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THE MEASUREMENT OF THE SURFACE AREA OF MINERALS WITH A MODIFIED PERKIN-ELMER SORPTOMETER

C. M. LAPOINTE

MINERAL SCIENCES DIVISION

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THE MEASUREMENT OF THE SURFACE AREA OF MINERALS WITH A MODIFIED PERKIN-ELMER SORPTOMETER

by

C.M. Lapointe*

ABSTRACT

The performance of a Model 212-D Perkin-Elmer Sorptometer has been studied for the measurement of surface areas in the range of specific surface areas between 200 cm^2/g and 1000 cm^2/g. It was found that, with some modifications to the instrument with regard to the transfer of the desorbed gas from the sample to the detector, the Sorptometer could be used for the surface area measurement of relatively large samples of mineral particles.

This Bulletin describes a simplification of the BET method that can be used for the routine measurement of surface areas on samples of similar characteristics by the one-point determination. The method can be extended to a two-point or a three-point determination in order to obtain a conventional BET plot.

A standard procedure is outlined for the calibration of the instrument, for the sample preparation, for the adsorption measurement, and for the calculation of the specific areas.

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LA MESURE DES AIRES DE SURFACE DES MINERAIS A L'AIDE D'UNE MODIFICATION DU SORPTOMETRE PERKIN-ELMER

par

C.M. Lapointe*

RÉSUMÉ

L'auteur évalue la performance d'un sorptomètre Perkin-Elmer, Modèle 212-D, pour la mesure des aires de surface de poudres allant de 200 cm^2/g à 1000 cm^2/g. Il a trouvé qu'après quelques modifications au mode de transport du gas désorbé de l'échantillon au détecteur, le sorptomètre convient à la mesure de l'aire de surface d'assez gros échantillons de minerais.

On décrit dans ce bulletin une simplification de l'équation BET que l'on peut utiliser au cours de mesures de routine sur une série d'échantillons semblables après détermination d'un seul point de l'isothèrme. Cette technique peut aussi être employée afin de tracer l'isothèrme conventionnel en effectuant deux ou trois mesures.

On trouvera en appendice descriptions 1) des techniques de calibration de l'instrument, 2) de la préparation des échantillons, et 3) du calcul des aires de surface.

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INTRODUCTION

In the course of a study on the flotation properties of cassiterite with oleic acid (1), a microscopic examination of the flotation products obtained under various experimental conditions showed definite differences between the surface structures of the float and the non-float fractions. More recent work performed on hematite has revealed that, for a highly pure, closely sized sample, an important factor governing the flotation efficiency at a given temperature, pH and collector concentration, is the surface roughness of the individual particles, that is, their specific surface areas. An investigation into the variation of the specific surface areas of flotation products obtained under different conditions was therefore desirable, and a search for a convenient method of measuring these areas has been conducted.

Several methods have been proposed for the measurement of the surface area of powdered material (2). The fatty-acid monomolecular adsorption method, its sensitivity greatly increased with the advent of C^{14}-tagged surfactants, has produced excellent results in some particular cases (3), but still requires extensive testing before becoming a routine laboratory technique. It is quite possible that, under carefully controlled experimental conditions, it may provide information not only on surface areas but also on the degree of reactivity of the surfaces, the knowledge of which is important in studies of adsorption and flotation.

The BET(Brunauer, Emmett and Teller) method (4) for surface area determination has been in use for a number of years as a standard procedure, but it has its limitations. Using nitrogen as the adsorbate at a temperature near its boiling point, the method is suitable for samples of total surface areas larger than 2000 cm^2. The use of krypton (5) instead of nitrogen as the adsorbate has extended the range of measurable surface areas down to about 100 cm^2 (6). Measurements with the krypton method, however, are time-

consuming and require close control of the laboratory temperature, along with excellent vacuum systems and skilled operation.

Although a krypton adsorption line was available in these laboratories for calibration purposes, it was decided to experiment with a more rapid technique designed for routine work, namely the Perkin-Elmer-Shell Sorptometer.

THE PERKIN-ELMER-SHELL SORPTOMETER

In 1958, Nelsen and Eggertsen (7) described a new surface area measurement technique based on the same theory as the BET method and using the BET equation. The proper instrumentation for this method was developed originally by the Shell Development Company at Emeryville in California, and a commercial instrument, the sorptometer, has been marketed by the Perkin-Elmer Corporation, Norwalk, Connecticut (8). Since the development of the technique and of the instrument, a number of papers have been published (listed in Reference 9), dealing with its applications and with improvements in the technique.

PRINCIPLES OF OPERATION

While the BET, or volumetric, method of determination of surface areas utilizes the measurement of a pressure decrease due to the adsorption of a gas on a solid from a known volume of that gas in a static system, the Sorptometer, or continuous-flow, method utilizes the measurement of the concentration change of the adsorbate in a continuous flow system.

A mixture of helium and nitrogen of known concentration flows through, or over, a sample which has previously been outgassed by heating in an inert gas flow. The thermal conductivity of the gas mixture is monitored differentially by means of thermal conductivity cells located before and after the sample cell, in a manner similar to that used in gas chromatography. When the sample is cooled with liquid nitrogen, it

adsorbs a certain amount of nitrogen from the gas mixture. As a result of the adsorption, the concentration of nitrogen in the mixture flowing past the sample cell decreases, and the difference between this concentration and the original concentration of the mixture flowing through the first cell of the detector located upstream of the sample is recorded as a peak on a chart recorder. After the adsorption equilibrium is reached, the recorder pen returns to its original baseline position. The coolant is then removed, leading to the desorption of the adsorbed nitrogen. The desorption increases the nitrogen concentration in the flowing mixture, and this is recorded as a peak in the direction opposite to the adsorption peak. After equilibrium is reached, a known volume of nitrogen is injected into the gas flowing through the sample, thus supplying a calibration peak.

For a given flow-rate of the gas mixture, the area under an adsorption (or desorption) peak is proportional to the volume of nitrogen adsorbed (or desorbed) or injected for calibration. So the simple relation:

$$\text{Volume adsorbed} = \frac{\text{Area of adsorption peak}}{\text{Area of calibration peak}} \times \text{Calibration volume}$$

can be used to plot the first point of the BET curve. By repeating the measurements at different He/N_2 ratios, the BET plot can be completed and the surface area of the sample can be calculated by graphical evaluation.

