INTERNATIONAL STANDARD

ISO 9277

Determination of the specific surface area of solids by gas adsorption — BET method

Détermination de l'aire massique (surface spécifique) des solides par adsorption de gaz — Méthode BET

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 24, *Particle characterization including sieving*, Subcommittee SC 4, *Particle characterization.*

This third edition cancels and replaces the second edition (ISO 9277:2010), which has been technically revised.

The main changes compared to the previous edition are as follows:

— the IUPAC classification of adsorption isotherms has been updated according to Reference [3];

— the description of dynamic vapour sorption (DVS) method in 6.3.6 has been added;

— Annex A has been revised;

— Annex B has been removed;

— the former Annex C (now Annex B) has been revised.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Gas adsorption allows for assessing surface area of nonporous materials and porous materials with accessible porosity (which depends on the chosen adsorptive) via the Brunauer, Emmett and Teller (BET) theory[1],[2]. The BET theory is applicable only to adsorption isotherms of type II (disperse, nonporous or macroporous solids) and type IV (mesoporous solids) (see Figure 1, Type II and Type IVa isotherms). However, in the case of Type IVb isotherms, caution is required since pore condensation can occur at quite low p/p_0 (see IUPAC recommendations[3]). The BET method cannot reliably be applied to solids which absorb the measuring gas. A strategy for BET area determination of microporous materials (type I isotherms) is described in Annex B.
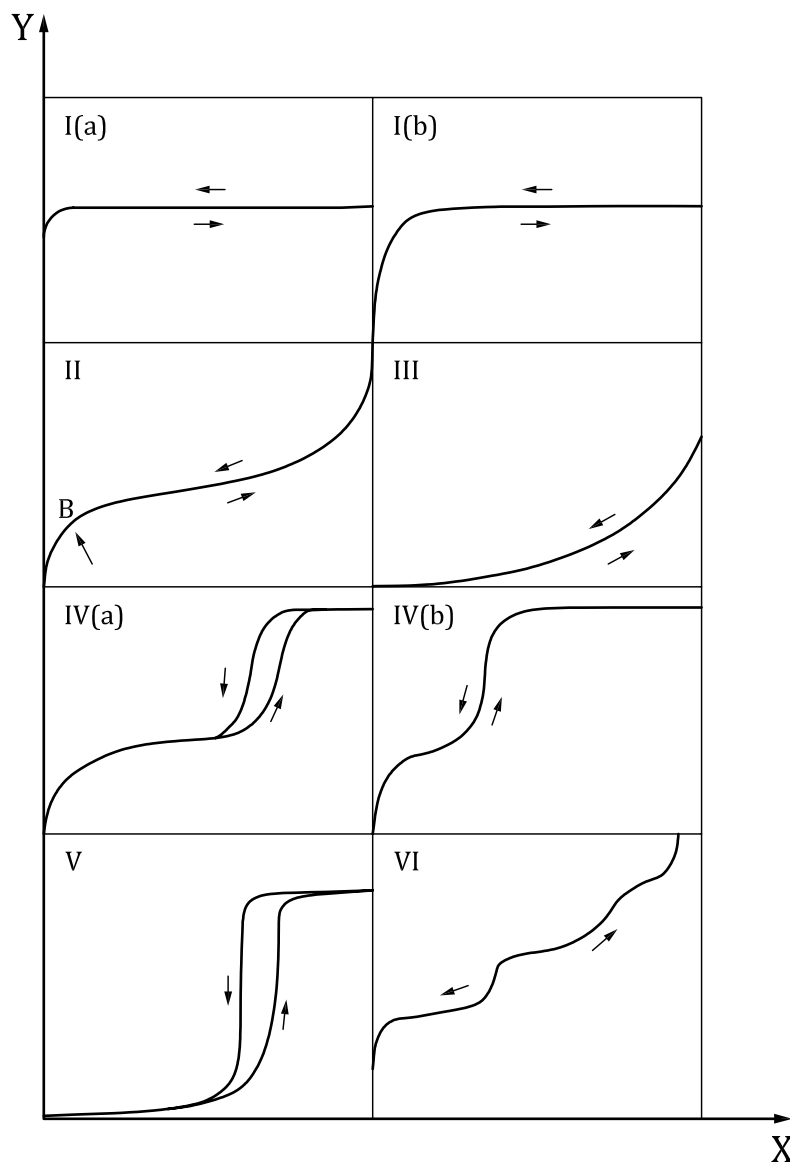
Key

