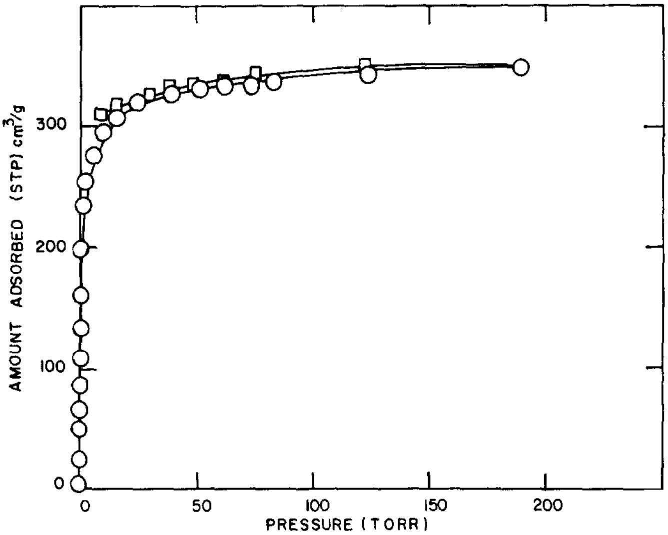

FIG. 1. Adsorption of argon on charcoal at 77.7 K. (○) Adsorption; (□) desorption.

pores contributing to the hysteresis was determined and it is shown in Fig. 7.

DISCUSSION

Charcoal is a very porous material having a wide distribution of pore sizes and therefore presents itself as a most complex surface as an adsorbent. In most active charcoals the pore sizes are distributed according to Dubinin (*7*) in three categories; macropores with diameters above about 200 Å, transitional or intermediate between 20 and 200 Å, and micropores below 20 Å. Hysteresis due to porous materials is discussed in detail by several authors (*8–15*) and actually the main contribution to the hysteresis is due to the transitional pores since micropores are

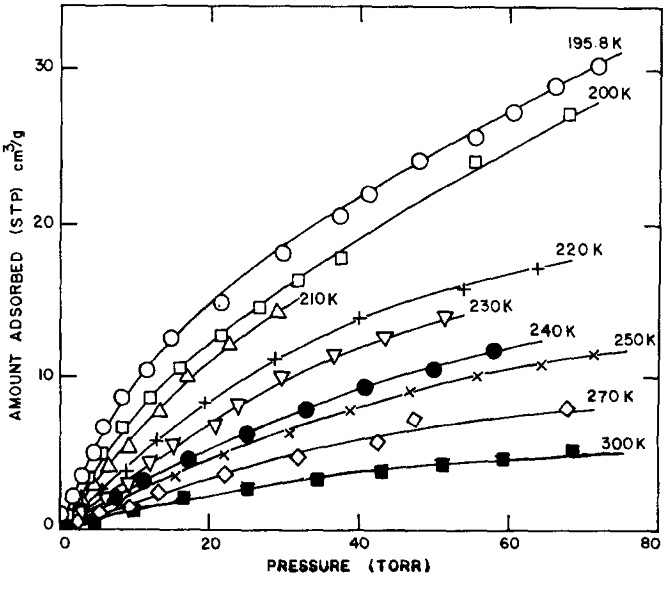

FIG. 2. Adsorption isotherms for NO on charcoal at indicated temperatures.

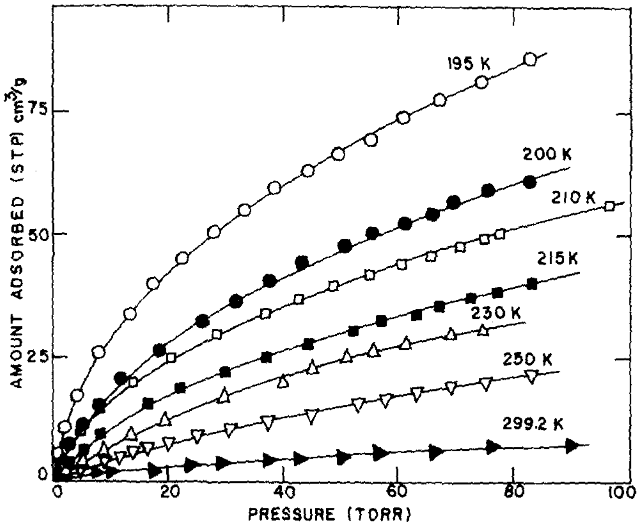

FIG. 3. Adsorption isotherms for N_2O on charcoal at indicated temperatures.

filled before the hysteresis starts, and macropores are easily emptied which doesn't occur with the transitional pores due to effects, such as the "ink bottle" effect, as discussed among others by Dacey (*10*). Almost all the isotherms measured in this work show hysteresis and since the charcoal used has pores with different shapes and sizes we felt that any quantity determined from our measurements is not absolute and therefore we called them surface area, apparent monolayer coverage, etc.

