<div align="center">**BRIEFING**</div>

⟨846⟩ **Specific Surface Area,** *USP 27* page 2385. The European Pharmacopoeia is the coordinating pharmacopeia for the international harmonization of the Specific Surface Area General Chapter, as part of the process of international harmonization of monographs and general analytical methods of the European, Japanese, and United States pharmacopeias. The following text represents the **ADOPTION STAGE 6** document. The EP draft was based in part on comments from the Japanese Pharmacopoeia and the United States Pharmacopeia in response to the Provisional Harmonized Text Stage 5A and 5B drafts prepared by the EP.

There are very few differences between the international harmonization **ADOPTION STAGE 6** document for Specific Surface Area and the current USP General Chapter, ⟨846⟩ *Specific Surface Area*. The fundamental principles have not changed.

(EMT: J. Lane)   RTS—41202-1

Change to read:

<div align="center">⟨846⟩ ~~**SPECIFIC SURFACE AREA**~~</div>

~~**Introduction** — The specific surface area of a powder is determined by physical adsorption of a gas on the surface of the solid and by measuring the amount of adsorbate gas corresponding to a single layer (monolayer) on the surface. Physical adsorption results from relatively weak forces (van der Waals forces) between the adsorbate gas molecules and the adsorbent surface of the test powder. The amount of gas adsorbed can be measured by a gravimetric, volumetric, or continuous flow procedure. Since the amount of gas adsorbed under a given pressure tends to increase on decreasing the temperature, adsorption measurements are usually made at a low temperature. Measurement is performed at 77 K, the boiling point of liquid nitrogen. The data are treated according to the Brunauer, Emmett, and Teller (BET) adsorption isotherm equation:~~

$$\frac{1}{\left[V_a\left(\frac{P_o}{P}-1\right)\right]} = \frac{C-1}{V_m C} \times \frac{P}{P_o} + \frac{1}{V_m C} \qquad (1)$$

~~where P, in mm of mercury, is the partial vapor pressure of adsorbate gas in equilibrium with the surface at 77 K, P_o, in mm of mercury, is the saturated pressure of the adsorbate gas, V_a, in mL, is the volume of gas adsorbed at standard temperature and pressure (STP, 273.15 K and 760 mm of mercury), V_m, in mL, is the volume of gas adsorbed at STP to produce an apparent monolayer on the sample surface, and C is a dimensionless constant that is related to the enthalpy of adsorption of the adsorbate gas on the powder sample. A value of V_a is measured at each of not less than three values of P/P_o. Then the BET value~~

$$1/\left[V_a\left(\frac{P_o}{P}-1\right)\right]$$

~~is plotted against P/P_o according to equation (1). This plot should yield a straight line. The data are considered acceptable if the correlation coefficient, r, of the linear regression is not less than 0.9975; that is, r^2 is not less than 0.995. From the resulting linear plot, the slope, which is equal to $(C-1)/V_m C$, and the intercept, which is equal to $1/V_m C$, are evaluated by linear regression analysis. From these values, V_m is calculated as $1/(slope + intercept)$, while C is calculated as $(slope/intercept) + 1$. From the value of V_m so determined, the specific surface area, S, in m^2 g^{-1}, is calculated by the equation:~~

$$S = V_m Na/22400m \qquad (2)$$

~~in which N is the Avogadro constant (6.023×10^{23} mole^{-1}), a is the effective cross-sectional area of one adsorbate molecule (0.162×10^{-18} m^2 for nitrogen or 0.195×10^{-18} m^2 for krypton), m is the mass, in g, of test powder, and 22400 is the volume, in mL, occupied by 1 mole of the adsorbate gas at STP, allowing for minor departures from ideality.~~

~~Some calculations and procedures, described below, require the absolute value of P_o, defined above, and of the barometric pressure, B, in mm of mercury. For liquid nitrogen open to the atmosphere in a Dewar vessel, P_o and B are taken to be equal to the measured atmospheric pressure (i.e., barometric pressure) plus 10 mm of mercury. Some instruments automatically perform the above measurements and computations. The upward correction of P_o and B allows for the elevation of the boiling point of nitrogen caused by impurities, such as oxygen, dissolved in the liquid nitrogen in the open Dewar vessel. This chapter describes the dynamic flow gas adsorption technique *(Method I)* and the volumetric gas adsorption technique *(Method II).*~~

<div align="center">~~**Outgassing**~~</div>

~~Before the specific surface area of the sample can be determined, it is necessary to remove gases and vapors that may have become physically adsorbed onto the surface after manufacture and during treatment, handling, and storage. If outgassing is not achieved, the specific surface area may be reduced or may be variable because an intermediate area of the surface is covered with molecules of the previously adsorbed gases or vapors.~~