X   relative pressure

Y   amount adsorbed

SOURCE   IUPAC Recommendations, 1994. Reproduced with the permission of the authors.[2]

Figure 1 — IUPAC (2015) classification of adsorption isotherms

Determination of the specific surface area of solids by gas adsorption — BET method

1   Scope

This document specifies the determination of the overall specific external and internal surface area of either disperse (e.g. nano-powders) or porous, solids by measuring the amount of physically adsorbed gas according to the method of Brunauer, Emmett and Teller method,[1] based on the 2015 International Union for Pure and Applied Chemistry (IUPAC) recommendations[3].

NOTE   For solids exhibiting a chemically heterogeneous surface, for example, metal-carrying catalyst, the BET method gives the overall surface area, whereas the metallic portion of the surface area can be measured by chemisorption methods.

2   Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 8213, *Chemical products for industrial use — Sampling techniques — Solid chemical products in the form of particles varying from powders to coarse lumps*

ISO 14488, *Particulate materials — Sampling and sample splitting for the determination of particulate properties*

3   Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
adsorption
enrichment of the adsorptive gas at the external and accessible internal surfaces of a solid material

3.2
physisorption
weak bonding of the *adsorbate* (3.2), reversible by small changes in pressure or temperature

3.3
adsorbate
adsorbed gas

3.4
adsorptive
gas or vapour to be adsorbed

3.5
adsorbent
solid material on which *adsorption* (3.1) occurs

3.6
isotherm
relationship between the amount of gas adsorbed and the equilibrium pressure of the gas, at constant temperature

3.7
volume adsorbed
volumetric equivalent of *adsorbed amount* (3.8) expressed as gas at standard conditions of temperature and pressure (STP)

3.8
adsorbed amount
number of moles of gas adsorbed at a given pressure and temperature

3.9
monolayer capacity
volumetric equivalent of monolayer amount expressed as gas at standard conditions of temperature and pressure

3.10
surface area
area of the external surface of a solid plus the internal surface of its accessible macro-, meso- and *micropores* (3.16)

3.11
specific surface area
absolute *surface area* (3.10) of the sample divided by sample mass

3.12
molecular cross-sectional area
molecular area of the *adsorbate* (3.2), i.e. the area occupied by an adsorbate molecule in the complete monolayer

3.13
nanopore
pore with width of about 100 nm or less

3.14
macropore
pore with width greater than approximately 50 nm

3.15
mesopore
pore with width between approximately 2 nm and 50 nm

3.16
micropore
pore with width of approximately 2 nm or less

3.17
relative pressure
ratio of the equilibrium *adsorption* (3.1) pressure, *p,* to the *saturation vapour pressure* (3.18), p_0, at analysis temperature

3.18
saturation vapour pressure
vapour pressure of the bulk liquefied adsorptive gas at the temperature of *adsorption* (3.1)

3.19
free space
head space
dead space
dead volume
volume of the sample holder not occupied by the sample

4 Symbols

Table 1 presents the symbols used in this document, together with their common units derived from the SI. For comparison purposes, the lUPAC symbols are also given. All specific dimensions are related to sample mass in grams.