SCHEMATIC OF THE INSTRUMENT

A schematic diagram of the Sorptometer is shown in Figure 1, where the gas flow can easily be followed. Both the carrier and adsorption gases enter the apparatus through drying tubes filled with Drierite and then through pressure regulators. Capillary restrictors are used in both lines to permit the operation of the pressure regulators in their optimum range. The two gases are mixed, and the mixture flow through a liquid nitrogen trap to condense any impurities in the gases, then through, in turn, a heat exchanger, the reference side of the detector, two calibration valves, the sample cell, a second heat exchanger, the sensing side of the detector, and, finally, a soap-bubble flow-meter which gives an exact measurement of the rate of flow of the gas mixture in the system.

The detector is a thermal conductivity cell with four tungsten filaments arranged in a Wheatstone bridge. To avoid temperature gradients in the detector block and the heat exchangers, these are immersed in a stainless steel bath filled with isopropyl alcohol.

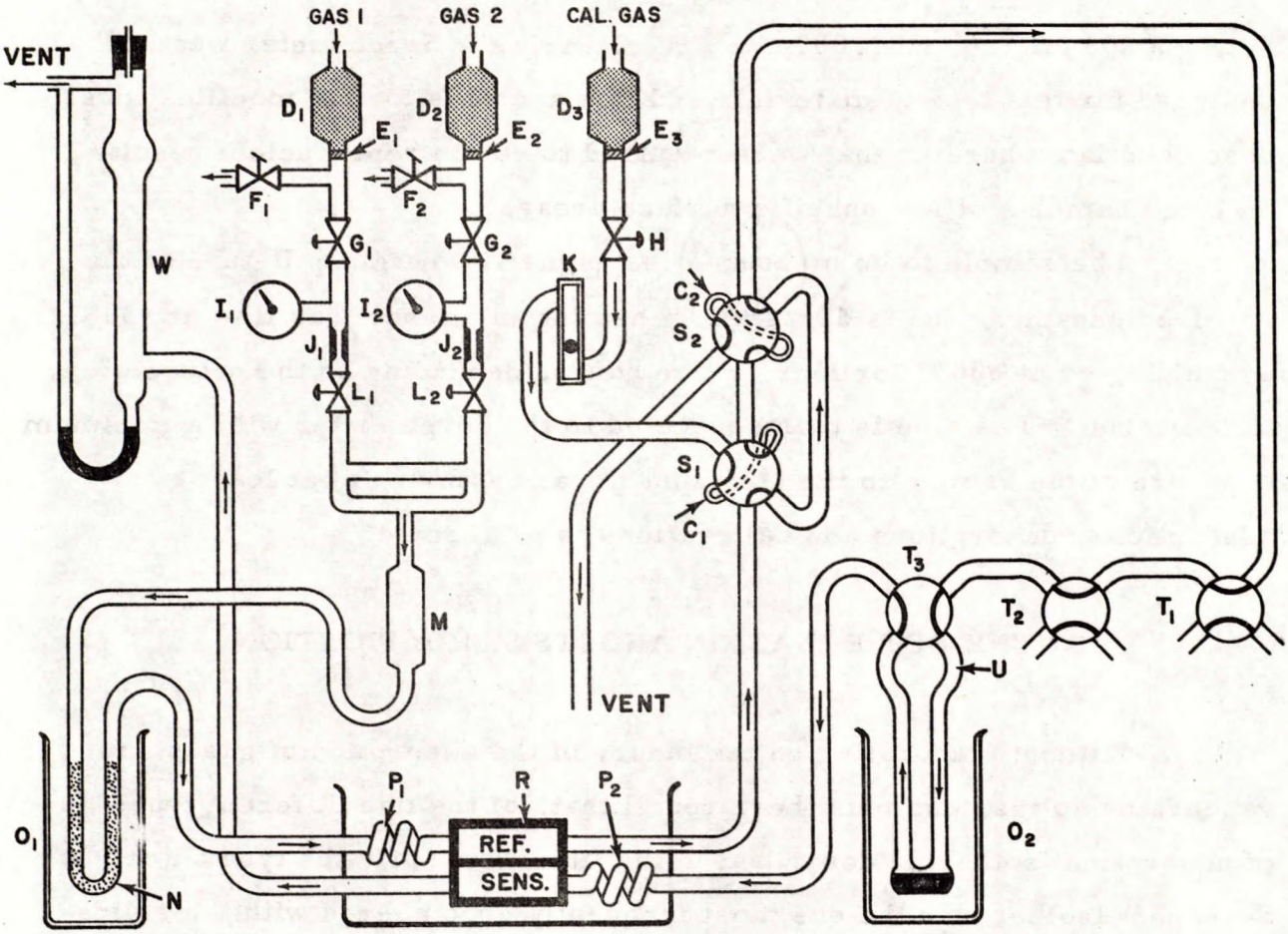
As mentioned previously, the volume of the adsorbed gas is calculated by comparison of the area of the adsorption peak with that of a peak obtained following the injection of a known volume of nitrogen into the gas stream. Because of the non-linearity of the instrument through its complete range (10), the two volumes to be compared should be as close as possible. In order to facilitate this comparison, the instrument contains two calibration valves with interchangeable loops. The calibration gas flows continuously through both valves. By opening one or both valves, the content of one or both loops may be injected into the gas stream, producing a peak of the desired magnitude on the recorder chart.

CALIBRATION

It is unfortunate that the Sorptometer, as received, is not calibrated as to the volumes of the calibration loops and of the flow-meter. The latter can be calibrated by weighing the amount of mercury required to fill the space between two fiduciary marks. The calibration loops, however, cannot be calibrated directly: a standard calibration cell (supplied) is first calibrated with mercury, and is then used to calibrate the built-in calibration loops. Details on the calibration procedure may be found in Appendix 1.