According to Everett (*11*) the hysteresis phenomena are frequently temperature dependent. Considering the adsorption–de-

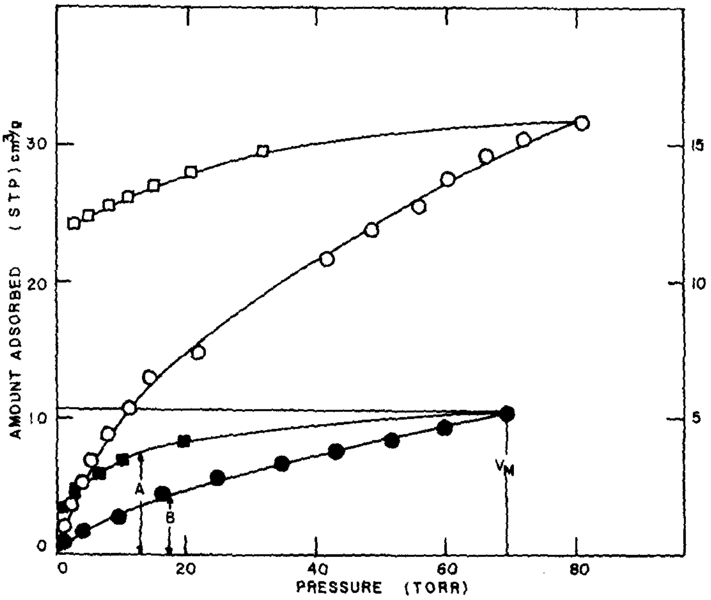

FIG. 4. Adsorption–desorption isotherms for NO on charcoal. (○) Adsorption, (□) desorption at 195.8 K, using left-hand scale. (●) Adsorption, (■) desorption at 300 K, using right-hand scale.

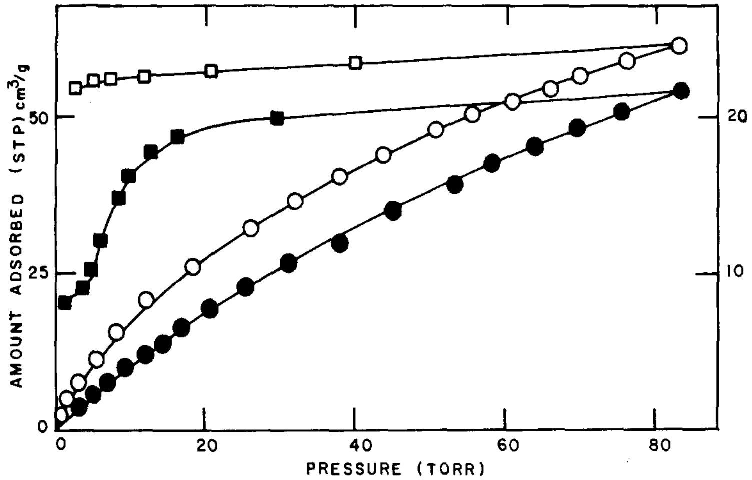

FIG. 5. Adsorption–desorption isotherms for N_2O on charcoal. (○) Adsorption, (□) desorption at 200 K, using left-hand scale. (●) Adsorption, (■) desorption at 250 K, using right-hand scale.

sorption isotherms obtained in this work we calculated from them the ratio of the amount of gas not released to the total amount which should have been released if the process were reversible. The quantities that appear in this ratio,

$$R = (A - B)/(V_M - B),$$

are indicated in Fig. 4 and the results obtained from Figs. 4 and 5 are given in Table 1 as a function of temperature. We considered R at 5 and 20% of the maximum pressure reached in each isotherm. It can be seen that, at 20%, where the desorption isotherms are quite flat, there is an almost constant value of R indicating that a very small amount of gas is being released. As smaller pressures are approached there is a rapid release which is larger at higher temperatures, i.e., the ratio decreases as the temperature increases indicating that the hysteresis ob-