Table 1 — Symbols

Symbol	Quantity	Unit
a_m	molecular cross-sectional area	nm^2
a_s	specific surface area	$m^2\,g^{-1}$
C	BET parameter [a]	1
L	Avogadro constant ($L = 6{,}022 \times 10^{23}$)	mol^{-1}
m	mass of the solid sample	g
m_a	specific mass adsorbed [a]	1
n_a	specific amount adsorbed	$mol{\cdot}g^{-1}$
n_m	specific monolayer capacity of adsorbate	$mol\,g^{-1}$
$n_{m,mp}$	specific monolayer capacity derived from multipoint measurement	$mol\,g^{-1}$
$n_{m,sp}$	specific monolayer capacity derived from single-point measurement	$mol\,g^{-1}$
p	pressure of the adsorptive in equilibrium with the adsorbate	Pa
p_0	saturation vapour pressure of the adsorptive	Pa
p/p_0	relative pressure of the adsorptive [a]	1
R	molar gas constant (= 8,314)	$J\,mol^{-1}\,K^{-1}$
r_s	radius of uniform nonporous spheres	nm
t	time	min
T	temperature	K
V_a	specific volume adsorbed	$cm^3\,g^{-1}$
$V_{p,micro}$	specific micropore volume	$cm^3\,g^{-1}$
ρ	(mass) density	$g\,cm^{-3}$
u_c	combined standard uncertainty for the certified specific surface area of a BET reference material	$m^2\,g^{-1}$
k	coverage factor for the combined standard uncertainty [a]	1
U	expanded uncertainty ($U = k\,u_c$) for the certified specific surface area of a BET reference material	$m^2\,g^{-1}$
[a] According to ISO 80000-1, the unit for any quantity of dimension one (at present commonly termed "dimensionless") is the unit one, symbol 1.		

5 Principle

The method specified involves the determination of the amount of adsorbate or adsorptive gas required to cover the external and the accessible internal pore surfaces of a solid (see Figure 2) with a complete monolayer of adsorbate. This monolayer capacity can be calculated from the adsorption isotherm using Formula (1) (see 7.1). Any gas may be used, provided it is physically adsorbed by weak bonds at the

surface of the solid (van der Waals forces) and can be desorbed by a decrease in pressure at the same temperature.
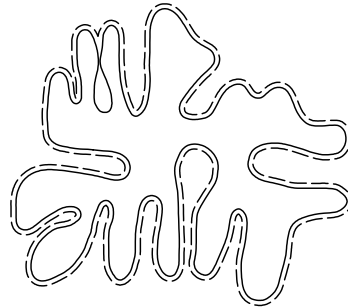
Figure 2 — Schematic cross-section of a particle with surface detected by the adsorption method shown by dotted line

Nitrogen at its boiling point (about 77 K) was for many decades the adsorptive generally used for the determination of the specific surface area, mainly because liquid nitrogen was readily available and relatively strong attractive adsorptive-adsorbent interactions for many systems. However, due to nitrogen's quadrupole moment the orientation of a nitrogen molecule is affected by the surface chemistry of the adsorbent. This leads to uncertainties in the surface area determination by nitrogen in the order of approximately 20 % for some surfaces. However, argon at 87 K is a great alternative because argon does, contrary to the diatomic nitrogen molecule, not exhibit a quadrupole moment. Hence, argon adsorption is less sensitive to the surface chemistry leading to a much more reliable surface area determination for many adsorbent surfaces. If the sensitivity of the instrument when using argon or nitrogen is insufficient for low specific surface areas of about 1 m^2 g^{-1} or lower, the application of krypton adsorption at liquid nitrogen temperature for the specific surface area analysis is recommended. As a consequence of the low p_0 of about 0,35 kPa for krypton at 77 K, the 'free space' correction (see 3.19) for unadsorbed gas is significantly reduced (to 1/300th) compared to the conditions of nitrogen adsorption at the same temperature and it becomes possible to manometrically measure low uptakes of adsorptive with acceptable accuracy. Although at 77 K krypton is about 38,5 K below its triple point temperature, there is some evidence from microcalorimetry and neutron diffraction studies that in the BET region, the adsorbate may well be in a liquid-like state and therefore the value of the supercooled liquid is recommended as the effective p_0 for the construction of the BET plot.

The results of measurements with different adsorptives may deviate from each other because of different molecular areas, different accessibilities to pores (classified into micro-, meso-, macro- and nanopores) and different measuring temperatures. Moreover, it is well known from the concepts of fractal analysis that experimental results for the quantities of length and area in the case of irregular complex structures – such as those which are found in most porous and/or highly dispersed objects – are not absolute but depend on the measurement scale i.e. the "yardstick" used. This means that less area is available for larger adsorbate molecules.

The adsorptive gas is admitted to the sample container, which is held at a constant temperature. The amounts adsorbed are measured in equilibrium with the adsorptive gas pressure p and plotted against relative pressure, p/p_0, to give an adsorption isotherm. Adsorption isotherms may be obtained by manometric (volumetric), by gravimetric or by the carrier gas method using continuous or discontinuous operation (see 6.3).