~~**Conditions** — The outgassing conditions must be demonstrated to yield reproducible BET plots, as discussed under *Introduction,* a constant weight of test powder, and no detectable physical or chemical changes in the test powder. The outgassing conditions are critical for obtaining the required precision and accuracy of specific surface area measurements on pharmaceuticals because of the sensitivity of the surfaces of the materials. The outgassing conditions defined by the temperature, pressure, and time should be so chosen that the original surface of the solid is reproduced as~~

closely as possible. Outgassing of many substances is often achieved by applying a vacuum or by purging the sample in a flowing stream of a nonreactive gas. In either case, elevated temperatures are sometimes applied to increase the rate at which the contaminants leave the surface. Outgassing by heating the test powder may change the nature of the surface and should be avoided unless specifically indicated in the individual monograph. The outgassing conditions stated in the monograph for each material have been derived where possible from studies of several materials from various manufacturers. If heating is employed, the recommended temperature and time of outgassing are as low as possible so as to achieve reproducibly high measures of specific surface area within an acceptable time span. For outgassing sensitive specimens the desorption-adsorption cycling method may be employed.

Procedure— To outgas the test specimen by the desorption-adsorption cycling method, proceed as follows. Allow the test powder to equilibrate with the adsorbate gas, nitrogen at $P/P_o = 0.30$ or krypton at $P/P_o = 1.038 \times 10^{-3}$, for at least one minute. Raise the Dewar vessel containing liquid nitrogen at 77 K up to a defined point on the sample cell. This level should be high enough above the level of the sample to ensure that the temperature drops to 77 K yet below any connections, such as O-rings in the cell holder, which could leak if cooled. At least one minute after vigorous boiling of liquid nitrogen has subsided, record or zero the gas detector-integrator signal according to *Method I,* or record the pressure signal according to *Method II* (adsorption signal). Lower the Dewar vessel from the sample cell, and surround the sample cell with a beaker of water at room temperature. Record the gas detector-integrator signal according to *Method I,* or record the pressure signal according to the *Method II* (desorption signal) when the signal has become constant. Repeat the cooling-heating cycle until three successive desorption signals differ by not more than 3%. If possible, reweigh the sealed sample cell containing the test powder and subtract the mass of the empty sample cell to obtain the actual mass, *m,* of the test powder. The sealed sample cell containing the test powder may be weighed after the measurement of the specific surface area, if necessary.

Standard Materials

The method employed for the determination of the specific surface area of the samples should be tested using reference standards of known surface area, such as alpha alumina, purchased together with a certificate of analysis from a scientifically accredited source. [*] The chosen reference standard should have a specific surface area as similar as possible to that of the powder sample and should be treated with the utmost care. If the measured specific surface area of the reference material does not fall within the range specified on the certificate of analysis from an accredited source, the same adsorbate gas being used, the elements of the method and the gas adsorption apparatus should be carefully examined to identify the cause of the discrepancy, which should then be eliminated.

METHOD I—THE DYNAMIC FLOW METHOD

Principles of the Method— In the dynamic flow method, the recommended adsorbate gas, is nitrogen or krypton, while helium is employed as a diluent gas, which is not adsorbed under the recommended conditions. For powder samples of surface area less than about 0.3 m^2 (or of specific surface area less than about 0.5 m^2 g-1) krypton is the preferred adsorbate gas, while for samples of greater surface area, nitrogen is preferred. A minimum of three mixtures of the appropriate adsorbate gas with helium are required within the P/P_o range 0.05 to 0.30, such as 0.100, 0.200, and 0.300 mole fraction of nitrogen or 3.46×10^{-4}, 6.92×10^{-4}, and 1.038×10^{-3} mole fraction of krypton, where P/P_o is the relative pressure of the adsorbate gas, P being the partial vapor pressure and P_o being the saturated vapor pressure of the adsorbate gas. These mixtures should be certified to within 1% (absolute) or may be obtained by using a suitable apparatus to mix the appropriate adsorbate gas with helium in proportions accurate to 1%. Nitrogen or krypton, at least 99.9 mole percent, is also required for calibrating the gas detector-integrator employed for measuring the volume or mass of the gas adsorbed, or desorbed, by the test powder. The gas detector-integrator should provide a signal that is approximately proportional to the volume of the gas passing through it under defined conditions of temperature and pressure. For this purpose, a thermal conductivity detector with an electronic integrator is one among various suitable types. A minimum of three data points within the recommended range of 0.05 to 0.30 for P/P_o should be determined.