SAMPLE PREPARATION

The amount of material required for a surface area determination varies with the expected specific surface area; the minimum surface area that can be measured with any reasonable accuracy is about 5,000 cm^2. For the minerals under study in this laboratory (oxides and sulphides of grain size varying between 65 and 200 mesh), the specific surface areas vary



GAS 1	–	ADSORBATE (NITROGEN) INLET PORT
GAS 2	–	CARRIER (HELIUM) INLET PORT
CAL. GAS	–	CALIBRATION GAS INLET PORT
W	–	SOAP BUBBLE FLOWMETER
D1, D2, D3	–	DRYERS
E1, E2, E3	–	FILTER DISCS
F1, F2	–	TOGGLE VALVES
G1, G2	–	PRESSURE REGULATORS
H	–	NEEDLE VALVE
I1, I2	–	PRESSURE GAUGES
J1, J2	–	RESTRICTORS
K	–	FLOWMETER
M	–	MIXING TANK
S1, S2	–	CALIBRATION VALVES (SHOWN IN "CHARGE" POSITION)
C1, C2	–	CALIBRATION VALVE LOOPS
N	–	COLD TRAP
O1, O2	–	DEWAR FLASKS
T1, T2, T3	–	SAMPLE BYPASS VALVES
U	–	SAMPLE TUBE
Q	–	CONSTANT TEMPERATURE BATH
P1, P2	–	HEAT EXCHANGERS
R	–	DETECTOR

Figure 1. - Flow diagram of Model 212-D Perkin-Elmer Sorptometer. (Courtesy of the Perkin-Elmer Corporation).

between 200 cm^2/g and 1,000 cm^2/g. Clearly the Sorptometer was not designed for this type of material, and this accounts for the modifications, described later herein, that were required to obtain reproducible results on large samples of low specific surface areas.

The sample to be measured is weighed into a glass U-tube of the required capacity, and is degassed by heating in an inert gas flow at 130°C overnight, or at 300°C for four or five hours, depending on the nature of the material. The tube is then connected to the Sorptometer with a minimum exposure of the sample to the atmosphere, and a series of at least two adsorptions, desorptions and calibrations is performed.

THE BET EQUATION AND ITS SIMPLIFICATION

Without elaborating on the theory of the adsorption of gases and vapours on solids, one must here recall that, of the five different types of adsorption isotherms described in the literature (11), the type II (or S-shaped) isotherm is the one most frequently encountered with the solids under study, and it is to this type of isotherm that the BET equation applies. This equation may be written as:

$$V_{ads} = \frac{V_m CP}{(P_o - P)\left[1 + (c-1)\,P/P_o\right]} \qquad \text{....(Eq. 1)}$$

where V_{ads} is the volume (cc STP/g sample) of the gas adsorbed at the partial pressure P, V_m is the volume (cc STP/g sample) of the gas required to cover the surface of the sample with one monolayer of adsorbed gas at a temperature near the boiling point of nitrogen, P_o is the saturation pressure of the gas at that temperature, and C is a constant related to the heat of adsorption.

Equation 1 can be rearranged in the following form:

$$\frac{P}{V_{ads}(P_o - P)} = \frac{(c-1)}{V_m C}\frac{P}{P_o} + \frac{1}{V_m C} \qquad \text{....(Eq. 2)}$$

which is the usual form of the BET equation.

Numerous tests have shown that the isotherms plotted according to Equation 2 (V_{ads} against P/P_o) are straight lines in the relative pressure range between 0.05 and 0.30. By using such a plot, Equation 2 can be evaluated graphically in the following way:

For a given system, V_m and C are constants; thus, the two corresponding fractions in the right-hand side of Equation 2 are constants, and can be expressed as:

$$\alpha = \frac{c-1}{V_m C} \quad \text{....(Eq. 3)}; \qquad \beta = \frac{1}{V_m C} \quad \text{....(Eq. 4)}$$

Equation 2 can now be written in the following form:

$$\frac{P}{V_{ads}(P_o - P)} = \alpha \frac{P}{P_o} + \beta, \quad \text{....(Eq. 5)}$$

which is a linear equation with two unknowns:

$$y = \alpha x + \beta, \quad \text{....(Eq. 6)}$$

where α is the slope and β is the intercept. A plot of $P/V_{ads}(P_o - P)$ against P/P_o will give, within practical limits, a straight line, as shown in Figure 2. Solving Equation 4 for C and substituting this value into Equation 3:

$$C = \frac{1}{V_m \beta} \quad \text{....(Eq. 7)}; \qquad \alpha = \frac{1}{V_m} - \beta \quad \text{....(Eq. 8)}$$

From Equation 8, V_m can be expressed in the following form:

$$V_m = \frac{1}{\alpha + \beta} \quad \text{....(Eq. 9)}$$

By extrapolation of the BET plot, as shown in Figure 2, Equation 9 gives the value of V_m, the volume of gas adsorbed as a monolayer on the sample surface. It remains only to convert this term from units of volume

to units of area by multiplying it by the area covered by a one-millilitre monolayer of adsorbate (s_o) at STP:

$$S = V_m s_o \qquad \text{....(Eq. 10)}$$

and the specific surface area, S_s, is obtained by dividing the total surface area S by the weight w of the sample:

$$S_s = \frac{V_m s_o}{w} \qquad \text{....(Eq. 11)}$$

With the continuous flow method, one generally measures the volume of adsorbed gas at three different nitrogen concentrations, corresponding to three different relative pressures, as is the rule with the standard BET method. However, for comparative measurements within a narrow range of surface areas, the one-point method can be used with a fair degree of accuracy and a notable saving of time.

Experience has shown that, with nitrogen as the adsorbate, most BET plots have relatively small intercepts on the ordinate. Therefore, if only a single point is determined in the relative pressure range of 0.25 - 0.30, and is then connected by a straight line to the origin (Figure 2), the value of V_m deduced from this graph will seldom differ by more than five per cent from the value determined by the three-point method. Furthermore, the specific surface area can be calculated directly from the measured parameters, without graphical interpretation.