6 Procedure

6.1 Sample preparation

Sampling shall be carried out in accordance with ISO 8213 and ISO 14488. Prior to the determination of an adsorption isotherm, remove physically adsorbed material from the sample surface by degassing, while avoiding irreversible changes to the surface. Ascertain the maximum temperature at which

the sample is not affected by thermogravimetric analysis (see Figure 3), by spectroscopic methods, or by trial experiments using different degassing conditions of time and temperature. When vacuum conditions are used, degassing to a residual pressure of approximately 1 Pa or better is usually sufficient. Degassing of the sample can also be performed at elevated temperature by flushing with an inert gas (e.g. helium, nitrogen, argon). Degassing is complete when a steady value of the residual gas pressure, p, of its composition or of the sample mass is reached.
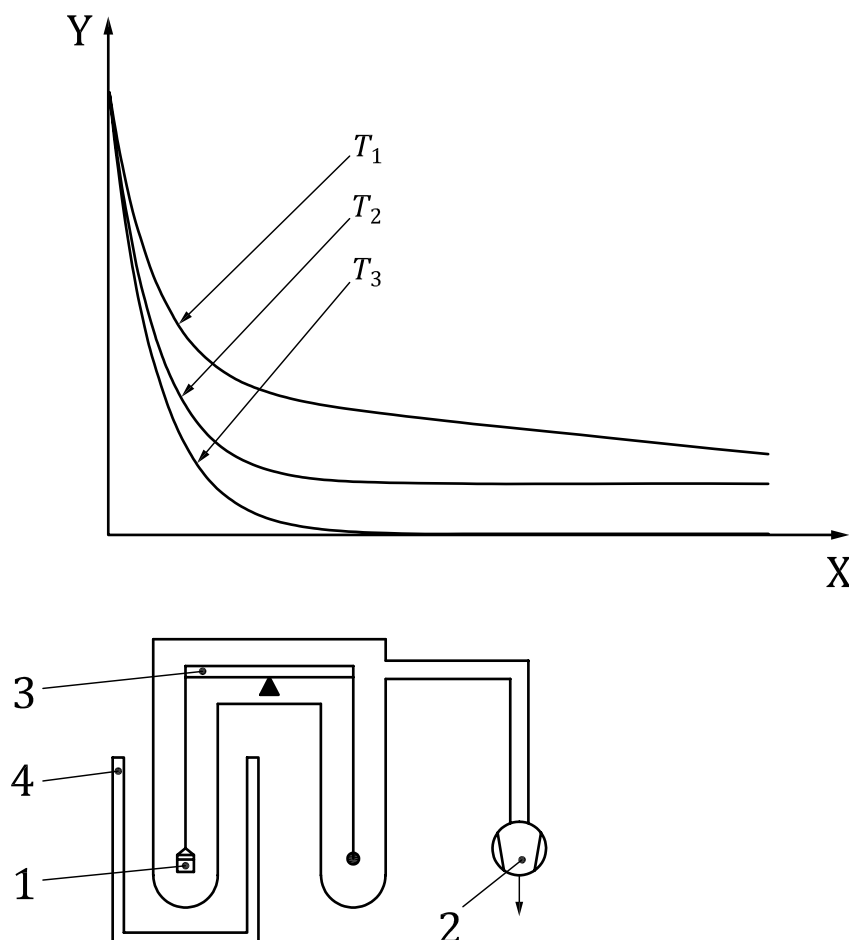
Key

X	degassing time	1	sample
Y	sample mass	2	vacuum generating system
T_1	temperature too low: long degassing time	3	balance
T_2	optimum temperature	4	oven
T_3	temperature too high: gas evolution due to decomposition of the sample		

Figure 3 — Thermogravimetric control of degassing

Using the vacuum technique, isolate the heated sample container from the pump and trap (at time t_i in Figure 4). If the pressure is nearly constant over a period of 15 min to 30 min, degassing is complete. This procedure also establishes the absence of leaks. The specific surface area should be related to the mass of the degassed sample.