Procedure— Accurately weigh a quantity of the test powder, such that the total surface area is at least 1 m^2, if possible, in a tared gas adsorption flow cell. [NOTE— Transfer the test powder carefully into the flow cell so that a clear path is provided for the flow of the gas. An approximate value of the mass, *m,* of the test powder to be taken may be calculated from the mean particle diameter, *d,* and the true or crystal density, ρ, assuming spherical particles by the equation:

$$m = Ad\rho/6. \qquad (3)$$

in which *A* is the surface area desired. Because of the assumptions on which it is based, this equation must not be employed to calculate the actual surface area.] Outgas the powder sample.

Pass the gas mixture containing the largest mole fraction of the adsorbate gas, nitrogen or krypton, within the recommended range over the test powder for at least 30 seconds. Raise the Dewar vessel containing liquid nitrogen at 77 K up to a defined point on the flow cell. As mentioned above, this level should be high enough above the level of the sample to ensure that the temperature drops to 77 K yet below any connections, such as O-rings in the cell holder, which could leak if cooled. Record or zero the gas detector-integrator signal (adsorption signal) at least one minute after vigorous boiling of liquid nitrogen has subsided. Lower the Dewar vessel from the flow cell, and surround the flow cell with a beaker of water at room temperature. Record the gas detector-integrator signal (desorption signal) when the signal becomes constant. Repeat the cooling-heating cycle until three successive desorption signals differ by not more than 3%. The data for the first point may be derived from the desorption-adsorption cycling method, provided that this method is employed for outgassing the powder sample.

Record the last three desorption values at the largest mole fraction of the adsorbate gas, and calculate the arithmetic mean. Calibrate the gas detector-integrator by injecting, from a gas-tight syringe, a known volume of adsorbate gas, measured to ±2%, so as to give a signal within 15% of the last three desorption signals. Calculate the corresponding volume of adsorbate gas, V_a (in mm of mercury), at standard temperature and pressure (STP, 273.15 K and 760 mm of mercury), from the calibrated detector-integrator signal by the equation:

$$V_a = V_c \times A_a \times B \times (273.15K)/A_c \times T \times (760 \text{ mm of Hg}) \qquad (4)$$

in which V_c is the volume, in mL, of gas injected for calibration, A_a is the detector-integrator response for the gas desorbed from the test powder, A_c is the detector-integrator signal response for the calibration volume, B is the measured barometric pressure, in mm of mercury without the correction (described above under *Introduction*), and T, in K, is the temperature of volume measurement (room temperature). If possible, weigh the sealed flow cell containing the test powder, and subtract the mass of the empty flow cell from this mass to obtain the actual mass, *m*, of the powder taken.

Prepare at least two other mixtures of the appropriate adsorbate gas with helium, as described above. For each of these gas mixtures, repeat the above cooling-heating cycle, beginning with "Pass the gas mixture." Repeat the measurements for each of the gas mixtures until three successive desorption signals differ by not more than 3%. Immediately after recording each gas mixture signal, calibrate the gas detector-integrator, and calculate V_a as directed in the previous paragraph.

If the BET plot is not linear, when using nitrogen as the adsorbate gas, or if the measured amounts of nitrogen adsorbed are not repeatable to within ±3%, lack of strict proportionality between the measured values and the actual amounts of nitrogen adsorbed may be suspected, perhaps because of the thermal diffusion effect of nitrogen. The magnitude of this effect increases, and the accuracy and precision of the measurements decrease, with decreasing specific surface area of the powder specimen. Under these circumstances, and especially if the surface area of the powder sample is less than 0.3 m^2 or if the specific surface area of the powder sample is less than 0.5 m^2 g^{-1}, as mentioned above, the thermal diffusion effect may be considerably reduced or eliminated by using an adsorbate gas that has a lower vapor pressure, such as krypton, instead of nitrogen. Since for krypton the saturated vapor pressure at 77 K is only 2.63 mm of mercury, the required mole fractions of krypton in the three mixtures of krypton with helium are less than those of nitrogen in its mixtures with helium by a factor of 2.63/760 = 0.00346. Since the cross-sectional area of the krypton molecule is not well defined, it is recommended that the standard value, a = 0.195 nm^2, be used in equation (2) when calculating the specific surface area, and that the name of the adsorbate gas employed be stated, if it is not nitrogen, when reporting the value of the specific surface area.