THE ONE-POINT METHOD

Since the intercept is now taken as zero, the BET equation can be written in the following form:

$$\frac{P}{V_{ads}(P_o - P)} \approx \frac{c-1}{V_{ads} C} \cdot \frac{P}{P_o} = \alpha' \frac{P}{P_o} \qquad \text{....(Eq. 12)}$$

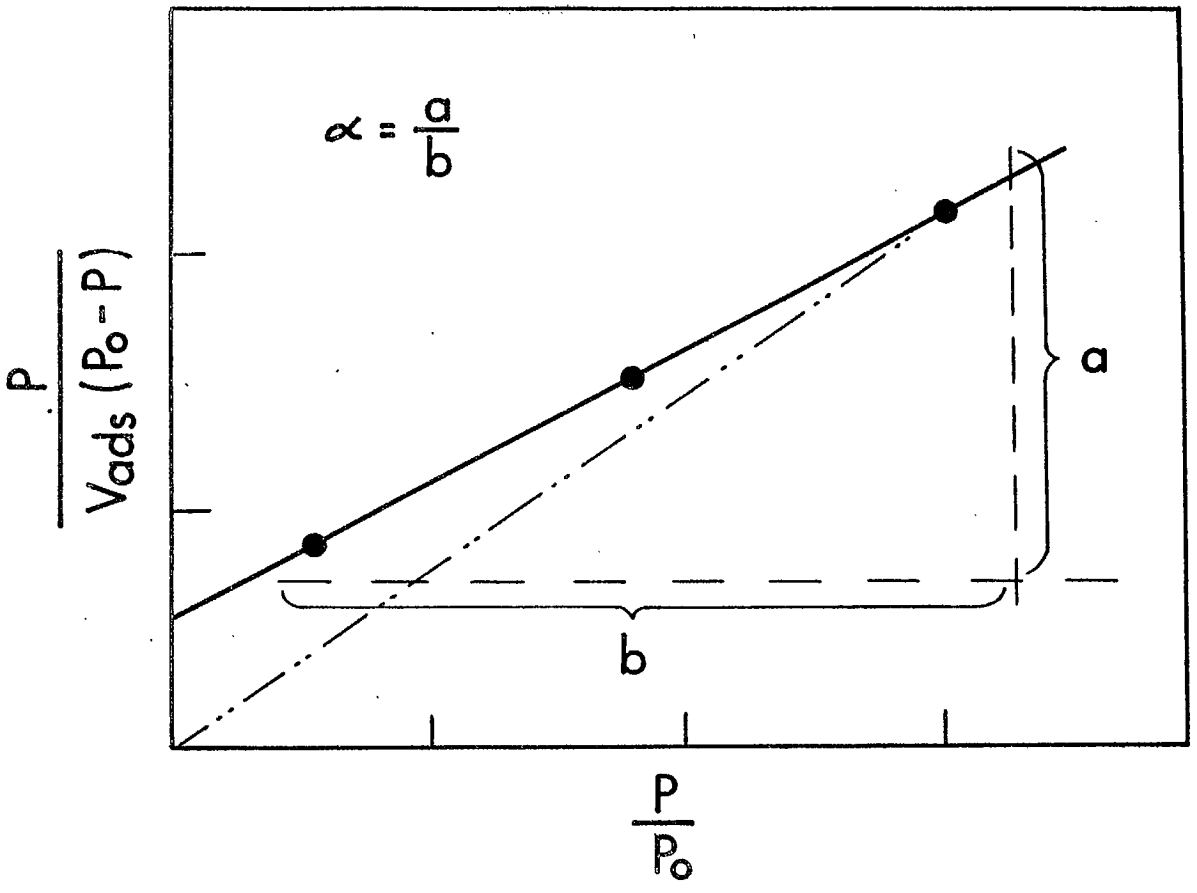


Figure 2. - A typical BET plot. The dashed line shows an extrapolation by the one-point method.

Expressing α' from this equation:

$$\alpha' = \frac{P_o}{V_{ads}(P_o - P)} \qquad \text{....(Eq. 13)}$$

Now, because $\beta = o$, V'_m can be expressed from Equation 9 as:

$$V_m = \frac{1}{\alpha'} = V_{ads} \frac{P_o - P}{P_o} \qquad \text{....(Eq. 14)}$$

Substituting Equation 14 into Equation 11, one obtains:

$$S'_s = \frac{V'_m S_o}{W} = V_{ads} \frac{P_o - P}{P_o} \cdot \frac{S_o}{W} \qquad \text{....(Eq. 15)}$$

If, instead of mixing helium and nitrogen in the instrument, one uses pre-mixed gases of known compositions, the partial pressure of nitrogen (P) can be calculated from the mole concentration in the mixture (c) and the barometric pressure (P_T):

$$P = \frac{c}{100} P_T \qquad \text{....(Eq. 16)}$$

Substituting P from Equation 16 into Equation 15, one obtains the working equation for the one-point method:

$$S_s = \frac{V_{ads}}{W} \cdot \frac{S_o}{P_o} \quad P_o - \frac{C}{100} P_T \qquad \text{....(Eq. 17)}$$

MEASUREMENT OF THE PARAMETERS OF EQUATION 17

The saturation pressure of nitrogen (P_o) and the area covered by a one-millilitre monolayer of the gas (s_o) are critically dependent on the temperature. For example, a 0.55°C variation in the boiling point of the liquid-nitrogen cooling bath will result in a 55-mm Hg (6.5%) change in the

saturation pressure of nitrogen in a vial immersed in the bath. The boiling point of commercial liquid nitrogen is by no means constant. It varies with the atmospheric pressure, but this could be allowed for. It also varies with the amount of impurities, especially oxygen, dissolved in the liquid nitrogen. Although some work has been done on the use of copper-constantan thermocouples and of thermistors for the measurement of low temperatures (12), the most reliable method of measuring the saturation pressure of nitrogen at the temperature of the cooling bath is to immerse a nitrogen manometer into the bath, immediately after desorption, as is the practice at the Shell Development Laboratories, or, better, during both adsorption and desorption, as is done in this laboratory. A description of the nitrogen manometer in use here may be found in Appendix 3, as well as a table (Table 1) showing the values of s_o and P_o as functions of the temperature.

The volume, V, of nitrogen adsorbed on the sample may be obtained by two different methods: a) by comparison of the area under the adsorption peak with the area under a peak obtained with a known volume of nitrogen injected through the sample under exactly the same conditions (flow rate, temperature, pressure) as prevailed during the adsorption; b) by adjustment of the adsorption peak area with the help of a family of curves obtained by instrument calibration.

The second method, initiated by the Shell Development group, is favoured when a large number of samples are processed daily. It is based on the fact that, although the peak area obtained with a given sample varies with the rate of gas flow, the product of peak area and flow-rate is constant ($\pm 1\%$) over the practical range of operation. The saving in time is appreciable: one minute for the measurement of the flow-rate against about 14 minutes for a calibration peak, plus the time required for the measurement of its area.