Key

X	time	$p_3(t)$	leak
Y	pressure	1	sample
t_1	time of sample isolation	2	vacuum generating system
$p_1(t)$	degassing complete, apparatus tight	3	manometer
$p_2(t)$	incomplete degassing	4	oven
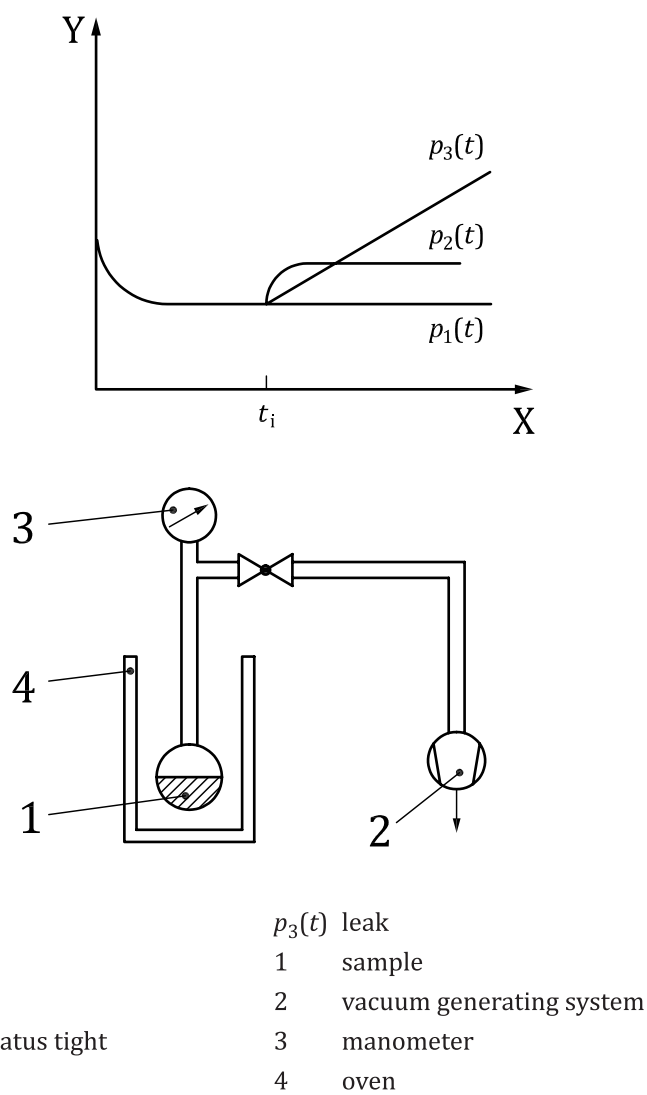
Figure 4 — Pressure control of degassing

After degassing, the sample container is cooled to the measuring temperature. It should be noted that, at low gas pressures, the temperature of the sample needs some time to equilibrate due to the reduced thermal conductivity within the sample cell.
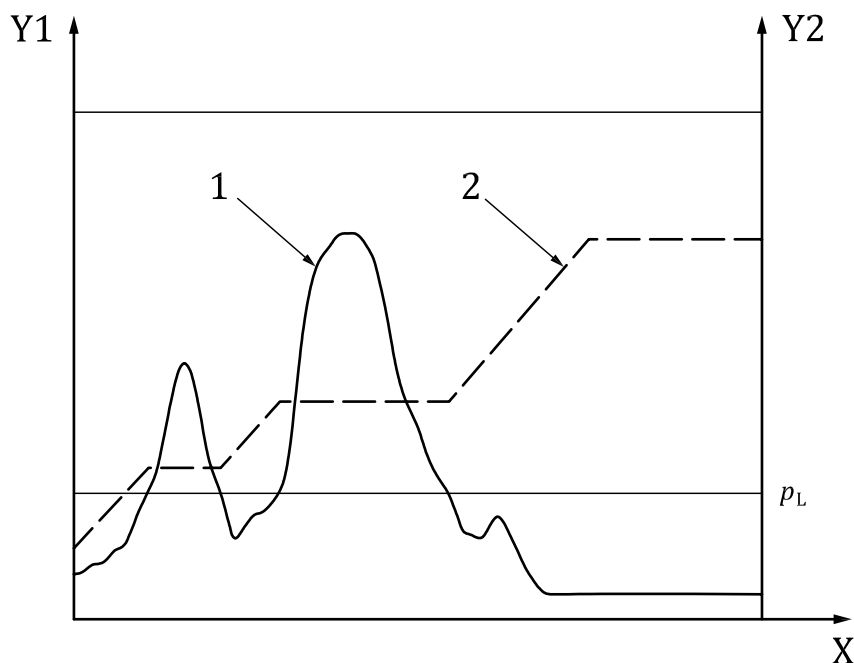
Key