METHOD II—THE VOLUMETRIC METHOD

Principles of the Method— In the volumetric method, the recommended adsorbate gas is nitrogen which is admitted into the evacuated space above the previously outgassed powder sample to give a defined equilibrium pressure, *P,* of the gas. The use of a diluent gas, such as helium, is therefore unnecessary, although helium may be employed for other purposes, such as to measure the void volume. Since only pure adsorbate gas, instead of a gas mixture, is employed, interfering effects of thermal diffusion are avoided in this method. Consequently, the use of an adsorbate gas possessing a low vapor pressure at 77 K, such as krypton, is unnecessary. Some instruments employ a balance tube to offset the effects of free space, thermal gradients, and non-ideal gas behavior. Other instruments claim other advantages. The use of equipment from any particular manufacturer is not specifically endorsed.

The volume of nitrogen admitted into the sample tube to give the equilibrium pressure, *P,* is equal to the sum of the volume of gas actually adsorbed, *V,* plus the volume of gas in the free space around and above the sample, V_f, which must be either corrected for by suitable adjustment of the instrument or balanced out. V is then converted by the following equation to the volume, V_a, occupied by the same amount of gas at standard temperature and pressure (STP, 273.15 K and 760 mm of mercury):

$$V_a = [V \times B \times (273.15 K)]/[T \times (760 \text{ mm Hg})]. \qquad (5)$$

Several instruments automatically perform the above measurements and computations. The instrument manual should always be consulted for guidance and for a complete description of the procedures for data acquisition and computation. A value of V_a is measured at each of not less than three values of P/P_o, and the data are plotted so as to provide a value of the specific surface area as described above under *Introduction.*

Procedure— Accurately weigh a quantity of the test powder, such that the total surface area is at least 1 m^2, if possible, in a tared gas adsorption tube. [To calculate an approximate value of the mass of the test powder to be taken, use equation (3).] Admit a small amount of dry nitrogen into the sample tube to prevent contamination of the clean surface, remove the sample tube, insert the stopper, and weigh it. Calculate the weight of the sample. Attach the sample tube to the dynamic volumetric apparatus. Cautiously evacuate the sample down to a pressure of 0.02 mm of mercury or less.

If the principle of operation of the instrument requires the determination of the void volume in the sample tube, for example, by the admission of a nonadsorbed gas, such as helium, this procedure is carried out at this point, followed by evacuation of the sample down to 0.02 mm of mercury or less. The adsorption of nitrogen gas is then measured as described below.

Raise a Dewar vessel containing liquid nitrogen at 77 K up to a defined point on the sample cell as directed under *Method I.* Admit a sufficient volume of nitrogen gas to give a relative pressure, P/P_o, equal to 0.10 ± 0.02. Measure the volume adsorbed, V_a. Repeat the measurement of V_a at P/P_o values of 0.20 ± 0.02 and 0.30 ± 0.02. A minimum of three data points is required. Additional measurements may be carried out, especially on those rare occasions when nonlinearity is obtained at a P/P_o value close to 0.3. Since nonlinearity is often obtained at P/P_o at or below 0.05, values in this region are not recommended. The test for linearity, the treatment of the data, and the calculation of the specific surface area of the sample are described above under *Introduction.*

Single-Point Measurement

Normally, at least three measurements of V_a, each at a different value of P / P_o, are required for the determination of specific surface area by *Method I* or *Method II.* However, under certain circumstances it may be acceptable to determine the specific surface area of a powder from a single value of V_a measured at a single value of P / P_o, such as 0.300 (corresponding to 0.300 mole of nitrogen or 0.001038 mole fraction of krypton), using the following equation for calculating V_m:

$$V_m = V_a \left(1 - \frac{P}{P_O} \right) \cdot \quad (6)$$

The specific surface area is calculated from the value of V_m by *equation (2)* stated above.

The single-point method may be employed directly for a series of powder samples of a given material for which the material constant, C, is much greater than unity. This circumstance may be verified by comparing values of specific surface area determined by the single-point method with that determined by the multiple-point method for the series of powder samples. Close similarity between the single-point values and multiple-point values suggests that $1/C$ approaches zero.

The single-point method may be employed indirectly for a series of very similar powder samples of a given material for which the material constant, C, is not infinite but may be assumed to be invariant. Under this circumstance, the error associated with the single-point method can be reduced or eliminated by using the multiple-point method to evaluate C for one of the samples of the series from the BET plot, from which C is calculated as (1 + *slope/intercept*). Then V_m is calculated from the single value of V_a measured at a single value of P / P_o by the equation:

$$V_m = V_a \left(\frac{P_O}{P} - 1 \right) \left[\frac{1}{C} + \frac{C-1}{C} \left(\frac{P}{P_O} \right) \right] \cdot \quad (7)$$

The specific surface area is calculated from V_m by equation (2) stated above.