The first method of direct calibration through the sample is to be preferred when the unit is not used continuously, and especially when it is used to measure the surface areas of powders of widely different characteristics. It is to be noted here that, although both the adsorption and the desorption curves

are integrated, only the desorption curve is used in the computation of the surface area. This procedure is adopted for the following reasons: 1) the desorption curve is, in most cases, more symmetrical; 2) the recorder's polarity for desorption is identical to that of the calibration curve; 3) in both desorption and calibration, nitrogen is added to the gas flow, resulting in an increase in concentration, while during adsorption the nitrogen concentration decreases; thus the conditions of desorption and calibration procedures are closely related.

MEASUREMENT OF PEAK AREAS

The various techniques in use for the measurement of the peak areas can be classified under two headings: manual and automatic.

Manual : Peak Height, Triangulation, Planimetry, Cut-and-Weigh.
Automatic: Disc Integrator, Electronic Integrator, Computer-and-Tape.

Although the automatic techniques are quite attractive and can handle several samples a day without too much attendance, because of their cost their use cannot be justified in a laboratory where the measurement of the surface area of the material being processed constitutes only one of several phases of processing.

A survey of the various methods of integration (13) has shown that of the manual methods, the Cut-and-Weigh method is the slowest but has the highest precision. It has been used with success in this laboratory, and will be standard practice until the number of samples to be measured warrants the installation of an electronic integrator ($2000.00).

PERFORMANCE OF THE MODEL 212-D SORPTOMETER

The Perkin-Elmer Sorptometer was designed primarily for the measurement of the surface areas of cracking catalysts used in the petroleum industry. The specific surface range for such material varies from 500 m^2/g

for fresh to 100 m^2/g for used catalysts. When operating with a mixture of 35 per cent nitrogen in helium at maximum sensitivity, a full-scale adsorption peak corresponds approximately to a total surface area of one square metre. One would expect that, with a suitable choice of sample containers and of sample weights, the instrument response would be the same for 10 g of material of specific surface area equal to 1000 cm^2 as for 1 g of material of specific surface area equal to 10,000 cm^2. It is not so: the peak areas are different, and, in the case of the larger sample, the desorption peak is usually followed by a peak in the opposite direction.

Such a behaviour has been traced to thermal diffusion within the larger sample and to a fluctuation in the effluent flow-rate during desorption (14). In order to correct for these disturbances, the instrument was modified as follows.

MODIFICATIONS TO THE SORPTOMETER

The obvious way of obtaining an acceptable desorption peak is to make sure that the desorbed nitrogen reaches the detector as a wave, without any tail effect, as happens when a measured volume of nitrogen is injected into the system for calibration. It has been suggested (15) that the desorbed gas be collected in a Töppler pump over mercury and, after thorough mixing, be swept towards the detector. This method was tried here without any significant success, because of the instability of the base line due to variations in the flow rate of the effluent.

The other alternative was to lengthen the gas path between the sample and the detector, by means of a mixing chamber (a brass tube 15 cm long and 1 cm in diameter) followed by a copper tube 3 metres long and 4 mm in diameter. This has proved to be very efficient, as can be seen in Figure 3, which shows a set of peaks obtained with a 15-g sample of hematite of specific surface area of 650 cm^2/g.

Even after the modifications mentioned, it was found that the day-to-day measurements showed fluctuations greater than expected. The Sorptometer

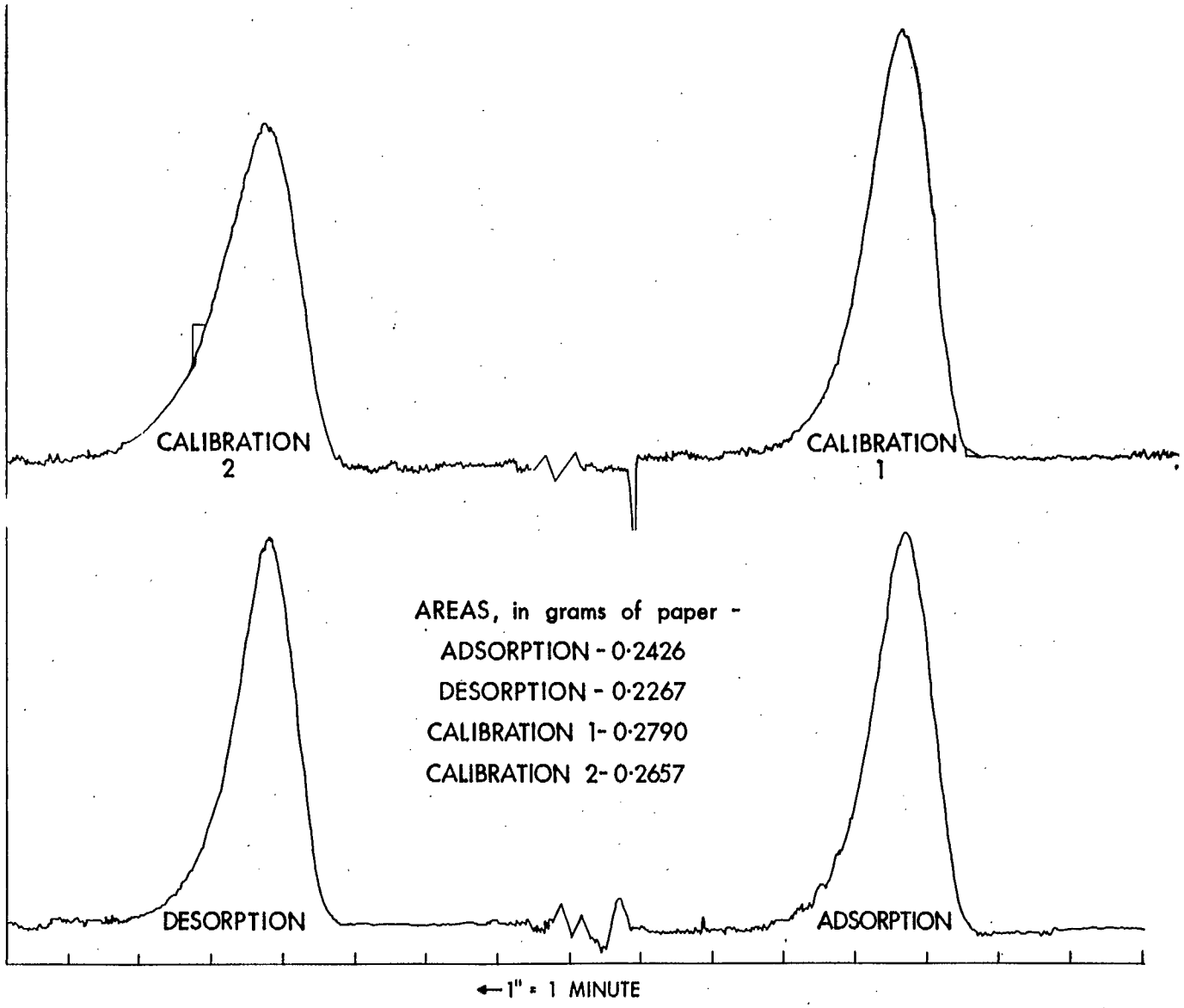


Figure 3. - Sorptograms for a 15-g sample of hematite of specific surface area of 650 cm^2/g.