X	time	p_L	fixed pressure limit
Y1	temperature	1	pressure curve
Y2	pressure	2	temperature curve

Figure 5 — Pressure controlled heating

For sensitive samples, a pressure-controlled heating (see Figure 5) is recommended. This procedure consists in varying the heating rate in relationship to the gas pressure evolved from a porous material during the degassing under vacuum conditions. When a fixed pressure limit p_L (usually around 7 Pa to 10 Pa) is overtaken due to the desorbed material from the sample surface, the temperature increase is stopped and the temperature is kept constant until the pressure falls below the limit, at that point the system continues the temperature ramp. This procedure is particularly suitable to avoid structural changes in microporous materials when fast heating rates can damage fragile structures due to a vigorous vapour release. In addition, the method is very safe in preventing sample elutriation when water or other vapour are released from the pores in very fine powder materials.

6.2 Experimental conditions

The precision of the measurement depends on the control of the following conditions.

a) The temperature or the p_0 value of the adsorptive should be monitored during the analysis.

b) The purity of the adsorptive and any helium used to calibrate volumes or as a carrier gas should be at least 99,999 %. If necessary, the gases should be dried and cleaned, for example, oxygen removed from nitrogen.

c) The saturation vapour pressure p_0 of the adsorptive at the measuring temperature can either be determined directly using a nitrogen vapour pressure thermometer, or it can be monitored and determined by measurement of the thermostat bath temperature.

d) The validity of the result depends on careful sampling and sample preparation.

In the discontinuous static procedure, at least three points within the relative pressure range for which the BET equation is valid (typically 0,05 to 0,3) should be measured in equilibrium. For continuous measurements, the deviation from equilibrium must be controlled either by occasional interruption of the gas flow or by control measurements using the discontinuous method.

6.3   Measuring methods for the assessment of the amount of adsorbed gas

6.3.1   General

The various types of apparatus used for the determination of physisorption isotherms may be divided into manometric and gravimetric methods, whereby static or dynamic techniques may be used in either case. The manometric method is generally considered the most suitable technique for undertaking physisorption measurements with nitrogen, argon and argon at cryogenic temperatures (i.e. 77 K and 87 K, the boiling point of nitrogen and argon respectively).

Gravimetric adsorption techniques are especially convenient for measurements with vapours (e.g. water vapour or some organic adsorptives) at temperatures not too far removed from ambient. At low temperatures (in particular at cryogenic temperatures), however, it can become difficult to control convection effects and to measure the exact temperature of the adsorbent.

