JOURNAL OF THE TENNESSEE ACADEMY OF SCIENCE
VOLUME 66, NUMBER 3, JULY 1991

FREON 12 AND FREON 22 ADSORPTION AND FREON 12 BET SURFACE AREAS FOR CARBON POWDERS

THOMAS R. RYBOLT, MICHAEL D. WALL, WILLIAM J. COULTER III, and PHILIP C. CLAIBORNE
The University of Tennessee at Chattanooga
Chattanooga, Tennessee 37403

ABSTRACT

Dichlorodifluoromethane, Freon 12, and chlorodifluoromethane, Freon 22 are shown to exhibit significant adsorption on activated carbon powders at room temperature. Freon 12 adsorption at 295 K gives BET surface areas for a series of five carbon powders that correlate with conventional surface areas from nitrogen adsorption at 77 K. These results suggest that room temperature Freon adsorption might be a useful method to determine surface areas in routine analysis of certain powders. In addition, the extent and rate of adsorption support the use of carbon powders to trap chorofluorocarbon molecules such as Freon 12 and Freon 22.

INTRODUCTION

There is considerable concern about the tendency of certain halogenated compounds to reduce the concentration of ozone in the stratosphere. It is well known that stratospheric ozone filters out ultraviolet radiation, and it has been estimated that for each 1% drop in ozone concentration there is a 2% increase in the most harmful ultraviolet radiation which reaches the earth (Zurer, 1988). While efforts are ongoing to replace the more widely used and harmful halogenated compounds with ones less damaging to the ozone layer and to reduce future use of these compounds, it is also desirable to gather more information about how these molecules might be trapped by solid adsorbents. We have studied the extent to which dichlorodifluoromethane, Freon 12, and chlorodifluoromethane, Freon 22, are adsorbed by carbon powders over a range of surface area.

A standard method for determining surface area is based on the BET, Braunauer-Emmett-Teller, equation (Lowell, 1979) and although variety of adsorbate gases at different temperatures have been used (Gregg, 1982) the method normally depends on nitrogen gas adsorption at liquid nitrogen temperature of 77 K.

In a previous study (Rybolt, 1986), adsorption of acetic acid from solution and gas-solid chromatography using an argon adsorbate were used to generate Langmuir and Henry's law virial surface areas, respectively. These areas were compared to nitrogen BET areas for five carbon powders. In the present investigation, the adsorption of Freon 12 at 295 K is used to determine BET surface areas that are compared to the conventional nitrogen BET method for these same five powders. The carbon powders span a range of surface area and porosity and include Mexican Graphite (MG), Aqua Nuchar (AN), Nuchar S-C (SC), Nuchar S-A (SA), and Super Sorb (SS).

The purpose of this investigation is to determine the extent to which Freon 12 is adsorbed on carbon powders and to compare and correlate the carbon powder BET areas obtained from Freon 12 with those obtained with nitrogen.

Previous investigations of adsorption have included Freon 12 (Skazyvaev, 1983) and Freon 22 (Diawara, 1986) on zeolites and Freon 22, 113 (Plokhov, 1977), Freon 113 (Drzal, 1976), Freon 12 (Skazyvaev, 1983), and Freon 112 (Ikezawa, 1972) on carbon powders. In addition, patents have been developed to use activated carbon powders to remove low concentrations of chlorofluorocompounds from the air in industrial processing situations (Hattori, 1978; Kurashiki, 1982; Asakura, 1987). In our work, we investigated the direct adsorption of large quantities of Freon 12 and Freon 22 from the pure gas.

THEORY

The BET equation may be written as

$$P/[N_a (P_o-P)] = 1/(N_m c) + [(c - 1)/(N_m c)] [P/P_o] \quad (1)$$

where N_a is the moles of gas adsorbed per gram of powder at a relative pressure of P/P_o, N_m is the moles adsorbed at monolayer coverage, P_o is the saturation pressure of the adsorbate, and c is a constant related exponentially to the magnitude of the adsorbent-adsorbate interaction (Brunauer 1938). The BET model assumes multilayer adsorption and the balancing of adsorption and desorption for each surface layer is used to derive Equation (1).