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*   A suitable scientifically accredited source is the National Institute of Standards and Technology, Gaithersburg, Maryland.

Add the following:

■ ⟨846⟩ SPECIFIC SURFACE AREA

INTRODUCTION

The specific surface area of a powder is determined by physical adsorption of a gas on the surface of the solid and by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface. Physical adsorption results from relatively weak forces (van der Waals forces) between the adsorbate gas molecules and the adsorbent surface of the test powder. The determination is usually carried out at the temperature of liquid nitrogen. The amount of gas adsorbed can be measured by a volumetric or continuous flow procedure.

BRUNAUER, EMMETT AND TELLER (BET) THEORY AND SPECIFIC SURFACE AREA DETERMINATION

Multipoint Measurement

The data are treated according to the Brunauer, Emmett and Teller (BET) adsorption isotherm equation:

$$\frac{1}{\left[V_a \left(\dfrac{P_o}{P} - 1 \right) \right]} = \frac{C-1}{V_m C} \times \frac{P}{P_o} + \frac{1}{V_m C} \qquad (1)$$

P = partial vapor pressure of adsorbate gas in equilibrium with the surface at 77.4 K (b.p. of liquid nitrogen), in Pa,
P_o = saturated pressure of adsorbate gas, in Pa,
V_a = volume of gas adsorbed at standard temperature and pressure (STP) [273.15 K and atmospheric pressure (1.013×10^5 Pa)], in mL,
V_m = volume of gas adsorbed at STP to produce an apparent monolayer on the sample surface, in mL,
C = dimensionless constant that is related to the enthalpy of adsorption of the adsorbate gas on the powder sample.

A value of V_a is measured at each of not less than three values of P/P_o.

Then the BET value

$$\frac{1}{\left[V_a \left(\dfrac{P_o}{P} - 1 \right) \right]}$$

is plotted against P/P_o, according to equation (1). This plot should yield a straight line usually in the approximate relative pressure range 0.05 to 0.3. The data are considered acceptable if the correlation coefficient, r, of the linear regression is not less than 0.9975; that is, r^2 is not less than 0.995. From the resulting linear plot, the slope, which is equal to $(C-1)/V_m C$, and the intercept, which is equal to $1/V_m C$, are evaluated by linear regression analysis. From these values, V_m is calculated as $1/(slope + intercept)$, while C is calculated as $(slope/intercept) + 1$. From the value of V_m so determined, the specific surface area, S, in m$^2 \cdot$g^{-1}, is calculated by the equation:

$$S = \frac{V_m N a}{m \times 22400} \qquad (2)$$

N = Avogadro constant (6.023×10^{23} mol^{-1}),
a = effective cross-sectional area of one adsorbate molecule, in square meters (0.162 nm^2 for nitrogen and 0.195 nm^2 for krypton),
m = mass of test powder, in g,
22400 = volume, in mL, occupied by one mole of the adsorbate gas at STP allowing for minor departures from the ideal.

A minimum of three data points is required. Additional measurements may be carried out especially when nonlinearity is obtained at a P/P_o value close to 0.3. Because nonlinearity is often obtained at a P/P_o value below 0.05, values in this region are not recommended. The test for linearity, the treatment of the data, and the calculation of the specific surface area of the sample are described above.

Single-Point Measurement

Normally, at least three measurements of V_a, each at different values of P/P_o, are required for the determination of specific surface area by the dynamic flow gas adsorption technique *(Method I)* or by volumetric gas adsorption *(Method II)*. However, under certain circumstances described below, it may be acceptable to determine the specific surface area of a powder from a single value of V_a measured at a single value of P/P_o such as 0.300 (corresponding to 0.300 mole of nitrogen or 0.001038 mole fraction of krypton), using the following equation for calculating V_m:

$$V_m = V_a \left(1 - \frac{P}{P_o} \right) \qquad (3)$$

The specific surface area is then calculated from the value of V_m by equation (2) given above.

The single-point method may be employed directly for a series of powder samples of a given material for which the material constant C is much greater than unity. These circumstances may be verified by comparing values of specific surface area determined by the single-point method with that determined by the multipoint method for the series of powder samples. Close similarity between the single-point values and multipoint values suggests that $1/C$ approaches zero.