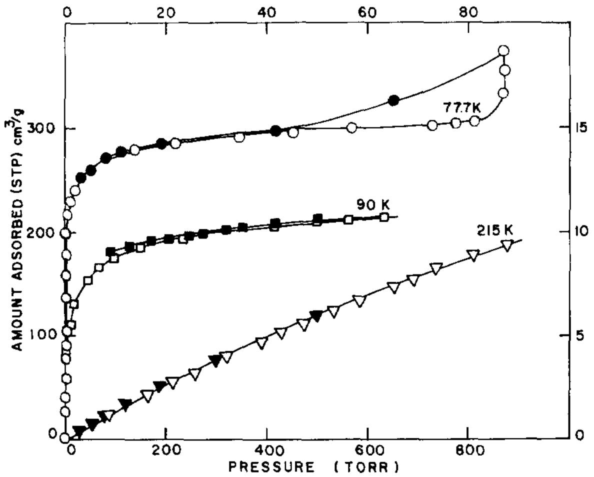

FIG. 6. Adsorption–desorption for N_2 on charcoal at indicated temperatures. Open symbols, adsorption; closed symbols, desorption. 215 K isotherm, right-hand and top scales; 90 K isotherm, left-hand and top scales.

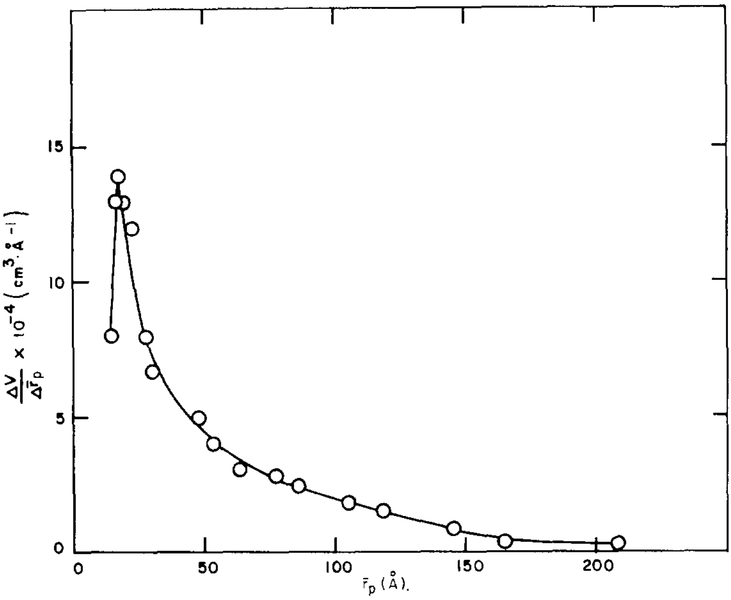

FIG. 7. Average pore size distribution curve from the nitrogen isotherm at 77.7 K.

tained is due mainly to pores which are being emptied faster as the temperature increases.

From the nitrogen desorption isotherm at 77.7 K, using Kelvin's equation,

$$\ln (p/p_o) = \frac{-2V\gamma}{r_K RT} \cos \phi,$$

where V (34.68 cm/mole) is the molar volume of the adsorbate in its liquid state, γ (8.72 dyne/cm) is the surface tension, and ϕ is the angle of contact between the liquid and the walls of the pores and is taken as equal to zero ($\phi = 0$) for simplification, we calculated the effective pore radius, r_K, for which the capillary condensation occurs at relative pressure p/p_o. Using the relation $V_s = X_s/\rho$, where V_s is the volume of all the pores which have radii up to and including r_s, X_s is the total amount on the isotherm at p_s/p_o, and ρ (0.81 g/cm³) is the liquid density, a curve of V_s as a function of r is constructed. This radius r is the radius calculated from Kelvin's equation corrected for the thickness, t, of the amount adsorbed on the pore walls ($r = r_K + t$).

$$t = 3.5\,[5/\ln (p_o/p)]^{\frac{1}{3}} \quad \text{[Ref. (6)]}.$$

From this curve the average pore size distribution $\Delta V/\Delta \bar{r}_p$ versus $\bar{r}_p$ is calculated taking slopes of this curve at small intervals of r. This distribution is shown in Fig. 7 where it can be seen that the main contribution to the hysteresis is from in-

TABLE 1

Ratio of the Amount of Gas not Released to the Total Amount Which Should Have Been Released at 5 and 20% of the Total Pressure