For many adsorbents a plot of $P/[N_a (P_o-P)]$ versus $[P/P_o]$ gives a linear region which is typically from $[P/P_o] = 0.05$ to 0.3. The slope and intercept are used to find N_m and c where $N_m = 1/(\text{slope}+\text{intercept})$ and $c = 1+(\text{slope}/\text{intercept})$. The specific surface area, A (m^2/g), is found from

$$A = N_m L a_m \quad (2)$$

where N_m is the moles adsorbed per gram of adsorbent, L is Avogadro's number, and a_m is the area occupied by one adsorbate molecule. For nitrogen adsorption at 77 K the value of a_m is generally taken to be 16.2×10^{-20} m^2/molecule (Sing 1985). Although the surface area for microporous adsorbents obtained from Eq. (2) is known to include contributions due to condensation in pores and thus to overestimate true surface area it is the most widely used method to compare powder areas.

MATERIALS AND PROCEDURES

The carbon powders used included Mexican Graphite (No. 25 Lubricating Graphite from the United States Graphite Co.), Aqua Nuchar, Nuchar S-C, Nuchar S-A (provided by Westvaco Chemical Division), and Super Sorb (provided by Amoco Research). The Nuchar S-C powder was filtered through an 80 mesh (177 micron) sieve to remove larger particles. The other powders were not filtered prior to use.

Nitrogen Gas Adsorption

Nitrogen BET surface areas were determined for each of the carbon powders with a Micromeritics Instrument Corporation Digisorb 2500 Automatic Pore Volume and Surface Area Analyzer. As discussed previously (Rybolt 1986), this instrument generates computer controlled nitrogen isotherm data at 77 K.

Dichlorodifluoromethane Gas Adsorption

The sample carbon powders were degassed under vacuum for two hours at temperatures greater than 400K. These conditions previously had been observed to be effective in removing adsorbed water vapor from these powders. (Rybolt 1981).

Samples of degassed powders in the range of 0.7 to 2.2 g and weighed to the nearest 0.001g with a Mettler PC180 balance were placed in 14x45mm glass vials and stoppered with glass wool. A set of vials representing all five samples was placed in a vacuum chamber, and a rotary vacuum pump was used to obtain a vacuum. Dichlorodifluoromethane, from a standard metal can of automotive DuPont Freon12, or chlorofluoromethane, from a can of fixed air conditioner refrigerant Freon 22, was admitted to the chamber, a Precision Thelco model 19 vacuum oven, until the desired initial pressure was obtained. (Caution: commercial cans of Freon should never be refilled or pressurized as the vessel is not designed for high pressure). The inlet valve was closed, and the adsorption allowed to take place for the desired time.

The vials were removed from the chamber for weighing. Masses of the sample vials before and immediately after adsorption were determined and the increase in mass used to determine the amount of gas adsorbed on the powder samples. Control vials with no powder were used to correct the mass gain for small amounts of Freon 12 in the empty space in the vials between the powder and glass wool.

Note that in this procedure it is possible to run many different sample powders simultaneously since each solid will reach its own equilibrium with the final observed pressure and many vials can be placed in the vacuum chamber at the same time. This would be ideally suited for a one point BET method since only one pressure reading is required.

The gas pressure was read from a gauge attached to the vacuum chamber. The relative gauge readings were converted to an absolute pressure based on a 13 point linear, correlation coefficient R=0.9999, calibration with a mercury manometer. The conversion is P(torr) = 762.8 - (24.90)G, where G is the gauge reading in inches of mercury vacuum.

Final equilibrium adsorption pressures for Freon 12 of 0.325, 0.466, 0.597, 0.761, and 0.804 atm were obtained at an adsorption temperature of 295K. These pressures correspond to relative pressures of 0.0550, 0.0788, 0.101, 0.129, and 0.136, respectively. These values are based on a saturation pressure of Freon 12 of 5.913 atm at T = 295 K which was obtained from the equation $P_o = 3.094 + 0.09156T + 0.001663T^2$ which is based on available data (Weast 1981) where T is the temperature in Celsius (T=22).