The single-point method may be employed indirectly for a series of very similar powder samples of a given material for which the material constant C is not infinite but may be assumed to be invariant. Under these circumstances, the error associated with the single-point method can be reduced or eliminated by using the multipoint method to evaluate C for one of the samples of the series from the BET plot, from which C is calculated as $(1 + slope/intercept)$. Then V_m is calculated from the single value of V_a measured at a single value of P/P_o, by the equation:

$$V_m = V_a \left(\frac{P_o}{P} - 1 \right) \left[\frac{1}{C} + \frac{C-1}{C} \times \left(\frac{P}{P_o} \right) \right] \qquad (4)$$

The specific surface area is calculated from V_m by equation (2) given above.

EXPERIMENTAL TECHNIQUES

This section describes the methods to be used for the sample preparation, the dynamic flow gas adsorption technique *(Method I)* and the volumetric gas adsorption technique *(Method II)*.

Sample Preparation

OUTGASSING

Before the specific surface area of the sample can be determined, it is necessary to remove gases and vapors that may have become physically adsorbed onto the surface after manufacture and during treatment, handling, and storage. If outgassing is not achieved, the specific surface area may be reduced or may be variable because an intermediate area of the surface is covered with molecules of the previously adsorbed gases or vapors. The outgassing conditions are critical for obtaining the required precision and accuracy of specific surface area measurements on pharmaceuticals because of the sensitivity of the surface of the materials.

The outgassing conditions must be demonstrated to yield reproducible BET plots, a constant weight of test powder, and no detectable physical or chemical changes in the test powder.

The outgassing conditions defined by the temperature, pressure, and time are chosen so that the original surface of the solid is reproduced as closely as possible. Outgassing of many substances is often achieved by applying a vacuum by purging the sample in a flowing stream of a nonreactive, dry gas or by applying a desorption-adsorption cycling method. In either case, elevated temperatures are sometimes applied to increase the rate at which the contaminants leave the surface. Caution should be exercised when outgassing powder samples using elevated temperatures to avoid affecting the nature of the surface and the integrity of the sample.

If heating is employed, the recommended temperature and time of outgassing are as low as possible to achieve reproducible measurement of specific surface area in an acceptable time. For outgassing sensitive samples, other outgassing methods such as the desorption-adsorption cycling method may be employed.

ADSORBATE

The standard technique is the adsorption of nitrogen of analytical quality at liquid nitrogen temperature.

For powders of low specific surface area (< 0.2 m^2g^{-1}) the proportion adsorbed is low. In such cases, the use of krypton at the liquid nitrogen temperature is preferred because the low vapor pressure exerted by this gas greatly reduces error. The use of larger sample quantities, where feasible (equivalent to 1 m^2 or greater total surface area using nitrogen), may compensate for the errors in determining low surface areas.

All gases used must be free from moisture.

QUANTITY OF SAMPLE

A quantity of the test powder is accurately weighed such that the total surface of the sample is at least 1 m^2 when the adsorbate is nitrogen and 0.5 m^2 when the adsorbate is krypton.

Lower quantities of sample may be used after appropriate validation.

Measurements

Because the amount of gas adsorbed under a given pressure tends to increase when the temperature is decreased, adsorption measurements are usually made at a low temperature. Measurement is performed at 77.4 K, the boiling point of liquid nitrogen.

Method I: The Dynamic Flow Method

PRINCIPLE

In the dynamic flow method (see *Figure 1*), the recommended adsorbate gas is dry nitrogen or krypton, while helium is employed as a diluent gas, which is not adsorbed under the recommended conditions.

A minimum of three mixtures of the appropriate adsorbate gas with helium are required within the P/P_o range 0.05 to 0.30.