was designed to operate at a constant ambient temperature, and the temperature in this laboratory is not controlled. In order to minimize the effect of temperature variations, a constant-temperature water bath was installed to feed water at 25 ± 0.2°C through two copper coils mounted in the isopropyl alcohol bath housing the sensing unit. This temperature control resulted in a definite improvement in stability and reproducibility of peak areas.

EXAMPLE OF CALCULATION OF THE SPECIFIC SURFACE AREA

A flotation test on a sample of Quebec-Cartier hematite, sized to -150 + 200 mesh, at pH 5.0, with the required amount of C^{14}-tagged oleic acid to float 58 per cent of the hematite, yielded enough flotation products for a surface area determination on the float and the non-float fractions. The fractions were heated at 375°C to remove the oleic acid chemisorbed on the hematite. Radiometric measurements showed that no C^{14} activity was present on the samples after heating.

A head sample was treated in a similar fashion for comparison. One-point surface area determinations were performed on the three samples with a pre-mixed gas containing 35.66 per cent nitrogen in helium. The results are summarized below: (The peak areas have been measured by the cut-and-weigh method, and are expressed in grams of chart paper.)

Sample	Adsorption	Desorption	Calibration	Barometric Pressure (mm Hg)	Saturation Pressure (mm Hg)	Temp.
Head	0.1294	0.1493	0.1935	747	755	25°C
14.5206g	0.1315	0.1462	0.1876	747	753	25°C
	0.1305	0.1477	0.1905	747	754	25°C

Specific Surface Area of Head Sample $= \dfrac{0.451 \times 0.1477 \times [754 - (0.3566 \times 747)] \times 4.372}{14.5206 \times 0.1905 \times 754}$

$= 680 \text{ cm}^2/\text{g}.$

Calculated similarly, the specific surface area of the

float fraction $= 570 \text{ cm}^2/\text{g}$, and of the

non-float fraction $= 855 \text{ cm}^2/\text{g}.$

A calculated surface area for the head sample, using a flotation efficiency of 58 per cent, gave 690 cm^2/g, which is considered to be in reasonable agreement with the measured value.

CONCLUSION

The Model 212-D Sorptometer, with the modifications and the ancillary equipment described, seems to be adequate for the measurements required in the type of research currently being conducted here. No doubt some further refinements will have to be introduced in the technique if the need for greater accuracy arises.

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APPENDIX 1

Calibration Procedure and Calculations

Calibration Procedure

The calibration cell supplied with the instrument consists of a Pyrex U-tube equipped with two three-way stopcocks and a by-pass tubulure. The nominal volume of the U-tube is one millilitre, but for accurate measurements an individual calibration is required. After a thorough cleaning of the cell and of the stopcocks with chromic acid and distilled water, the parts are dried and re-assembled with a minimum of stopcock grease and the assembly is weighed. It is then filled with redistilled mercury and allowed to reach room temperature. The stopcocks are closed and the excess mercury in the upper branches is removed by means of a vacuum pump equipped with a trap and a flexible length of fine tubing. The mercury-filled cell is weighed, and from the net weight of mercury and its density at room temperature, the volume of the standard cell is calculated. For the cell in use here, the volume was found to be 1.040 ml. The cell is then emptied and cleaned from any remaining mercury.

The built-in calibration valve loops of the Sorptometer, as shipped, have a nominal volume of 0.4 ml. They can be accurately calibrated as follows. The calibrated standard cell is mounted on the third set of sample ports on the right side of the instrument. With only the nitrogen gas supply on and the by-pass valve in the SAMPLE position, the cell is purged and filled with pure nitrogen and the stopcocks are closed. If the Sorptometer has not been in operation, it is turned on according to the following steps, recommended by the manufacturer: (One must remember that the sensing elements are fine tungsten filaments and that no current should be allowed to flow through them when a trace of oxygen is present in the system.)

1. Turn on the recorder and allow it to warm up.

2. Turn on the helium, nitrogen, and pre-mixed gas supplies and set the pressure valves at 20 psi. Set the helium and nitrogen pressure regulators at about 30 inches of water.

3. Turn the calibration gas flow needle valve until a small nitrogen flow is indicated by the calibration gas-flow indicator on the front panel. This ensures that the calibration loops in the CHARGE position will always be filled with nitrogen at room temperature and pressure.

4. When the system has been purged of any trace of oxygen (about 10 minutes), turn on the recorder-chart-drive and the bridge power. Set the ATTENUATION switch to the bridge (B) position, set the detector current by adjusting the DETECTOR CURRENT control to give a 30- to 40-per cent deflection of the recorder pen on the 1-mv full-scale position; this corresponds to a bridge current of approximately 70 ma.

5. Set the ATTENUATION switch to the position of least sensitivity (X64) and bring the recording pen to zero with the ZERO control. Repeat this step at increasing sensitivities until the recorder is zeroed at XI attenuation.

6. Turn the third sample valve to the SAMPLE position in order to sweep-off the nitrogen trapped above the charged volume in the tubing of the standard cell.

7. When the recorder indicates a steady baseline at about 0.1 mv, turn both standard cell stopcocks simultaneously to open, thus flushing the pure nitrogen from the standard cell into the system. A peak will appear on the recorder chart. Make sure that the POLARITY switch is on the DESORPTION position. Recharge the standard cell with nitrogen and repeat the above procedure several times, thus recording a series of peaks.