RESULTS AND DISCUSSION

Nitrogen and Dichlordifluoromethane BET Experiments

Table 1 reports the slope, intercept, and correlation coefficient R values for BET plots based on Eq. (1). The BET plot for each powder was based on five adsorption points in the P/P_o range of 0.05 to 0.22 obtained from the Digisorb 2500 Analyzer with the sample at liquid nitrogen temperature, 77 K. Following the procedure discussed previously, the slope and intercept values were used to calculate the c and N_m values shown in Table 1.

The Freon 12 adsorption data shown in Table 2 was analyzed using Eq. (1) in a manner analogous to the conventional nitrogen BET treatment. The BET plot for each powder was based on five adsorption points in the P/P_o range of 0.05 to 0.14 obtained from mass differences before and after 120 minutes of exposure to Freon 12 at a temperature of 295 K. Despite the simple approach and the fact that each pressure measurement was carried out on different samples of the powders on different days, the results as judged by the R values are quite consistent.

The surface area occupied by a single nitrogen molecule is normally taken to be 16.2×10^{-20} m²/g. Substituting this value and the moles of nitrogen at monolayer coverage from Table 1 into Eq. (2) resulted in the nitrogen surface areas shown in Table 3. Note that the Mexican Graphite is primarily a nonporous sample, whereas, the other powders have significant porosity.

Figure 1 shows a plot of the nitrogen surface areas versus the moles of Freon 12 adsorbed. This plot has a slope of 314682 m²/mol and R=0.9984. The value of the slope was used in conjunction with Eq. (2) to determine the Freon 12 surface areas shown in Table 3. These specific surface areas are associated with an effective area per dichlorodifluoromethane molecule of 52.3×10^{-20} m²/g. The agreement between the Freon 12 and nitrogen surface areas is indicated in Table 3 by the absolute difference and percentage difference of the Freon 12 values relative to the nitrogen values.

With the exception of the Mexican Graphite all the Freon surface area values are within 10% of the standard nitrogen values. Since the Mexican Graphite has the smallest specific surface area, it is expected to have the largest uncertainty in determining the mass increase due to adsorbed Freon 12. However, it is also possible that the difference between the MG and other four powders is because a difference in packing and effective molecular surface area on porous and nonporous carbons.

Table 4 shows the ratio of the adsorbed moles of nitrogen divided by the adsorbed moles of Freon 12. The effective molecular Freon 12 area for each carbon was calculated based on these ratios to give for the MG, AN, SC, SA, and SS powders values of 34.3, 48.0, 47.5, 54.5, and 52.5 $\times 10^{-20}$m², respectively. The four porous carbons are clearly grouped higher than the nonporous Mexican Graphite. The four porous carbons have an value of 50.6 with a standard deviation of 3.4.

This combined average molecular Freon 12 area was used in Eq. (2) to calculate the porous carbon surface areas shown in Table 4 along with the absolute difference and percentage difference of the Freon 12 values relative to the nitrogen values. Note that the four porous carbon Freon 12 areas are within 7% of the standard nitrogen values which suggest that Freon 12 adsorption at room temperature might be useful as a routine method of surface area analysis.

Repeat measurements of Freon 12 surface area for the microporous carbons AN, SC, and SS at the same temperature yielded values within 3% and repeat measurements at a slightly lower

Table 1. BET nitrogen adsorption results from $P/[N_a(P_o-P)]$ versus P/P_o plots at T=77K.

Solid	Slope (g/mol)	Intercept (g/mol)	R	c	N_m (mol/g)
MG	3744.0	19.68	0.9999	191.2	0.0002657
AN	127.8	-0.9800	0.9993	-129.4	0.007885
SC	107.7	0.1668	0.9998	646.7	0.009271
SA	58.32	0.3782	0.9999	155.2	0.01704
SS	30.39	0.3746	0.9998	82.13	0.03250

Table 2. BET Freon-12 adsorption results from $P/[N_a(P_o-P)]$ versus P/P_o plots at T=295K.

Solid	Slope (g/mol)	Intercept (g/mol)	R	c	N_m (mol/g)
MG	8221.0	107.200	0.9803	77.69	0.0001201
AN	374.4	0.5176	0.9997	724.30	0.002667
SC	312.9	3.263	0.9994	96.89	0.003163
SA	193.4	3.641	0.9970	54.12	0.005075
SS	98.32	1.399	0.9996	71.28	0.01003

Table 3. Comparison of nitrogen and Freon 12 surface areas based on area of 52.3×10^{-20} m^2/g for Freon 12.