The gas detector-integrator should provide a signal that is approximately proportional to the volume of the gas passing through it under defined conditions of temperature and pressure. For this purpose, a thermal conductivity detector with an electronic integrator is one among various suitable types. A minimum of three data points within the recommended range of 0.05 to 0.30 for P/P_o is determined.
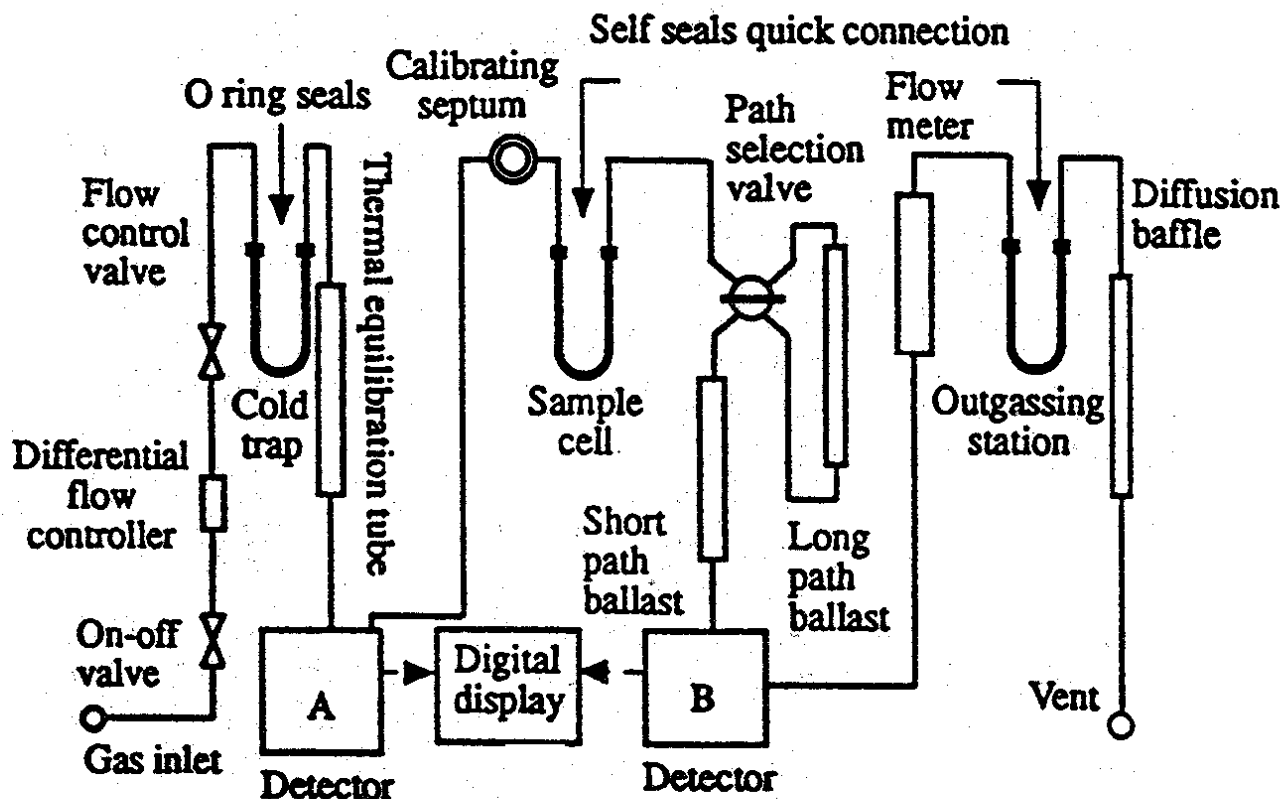
Fig. 1. Schematic diagram of the dynamic flow method apparatus.

PROCEDURE

A known mixture of the gases, usually nitrogen and helium, is passed through a thermal conductivity cell, through the sample again, through the thermal conductivity cell, and then to a recording potentiometer.

The sample cell is immersed in liquid nitrogen, and the sample adsorbs nitrogen from the mobile phase. This unbalances the thermal conductivity cell, and a pulse is generated on a recorder chart.

The sample is removed from the coolant; this gives a desorption peak equal in area and in the opposite direction to the adsorption peak. Because this is better defined than the adsorption peak, it is the one used for the determination.

To effect the calibration, a known quantity of adsorbate, sufficient to give a peak of similar magnitude to the desorption peak, is injected into the system, and the proportion of gas volume per unit peak area is obtained.

A mixture of nitrogen and helium is used for a single-point determination; and several such mixtures or premixing two streams of gas are used for a multipoint determination.

The calculation is the same as the volumetric method.

Method II: The Volumetric Method

PRINCIPLE

In the volumetric method (see *Figure 2*), the recommended adsorbate gas is nitrogen, which is admitted into the evacuated space above the previously outgassed powder sample to give a defined equilibrium pressure, P, of the gas. The use of a diluent gas, such as helium, is therefore unnecessary, although helium may be employed for other purposes, such as to measure the dead volume.