8. Turn the sample by-pass valve to the BY-PASS position and turn one calibration valve to INJECT, thus flushing the pure nitrogen from the calibration valve into the system. Recharge the calibration loop and repeat the injection several times. Then proceed in the same fashion with the second calibration loop.

9. Set the ATTENUATION one step up (lower sensitivity) and repeat the same procedure, but this time injecting the nitrogen from both loops simultaneously.

Calculations

Using the Cut-and-Weigh method, the average values for the peak areas obtained with the standard cell and with the calibration loops are converted into the true volume of the calibration loops, as follows:

$$\frac{V_{cal}}{V_{cell}} = \frac{A_{cal}}{A_{cell}} \; ; \quad \text{hence } V_{cal} = V_{cell} \frac{A_{cal}}{A_{cell}} \qquad \text{....(Eq. 18)}$$

where V_{cal} = the volume of nitrogen in the calibration-valve loop (ml),

A_{cal} = the peak area produced by nitrogen in the calibration valve loop (g),

V_{cell} = the volume of nitrogen in the standard cell (ml), and

A_{cell} = the peak area produced by nitrogen in the standard cell (g).

The volume of the calibration-valve loops must be expressed at identical conditions (room temperature and barometric pressure) as the volume of adsorbed gas. It is therefore convenient to convert V_{cal} to STP conditions and to record this volume. When performing surface area calculations this STP value is corrected for atmospheric conditions existing at the time of the measurement. If V_{cal} expresses the determined volume of the calibration loop corrected to 0°C and 760 mm Hg, and if V_{cal} expresses the volume of this loop at temperature T_R (°K) and pressure P_T (mm Hg), then:

$$V_{cal} = V_{cal} \frac{760\ T_R}{273\ P_T} \qquad \text{....(Eq. 19)}$$

APPENDIX 2

Procedure for Measurement of Surface Areas

The most important part of the procedure for the measurement of surface areas is the preparation of the sample. One must make sure that the particles are free from any surface contamination that can interfere with the adsorption of nitrogen at the surfaces. This is usually accomplished by repeated extraction or washing with suitable solvents, and then outgassing the sample at high temperature in a flow of inert gas. The temperature and time required for outgassing depend on the nature of the sample. Temperatures may vary between 100° and 500°C, and heating periods may last from one hour to six hours. The criterion in the choice of temperature and duration of heating should be a complete removal of moisture and gases without causing physical or chemical changes in the sample.

In this laboratory, three sample containers, attached to a manifold through which argon is used as a sweeping inert gas, are heated in three baths consisting of Glass-Col heaters filled with sand and controlled with Variac transformers. After suitable outgassing, the heat is turned off and the samples are allowed to cool in the gas stream. The sample containers are then removed from the manifold and quickly sealed with rubber policemen.

The sample container, fitted with policeman, had been previously weighed. It is now weighed with the sample in order to obtain the weight W of Equation 17, and the Sorptometer is now made ready for the actual adsorption measurement.

1) A Dewar flask filled with liquid nitrogen is installed around the stainless steel cooling trap located upstream of the system, in order to remove any moisture or contaminant present in the gases. The liquid nitrogen level should be kept reasonably constant, in order to prevent shifts of the baseline.

2) The helium supply is turned on and the cylinder regulator is set at about 20 psi.

3) The pre-mixed gas cylinder is turned on, and the cylinder regulator is set at a pressure of 20 psi.

4) The gas flow is adjusted by setting the GAS MIXTURE regulator so that the gauge indicates 30 inches of water. The gas flow, once set, should be kept constant throughout each surface area measurement, including calibration.

5) Before connecting the sample tube to the sample port, the sample by-pass valve should be switched to the SAMPLE position for a few seconds, in order to purge the valve and sample tube adapter. The sample tube is then connected to the sample port, the fitting being finger-tight only.

6) The ATTENUATION switch is now turned in position B, and the unit allowed to warm up. Zeroing of the recorder is accomplished as described in the calibration procedure, until a stable baseline is obtained.

7) With the ATTENUATION switch at maximum sensitivity, the POLARITY switch at ADSORPTION and the recorder pen adjusted at 0.1mv and drawing a stable baseline, a Dewar flask filled with liquid nitrogen is raised to a well defined position around the sample tube, and adsorption takes place on the sample. It is very important that the liquid nitrogen level be maintained constant throughout the adsorption, in order to prevent shifting of the baseline. The ATTENUATION switch should be set so as to obtain an adsorption peak about half of full scale on the chart.

8) When adsorption equilibrium has been reached, the recorder pen returns to the baseline. The POLARITY switch is then reversed to DESORPTION, the baseline is re-adjusted to 0.1 mv, and the desorption process is initiated by removing the Dewar flask from the sample.

9) After completion of the desorption, a calibration peak is produced by injecting the nitrogen content of one or two loops into the sample. The size of the peak produced for calibration should be comparable to that of the desorption peak, and the same attenuation, or attenuations adjacent to one another should be used when producing both peaks.

It is the practice in this laboratory to run three cycles of adsorption-desorption-calibration. During these runs, the ambient temperature and the

barometric pressure are recorded alongside the peaks on the recorder chart, as well as the saturation pressure of nitrogen as read on the nitrogen manometer. A conversion table, supplied by the manufacturer, gives the temperature of the liquid nitrogen bath and the area covered by a one-ml nitrogen monolayer as a function of the saturation pressure of nitrogen monolayer as a function of the saturation pressure of nitrogen.

The procedure outlined here for the one-point method of surface area determination can be followed for a two- and three-point determination simply by using gas mixtures of different ratios, in order to obtain a true BET plot.

APPENDIX 3

A Nitrogen Manometer for the Measurement of the Saturation Pressure of Nitrogen at the Temperature of a Liquid Nitrogen Bath

In surface area measurements, an accurate knowledge of the saturation pressure of nitrogen at the temperature of the liquid nitrogen bath is essential, because the relative pressures of nitrogen and of helium are critical factors in the BET equation.

As was mentioned earlier, commercial liquid nitrogen is never pure, and while in use, it absorbs oxygen, carbon dioxide and water vapour at such a rate that one cannot rely on a simple correction for barometric pressure for estimating the true temperature of a liquid nitrogen bath, and hence the saturation pressure of nitrogen in the sample container immersed in the bath.