6.3.2   Static manometric (volumetric) method

In the static manometric method, a known amount of gas is admitted to a sample bulb thermostated at the adsorption temperature (see Figure 6). Adsorption of the gas onto the sample occurs, and the pressure in the confined volume continues to fall until the adsorbate and the adsorptive are in equilibrium. The amount of adsorbate at the equilibrium pressure is the difference between the amount of gas admitted and the amount of adsorptive remaining in the gas phase. Measurement of the pressure is required together with temperatures and volumes of the system. The volumes are most easily determined by gas expansion of an inert gas such as helium. The free space volume must be determined before or after the measurement of the adsorption isotherm. The calibration of the volumes of the system is done manometrically using helium at the measuring temperature. It should be noted that some materials can adsorb and/or absorb helium. In this case, corrections can be made after measuring the adsorption isotherm. If the measurement of the free space volume can be separated from the adsorption measurement, the use of helium can be avoided. The void volume of the empty sample cell is measured at ambient temperature using nitrogen. Subsequently, a blank experiment (with the empty sample cell) is performed under the same experimental conditions (temperature and relative pressure range) as the sorption measurements. The required correction for the sample volume is made by entering the sample density or by pycnometric measurement with nitrogen at ambient temperature at the start of the adsorption analysis (in case nitrogen adsorption effects can be neglected). The determination of the free space volume may be avoided using difference measurements, that is, by means of a reference and sample tube connected by a differential transducer. During sample measurement and determination of the dead volume, it is recommended that the liquid level in the cooling bath be maintained, unless otherwise compensated, at least 15 mm above the sample and constant to within 1 mm.
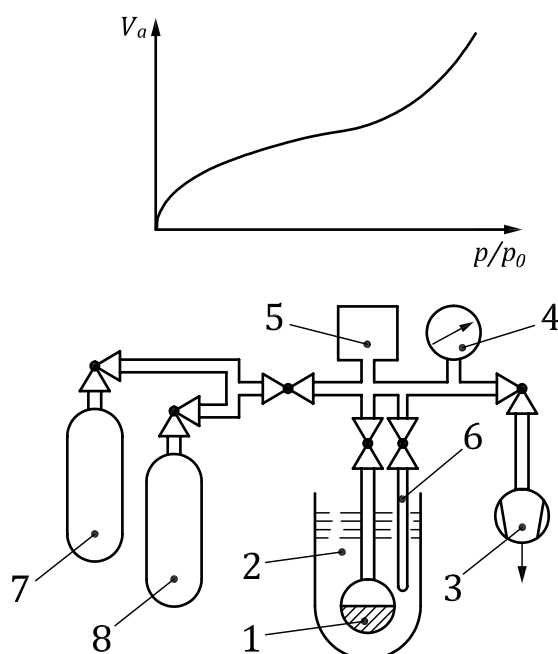
6.3.3   Flow manometric (volumetric) method

The flow manometric method is similar to the static manometric method, the difference is such that gas is continuously fed to the sample at a relatively low flow rate rather than the series of batch doses. By this method, the change in cell pressure is continuously measured at a controlled flow rate. The adsorbed amount is determined by comparing the rate of pressure rise with the adsorptive gas to that with a non-adsorbing gas such as helium used for calibration. An alternative approach, which directly determines the quantity of gas adsorbed, is to measure the pressure difference between the reference and sample tubes at the same volume of adsorptive gas fed. One volume is connected via a flow control valve to the sample tube while the other volume is similarly connected to a balance tube without sample. Because gas is continuously introduced, the analysis can, under some circumstances, be completed in a shorter period than using a static manometric method. However, special care has to be taken to ensure that the flow rate is low enough so that the adsorptive and adsorbate are close to equilibrium at all times. Determination of the dead volume and control of the liquid level in the cooling bath are recommended using the same requirements as described in 6.3.1.

6.3.4 Gravimetric method

In the continuous gravimetric method, the mass of gas adsorbed is measured as a function of the gas pressure in the sample container using a microbalance (see Figure 7). Before measurement of the adsorption isotherm, the buoyancy of the balance in the adsorptive should be measured at room temperature and at measurement temperature. The buoyancy of the sample should be measured at room temperature in helium. By using an equal-arm instrument, the buoyancy of the balance is eliminated and that of the sample compensated for using a compact counterweight of the same density as the sample. Because the sample is not in contact with the thermostat, it is necessary to ensure that it is always at the measuring temperature. The sample temperature should be monitored.

The zero point of the isotherm should be measured at a vacuum better than 10^{-2} Pa because disturbances due to thermal gas flow exhibit a maximum at about 1 Pa.

In the discontinuous gravimetric procedure, the adsorptive is admitted stepwise and the pressure is kept constant until the sample mass reaches a constant value.