Because only pure adsorbate gas, instead of a gas mixture, is employed, interfering effects of thermal diffusion are avoided in this method.
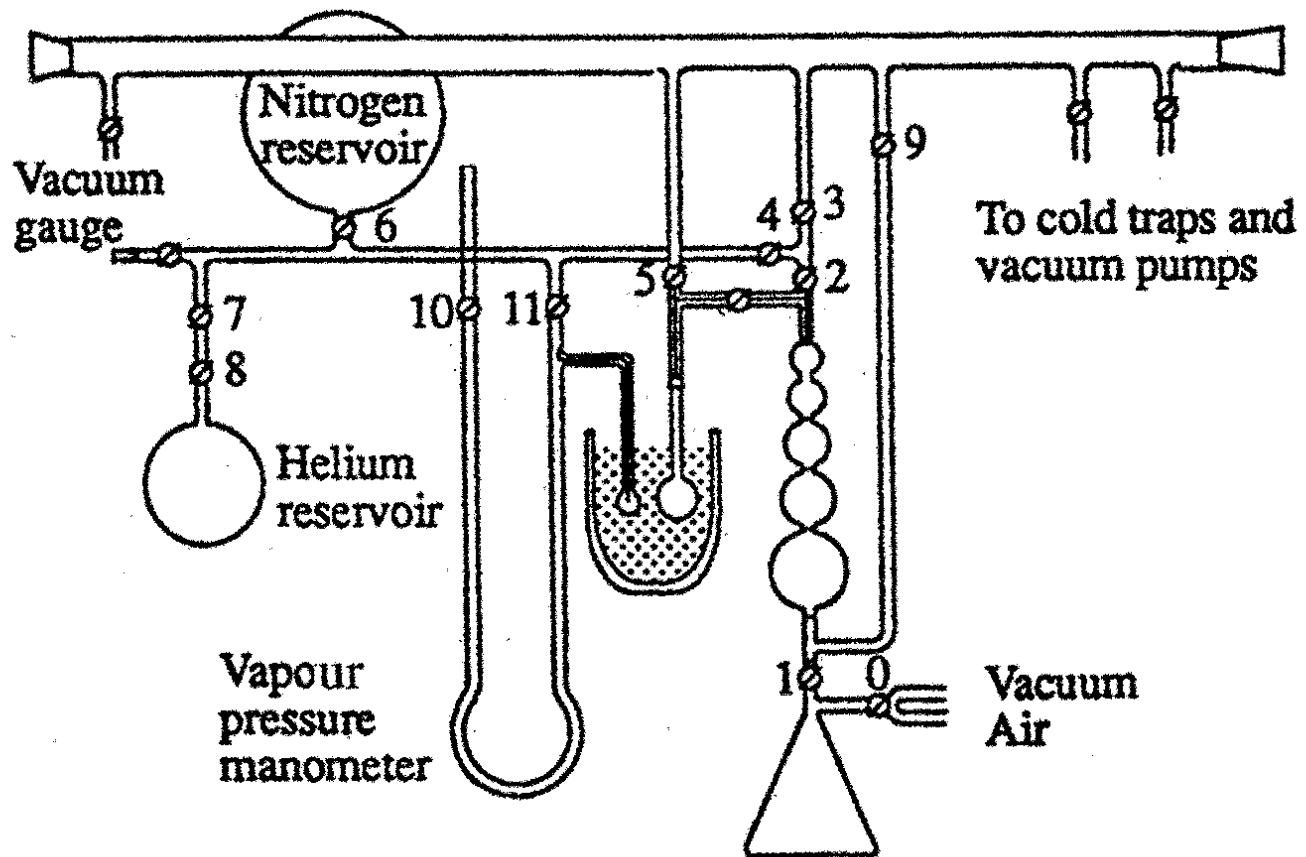

Fig. 2. Schematic diagram of the volumetric method apparatus.

PROCEDURE

A small amount of dry nitrogen is admitted into the sample tube to prevent contamination of the clean surface, the sample tube is removed, a stopper is inserted, the tube is weighed, and the weight of the sample is calculated. Then the sample tube is attached to the volumetric apparatus. The sample is cautiously evacuated down to the specified pressure (e.g., between 2 Pa and 10 Pa). Alternately, some instruments are operated by evacuating to a defined rate of pressure change (e.g., less than 13 Pa/30 s) and by holding for a defined period of time before commencing the next step.

If the principle of operation of the instrument requires the determination of the dead volume in the sample tube, for example, by the admission of a nonadsorbed gas, such as helium, this procedure is carried out at this point, followed by evacuation of the sample. The determination of dead volume may be avoided using difference measurements: that is, by means of reference and sample tubes connected by a differential transducer. The adsorption of nitrogen gas is then measured as described below.

Raise a Dewar vessel containing liquid nitrogen at 77.4 K up to a defined point on the sample cell. Admit a sufficient volume of adsorbate gas to give the lowest desired relative pressure. Measure the volume adsorbed, V_a. For multipoint measurements, repeat the measurement of V_a at successively higher P/P_o values. When nitrogen is used as the adsorbate gas, P/P_o values of 0.10, 0.20, and 0.30 are often suitable.

Reference Materials

Periodically verify the functioning of the apparatus using appropriate reference materials of known surface area that has a specific surface area similar to that of the sample to be examined.

■1S (*USP28*)