Low-temperature thermometers have been described in the literature (12) but they do not seem to be practical. The Shell Development Company has been using a closed mercury manometer filled with nitrogen to measure the saturation pressure of the liquid nitrogen bath before and after nitrogen adsorption on the samples. In this Laboratory, a slight modification of the instrument allows the measurement of the saturation pressure of nitrogen at the time of adsorption. Figure 4 shows the manometer "in situ", while Figure 5 is a diagram of the manometer.

The instrument consists of a one-metre-long manometer filled to about 50 cm with redistilled mercury. The bulb, which is the sensing part of the device, is connected to the manometer by means of a stainless steel flexible coupling, so as to permit positioning of the bulb between the legs of the U-shaped sample container in the Dewar cooling flask.

After the manometer has been filled to 50 cm with mercury, it is attached to a high vacuum line at points A and B, and evacuated. The whole assembly is gently flamed in order to remove any occluded gas, until the

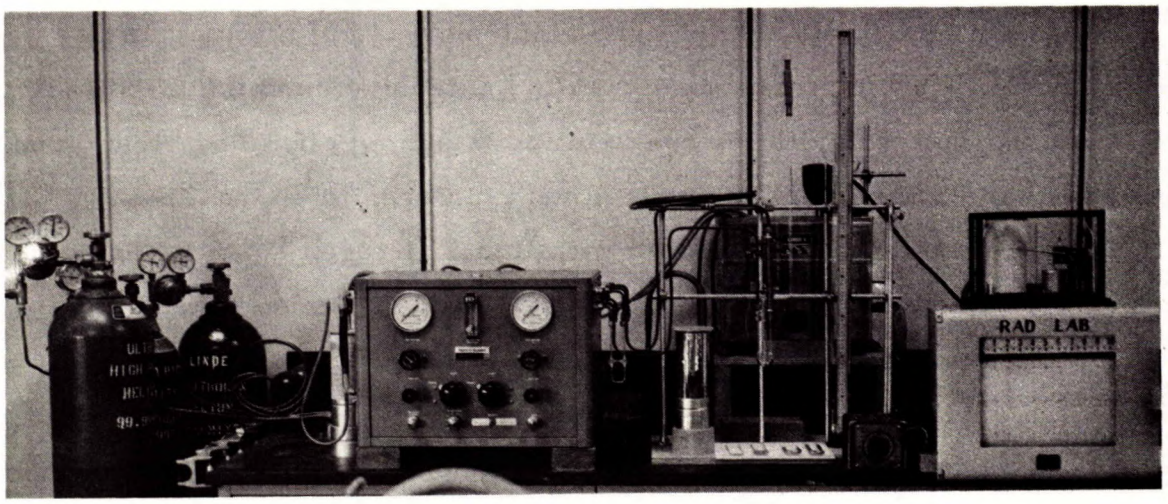

Figure 4. - Photograph of instrumentation used for the measurement of surface areas. From left to right: gas cylinders; sorptometer; nitrogen manometer and constant temperature bath; and recorder and barograph.

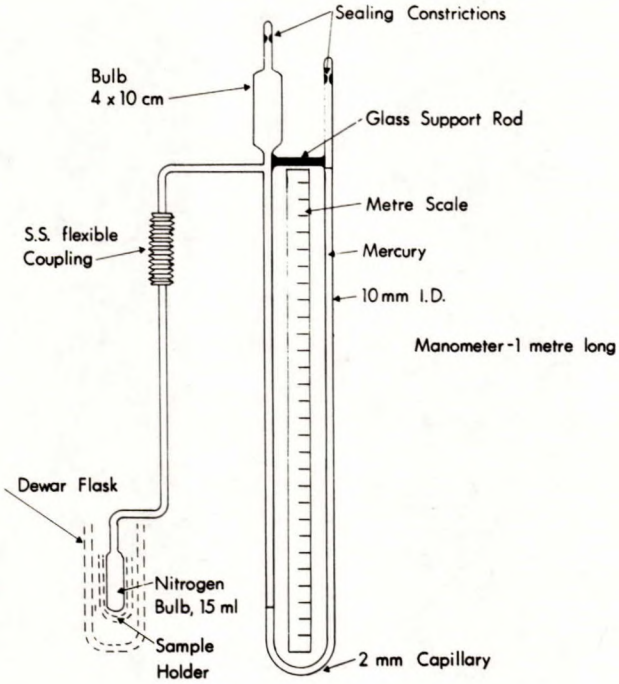

Figure 5. - Diagram of the nitrogen manometer.

mercury column is perfectly clear. The right-hand leg of the manometer is then filled with high-purity nitrogen. After extensive pumping at point A down to about 10^{-5} mm Hg, the A constriction is sealed off. The right-hand leg of the manometer is then pressurized with nitrogen to approximately 900 mm Hg, the sensing bulb is cooled with liquid nitrogen so as to reduce the pressure to atmospheric, and the constriction B is sealed off.

This manometer has given the desired accuracy ($\pm$ 0.03°K) and, if properly filled, should not require any maintenance.

Table 1 shows the relation between the boiling point and the saturation pressure of nitrogen, the cross-sectional area of one nitrogen molecule, and the area covered by a 1-cc nitrogen monolayer.

TABLE 1*

Saturation Pressure of N_2, Cross-sectional Area of One N_2 Molecule, and the Area Covered by a 1-cc Monolayer

Temperature		Saturation Pressure of Nitrogen	Cross-sectional Area of One N_2-Molecule	Area Covered by 1-cc N_2 Monolayer
T		P_o		s_o
°C	°K	mmHg	Å/molecule	m^2/ml (STP)
-195.80	77.36	760	16.268	4.3721
-195.69	77.47	770	16.275	4.3739
-195.57	77.59	780	16.281	4.3756
-195.47	77.69	790	16.287	4.3773
-195.36	77.80	800	16.294	4.3790
-195.25	77.91	810	16.301	4.3808
-195.14	78.02	820	16.308	4.3826
-195.04	78.12	830	16.315	4.3844
-194.93	78.23	840	16.321	4.3862
-194.83	78.33	850	16.327	4.3880
-194.73	78.43	860	16.334	4.3898
-194.63	78.53	870	16.340	4.3915
-194.53	78.63	880	16.346	4.3932
-194.43	78.73	890	16.353	4.3949
-194.33	78.83	900	16.359	4.3966

(*Courtesy of the Perkin-Elmer Corporation, Norwalk, Conn.)

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