Solid	Area Nitrogen (m^2/g)	Area Freon 12 (m^2/g)	Comparison of Freon 12 to Nitrogen Surface Areas: Absolute (m^2/g)	Relative (%)
MG	26	38	+12	+46.2
AN	769	839	+70	+9.1
SC	904	995	+91	+10.1
SA	1662	1597	-65	-3.9
SS	3171	3156	-15	-0.5

temperature for SA and SS yielded values with 6% of those reported previously.

McClellan and Harnsberger (1967) compiled a list of 128 substances that had been used as adsorbates in two or more surface area determinations, but they recommended nitrogen, argon, krypton, n-butane, and benzene as the most useful. Freon 1, dichlorofluoromethane, has been used as an adsorbate (Davis, 1947) and found to have an effective molecular surface area of $40.1\times10^{-20}m^2$ as compared to an area calculated from liquid density packing of $26.4\times10^{-20}m^2$.

It is interesting to note that the estimated molecular area for Freon 12 based on liquid density packing is $31.2\times10^{-20}m^2$ from (Gregg, 1982)

$$a_m = 1.091(M/d\ L)^{2/3} \quad (3)$$

where M is the molar mass, d is the density (for Freon 12 d=1.311g/cm^3, Weast, 1985), and 1.091 is the packing factor based on six near neighbors on a plane surface. This value compares well to the value

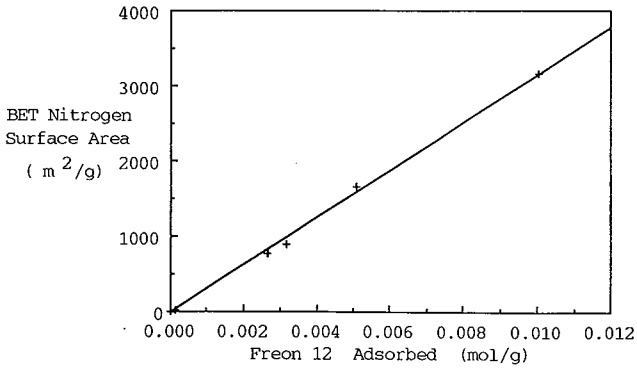

Figure 1. Nitrogen BET Surface Areas versus Moles of Freon 12 Adsorbed for Carbon Powders.

Table 4. Ratio of moles adsorbed for nitrogen to Freon 12 $N_m(N_2)/N_m(F12)$ and carbon surface areas based on area of $50.6\times10^{-20}m^2/g$ for Freon 12.

Solid	$N_m(N_2)/N_m(F12)$	Area Freon 12 (m^2/g)	Comparison of Freon 12 and Nitrogen Surface Areas: Absolute (m^2/g)	Relative (%)
MG	2.12			
AN	2.96	813	+44	+5.7
SC	2.93	964	+60	+6.6
SA	3.36	1546	-116	-7.0
SS	3.24	3056	-115	-3.6

we found for the MG surface of $34.3\times10^{-20}m^2$ whereas the average porous carbon value was $50.6\times10^{-20}m^2$. The ratio of our larger Freon 12 value to one based on liquid packing density is 1.62 whereas the same ratio for the reported Freon 1 value is 1.52. These comparison support our observed molecular areas.

Spectroscopic Observations

In addition to using adsorbent mass differences or pressure differences based on Freon 12, it might also be possible to use infrared spectroscopic measurements of gas phase Freon 12 to determine the amount present before and after exposure to a carbon powder. While this is an area where more work is needed, we wish to report our Beer-Lambert observations for gas phase Freon 12.

For Absorbance=(constant)(pressure) we found for a 10 cm path length gas cell with NaCl salt plates that the constant is $9.75\times10^{-3}kPa^{-1}$ where P is in units kPa. This value is based on 17 data points in the range of 5 to 90 kPa giving a straight line plot with R=0.999 using the 1240 cm^{-1} IR peak. A gauge calibrated with a mercury manometer was used to measure pressure and a Perkin Elmer 1310 IR spectrophotometer was used to determine corrected absorbance values. A similar plot for the 1380 cm^{-1} peak gave a constant of $3.91\times10^{-3}kPa^{-1}$ with R=0.996. The 1380cm^{-1} and 1240cm^{-1} peaks have been reported as weaker peaks that are a combination of fundamental peaks (Thompson, 1948; Zobel, 1955).

