

EXPERTS IN SIZE AND CRYSTALS

BET theory

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BET theory

The specific surface area of a powder is determined by the physical adsorption of a gas on the solid's surface and by the calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface. The physical adsorption result from relatively weak van der Waals forces between the adsorbate gas molecules and the adsorbent surface area of the test powder. Usually, the determination is performed at the temperature of liquid nitrogen. Typically the amount of gas adsorbed is measured by a volumetric or continuous flow procedure.

Multi-point measurements

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

$$\left[\frac{1}{V_a \left(\frac{P_0}{P} - 1 \right)} \right] = \frac{C-1}{V_m C} \times \frac{P}{P_0} + \frac{1}{V_m C}$$

P	=	The partial vapour pressure of adsorbate gas in equilibrium with the surface at 77.4 K (b.p. of liquid nitrogen), in pascals.
P_0	=	The saturated pressure of adsorbate gas, in pascals.
V_a	=	The volume of gas adsorbed at standard temperature and pressure (STP) [273.15 K and atmospheric pressure (1.013×10^5 Pa)], in millilitres.
V_m	=	The volume of gas adsorbed at STP to produce an apparent monolayer on the sample surface, in millilitres.
C	=	The dimensionless constant related to the enthalpy of adsorption of the adsorbate gas on the powder sample.



The value of V_a is measured at each 3 values of P/P_0 .

$$\frac{1}{V_a \left(\frac{P_0}{P} - 1 \right)}$$

The BET value is plotted against P/P_0 according to equation (1). This plot should yield a straight line, usually in the approximate relative pressure range of 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 $1/(\text{slope} + \text{intercept})$, while C is calculated as $(\text{slope}/\text{intercept}) + 1$. From the value of V_m so determined, the specific surface area, S , in $\text{m}^2 \cdot \text{g}^{-1}$, is calculated by the equation:

N	=	The Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$).
a	=	The effective cross-sectional area of one adsorbate molecule, in square metres (0.162 nm^2 for nitrogen and 0.195 nm^2 for krypton).
m	=	The mass of test powder, in grams.
22400	=	The volume occupied by 1 mole of the adsorbate gas at STP allowing for minor departures from the ideal, in millilitres.

A minimum of 3 data points is required. Additional measurements may be carried out, especially when non-linearity is obtained at a P/P_0 value close to 0.3. Because non-linearity is often obtained at a P/P_0 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

Typically, at least 3 measurements are required of V_a . Each at a different value of P/P_0 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_0 such as 0.300 (corresponding to 0.300 moles of nitrogen or 0.001038 moles fraction of krypton), using the following equation for calculating V_m :

$$S = \frac{V_m N_a}{m \times 22400}$$

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 the specific surface area determined by the single-point method with that determined by the multiple-point method for the series of powder samples. The 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 these circumstances, the error associated with the single-point method can be reduced or eliminated by using the multi-point method to evaluate C for one of the samples of the series from the BET plot, from which C is calculated as $(1 + \text{slope}/\text{intercept})$. Then V_m is calculated from the single value of V_a measured at a single value of P/P_0 by the equation:

$$V_m = V_a \left(1 - \frac{P}{P_0} \right)$$

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

The following 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 vapours 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 vapours. 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.

Conditions: 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 should be 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 non-reactive, 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.

The volumetric method (Ph. Eu.2.9.26 Method II)

Principle: In the volumetric method (see Figure 2.9.26.-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.

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

Procedure: 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 volumetric apparatus. Cautiously evacuate the sample down to the specified pressure (e.g. between 2 Pa and 10 Pa). Alternatively, some instruments operate by evacuating to



a defined rate of pressure change (e.g. less than 13 Pa/30 s) and 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 non-adsorbed 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 multi-point measurements, repeat the measurement of V_a at successively higher P/P_0 values. When nitrogen is used as the adsorbate gas, P/P_0 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, such as α -alumina, which should have a specific surface area similar to that of the sample to be examined.

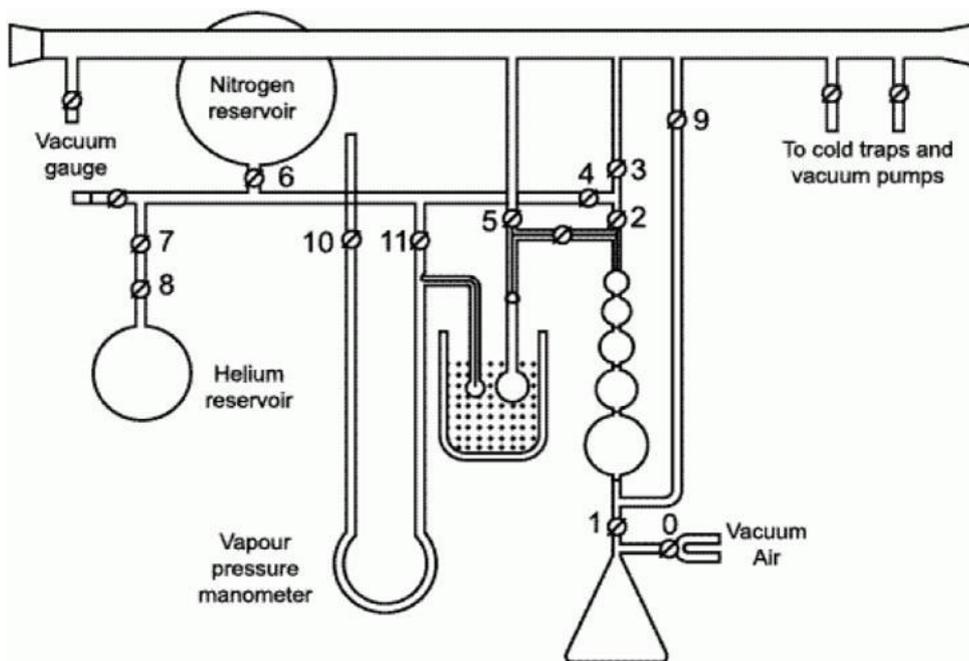


Figure 2.9.26.-1. — Schematic diagram of the dynamic flow method apparatus dynamic flow method apparatus