T (K)	R for NO		R for N_2O	
	(5%)[a]	(20%)	(5%)	(20%)
195.8	0.74	0.77	—	—
200.0	—	—	0.88	0.86
215.0	—	—	0.89	0.88
220.0	0.71	0.74	—	—
230.0	—	—	0.62	0.80
240.0	0.68	0.79	—	—
250.0	0.66	0.79	0.39	0.81
270.0	0.44	0.71	—	—
299.2	—	—	—	—
300.0	0.38	0.54	—	—

[a] Percentage of total pıessure.

termediate pores, according to Dubinin's classification, as expected. Kelvin's equation was used even knowing its limitations as discussed by Gregg and Sing (*6*), but, as was said before, charcoal has a very complex structure and no known equation would describe exactly the pore distribution; therefore Kelvin's equation was considered a reasonable approximation and the result obtained seems to indicate once more that the main contribution to the hysteresis is due to the pores and not to chemisorption.

Smith *et al.* (*1*) measured isotherms of NO on Graphon and Su-60 substrates and found that, for Su-60 (activated sugar charcoal, a highly porous material), the isotherms at 195 and 273 K showed a hysteresis not obtained with Graphon. They attributed their results to chemisorption and, from the analysis of the adsorbed gas at 195 and 273 K, concluded that NO reacts with the carbon resulting in CO_2, CO, and mostly N_2 having no reaction at 119 K. The authors didn't mention if they checked the 119 K isotherm on Su-60 for hysteresis. Also because no other authors found hysteresis in their adsorption measurements of NO on nonporous carbon surfaces we are led to conclude that the hysteresis found in this work is *mainly* due to the charcoal's porosity and not to chemisorption although we believe that some chemisorption takes place but at a small rate. The shape of our isotherms indicate that they might be a combination of physical adsorption on top of chemical adsorption as discussed by Emmett and Brunauer (*16*) and also by Adam (*15*). This shouldn't be a surprise because the charcoal's surface is probably mostly oxidized to begin with, and most of the oxygen is not removed by the heat treatment given before each measurement; therefore there is only a minor area of the surface where NO might be directly chemisorbed on the charcoal. The oxygen layer not only influences the properties of the charcoal surface but also reduces the sizes of the pores which in turn dictates the shapes of the hysteresis curves as discussed by Adam (*15*). If the coverage of the oxygen on the charcoal is very extensive one might say that the surface behaves more like a carbon oxide than a carbon surface. The apparent adsorption energies, $E_1 = E_1(T)$, for N_2O were obtained from the BET equation,

$$\left(\frac{p}{p_0 - p}\right)\frac{1}{V} = \frac{1}{V_m C} + \left(\frac{C-1}{V_m C}\right)\frac{p}{p_0},$$

where $C = \exp(E_1 - E_v/RT)$. E_v is the heat of vaporization given as a function of temperature (*17*). The apparent integral adsorption energies were calculated from the Langmuir–Fowler (*18*) equation,

$$p/V = (1/bV_m) + (p/V_m),$$

with $b = \{h^3/[(2\pi m)^{\frac{3}{2}}(kT)^{\frac{5}{2}}]\}e^{U/kT}$, where U is the integral adsorption energy, being the difference between the total energies of the molecule in its gaseous and adsorbed phases. The values obtained for these energies are presented in Table 2. The only data found in the literature for the adsorption of NO on charcoal with which we could compare our results are

TABLE 2

Apparent Energies for N_2O and NO[a]

T (K)	E_{BET} (kcal/mole)	E_{INT} (kcal/mole)	
	N_2O	N_2O	NO
195.0	4.90	7.15	—
200.0	4.98	7.30	7.06
210.0	5.14	7.68	—
215.0	5.25	7.87	—
220.0	—	—	7.58
230.0	5.20	8.13	7.88
240.0	—	—	7.96
250.0	5.60	8.87	8.20
270.0	—	—	8.80
299.2	6.10	10.90	—

[a] For explanation, see text.

those by Favre (*2*) who reported a value of 7.40 kcal/mole at room temperature for the heat of adsorption (not specifying which heat of adsorption) and by Gregg (*3*) who found differential heats of adsorption of 7.18 kcal/mole at 273 K and 7.44 kcal/mole at 313.4 K.

For the NO we used only Langmuir–Fowler equation since our experimental temperature interval is above its critical temperature. The reference found in the literature for the same temperature interval was that of Smith *et al.* (*1*) but they do not give any values for adsorption energy.

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