Other Adsorption Experiments

Other experiments using the same basic procedures outlined previously have shown the extent of adsorption of Freon 22 (molar mass of 86.5g/mol) like Freon 12 is related to the powder surface area. Exposure of powders to Freon 22 for 42 minutes at T=293 K

with a final equilibrium pressure of 0.76 atm resulted in 0.370, 0.509, and 1.01 g of Freon 22 adsorbed per g of SC, SA, and SS, respectively. From Table 2 we can calculate that for the SC, SA, and SS powders the amounts for Freon 12 (molar mass 120.9 g/mol) adsorbed are 0.382, 0.614, and 1.21 g of Freon 12 per g of powder.

It is interesting to note that the largest surface area powder, Super Sorb, can adsorb more than its own weight of either Freon 12 or Freon 22. Freon 12 and Freon 22 are rather similar in molar amounts that are adsorbed; however, the Freon 12 is greater in mass adsorbed primarily due to its greater molar mass.

About 137 million kilograms of Freon 12 (major use: air conditioning, refrigeration, blowing rigid foam) and 99 million kilograms of Freon 22 (major use: air conditioning) are used in annually in the United States (Monastersky, 1988). Automobile air conditioners use Freon 12 (a little more than a kilogram is required to fill the typical automotive air conditioner system) while central and window air conditioners use Freon 22 as a coolant. Freon 12 is about 20 times more harmful with respect to its ozone depletion effect than Freon 22 and efforts are underway in some parts of the country to recycle Freon 12 when automobile air conditioners are serviced (Zurer, 1989). It has been suggested that activated carbon could be widely used to trap chlorofluorocarbons, and that both the carbon powder and chlorofluorocarbons could be recycled (Navratil, 1989).

We have tried recycling the powders and have found that chlorofluorocarbons can be removed by degassing under the heated vacuum conditions indicated previously and that the powders are just as effective in additional adsorption experiments. This indicates that such powders can be recycled for multiple uses.

We monitored the extent of Freon 22 desorption in capped and uncapped glass flasks. After 28 days 97% of Freon 22 and 98% of Freon 12 remained adsorbed on the solid and there was no observed build up of pressure inside the closed flask. Uncapped flasks retained about 28% of Freon 22 after 5 days and10% of Freon 22 after 14 days (may have been some weight gain due to water). This indicates that the adsorption is physical adsorption based on Van der Waals forces, is reversible and is based on an equilibrium between the gas phase and the adsorbed phase.

The rate of adsorption of Freon 22 on Super Sorb carbon at room temperature was observed by following the pressure drop with time and determining the percent of maximum adsorption. After 10 minutes the adsorption was 60% complete, and after 25 minutes it was more than 80% complete.

In another series of experiments either argon or Freon 22 was flowed through either an empty or powder (5.46g of SS) filled tube. The flow rate was monitored with a soap bubble flow meter. With argon the flow rate through the powder packed column was only 50% of the empty tube. The reduction in flow rate is due the constriction in the path. However, for Freon 22 the flow rate was reduced to 0% (0.161 to 0.00 ml/s) or 3% (1.96 to 0.063 ml/s) through the powder packed column as compared to the empty column. During these flow experiments the powder adsorbed about 0.640 g of Freon 22 per g of powder.

The results of these experiments suggest that chlorofluorocarbon molecules can be effectively trapped on porous carbons through either static or flow adsorption. These results support the use of high surface area carbon powders to trap Freon molecules which could then be either recycled or destroyed rather than vented directly into the atmosphere.

Further studies should focus on the variation in molecular packing of Freon 12, the possibility of correlating a wider range of Freon 12 adsorbent surface areas with conventional nitrogen areas, and the gathering of more information on the role of adsorbents in trapping chlorofluorocarbon compounds.

ACKNOWLEDGEMENTS

We wish to thank Dr. Don Blankenship for assistance in obtaining the Digisorb 2500 BET adsorption measurements.

LITERATURE CITED

Asakura, S. and T. Kishimoto. 1987. Adsorption of halohydrocarbons, Jpn. Kokai Tokyo Koho JP 87 132,523.

Brunauer, S., P.H. Emmett, and E. Teller. 1938. Adsoption of Gases in Multimolecular Layers. *J. Am. Chem. Soc.* 60:309-319.

Davis, R. T., T. W. DeWitt and P. H. Emmett. 1947. Adsorption of Gases on Surfaces of Powders and Metal Foils. *J. Phys. Chem.* 51:1232-1248.

Diawara, B., L. C. Dufour, R. De Hartoulari, M. Moutabid, and M. Vareille. 1986. A simple microbalance for investigating the reactions of solids with ammonia and Freons at pressures up to 10 bars, Thermochim. Acta. 103:15-20.

Drzal, L. T and T. Fort, Jr. 1976. Adsorption of Freon 113. I. Comparison of the adsorption of krypton and 1,1,2-trichloro-1,2,2- trifluoroethane on graphitized carbon black. Colloid Polym. Sci. 254:795-802.

Gregg, S. J. and K. W. S. Sing. 1982. "Adsorption, Surface Area and Porosity," 2nd ed. Academic Press, London.

Hattori, T., T. Sakaino. 1978. Recovery of Freon in foaming of polyurethane. Japan. Kokai JP 78 66,999.

Ikezawa, Y., S. Kitani,Y. Yoshida, M. Kozuka, and H. Takeda. 1972. Measurement of leaks in activated charcoal filter systems using Freon 112. Nippon Genshiryoku Gakkaishi, 14:106-12.

Kurashiki Spinning Co., Ltd.1982. Recovery of Freon from gases evolved from polyurethane foams during manufacture. Jpn. Kokai Tokyo Koho JP 82 18,742.

Lowell, S., 1979. "Introduction to Powder Surface Area," John Wiley and Sons, New York.

McClellan, A. L. and H. F. Harnsberger. 1967. Cross-sectional Areas of Molecules adsorbed on Solid Surfaces. *J. Colloid Interface Sci.* 23:577-599.

Monastersky, R. 1988. Decline of the CFC Empire. *Sci. News.* 133:234-236.

Navratil, J. D. 1989. Recycling Chlorofloruocarbons, letter to editor. C&EN News, June 12, p. 3.

Plokhov, Yu. M., G. A. Musakin, T. G. Plachenov. 1977. Effect of structure parameters of carbon adsorbents on the adsorption capacity with respect to poorly sorbed organic substances at low concentrations in an air stream. Deposited Doc., VINITI 15-78, 201-7.

Rybolt, T. R. 1981. "The Gas-Solid Joule-Thomson Effect," Ph.D. Thesis, Georgia Institute of Technology.

——— 1986. A Comparison of BET, Langmuir, and Virial Surface Areas for Carbon Powders. *J. Tenn. Acad. Sci.* 61:66-69.

Sing, K. W. S., D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, and T. Siemieniewska. 1985. Reporting Physisorption Data for Gas/Solid Systems, IUPAC Recommendations. *Pure Appl. Chem.* 57:603-619.

Skazyvaev, V. E., S. S. Khvoshchev, and L. N. Rozanov. 1983. Study of Freon 12 adsorption by porous adsorbents. *Zh. Prikl. Khim.* (Leningrad) 56:1191-3.

Thompson, H. W. and R. B. Temple. 1948. The Vibrational Spectra and Thermodynamic Properties of Chlorofluoromethanes. *J. Chem. Soc.* 1948:1422-1436.

Weast, R. C., M. J. Astle, and W. H. Beyer, eds. 1985. "CRC Handbook of Chemistry and Physics," CRC Press, Boca Raton, Florida, p. E-28.

Zobel, R. and A. B. F. Duncan. 1955. Vacuum Ultaviolet Absorption Spectra of Some Halogen Derivatives of Methane. Correlation of the Spectra. 77:2611-2615.

Zurer, P. S. 1988. Ozone Layer: Study finds alarming global losses. C&EN News, March 21, p. 6-7.

——— 1989. Producers, Users Grapple with Realities of CFC Phaseout. C&EN News July 24, p. 7-13.