Key

1	sample	5	calibrated volume (gas burette)
2	dewar vessel with cooling bath	6	saturation pressure tube
3	vacuum-generating system	7	adsorptive
4	manometer	8	gas for dead space measurement (e.g. He)

Figure 6 — Manometric (volumetric) method
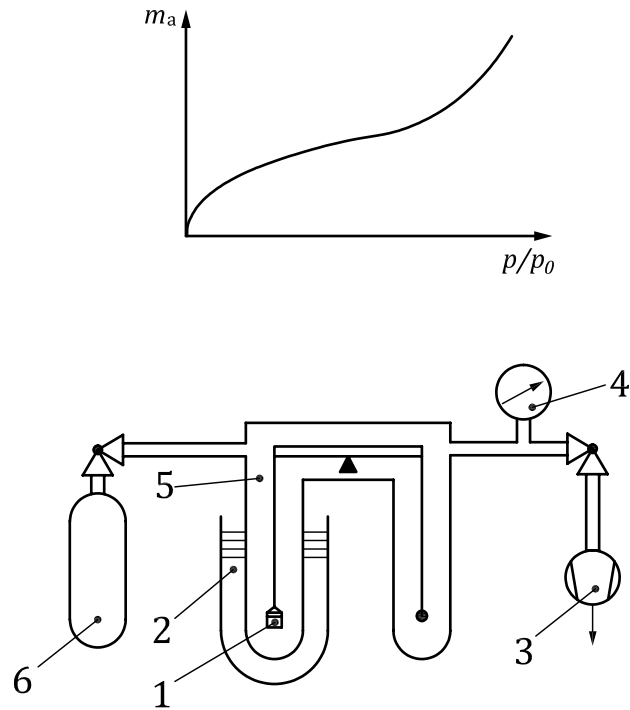
Key

|			
1	sample	4	manometer
2	cooling bath	5	balance
3	vacuum-generating system	6	adsorptive

Figure 7 — Gravimetric method

6.3.5 Carrier gas method

In the carrier gas method, a range of mixtures of known concentrations of adsorptive in a non-adsorbable gas (helium) is admitted to the sample (see Figure 8). As a result of adsorption on the sample, the concentration of adsorptive decreases. The decrease in concentration in comparison to that of the initial mixture generates a peak in the signal recorded as a function of time by means of a gas detector, usually a thermal conductivity cell. After removal of the cooling bath, a desorption peak is recorded. The sharper desorption peak can be better integrated and is preferred for the evaluation of the gas amount initially adsorbed. Care must be taken that the signal is not disturbed by thermal diffusionand to ensure proper calibration of the gas detector.[4]
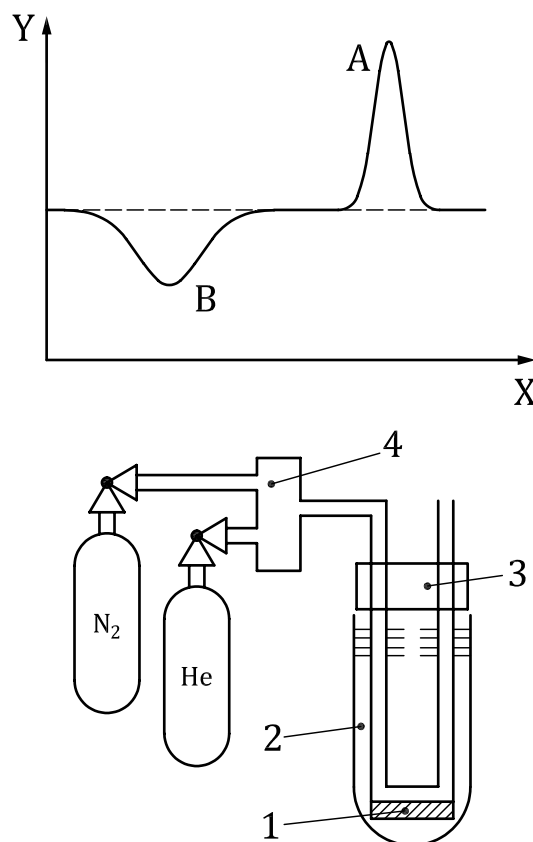
Key

X	time	1	sample
Y	detector signal	2	dewar vessel with liquid nitrogen
A	desorption	3	heat conductivity detector
B	adsorption	4	gas mixer

Figure 8 — Carrier gas method

6.3.6 Dynamic vapour sorption method

In the dynamic vapour sorption (DVS) both, the gravimetric and carrier gas method is combined. Typically, helium, nitrogen or another inert gas are used as carrier gases via mass flow controllers or injection, a dry carrier gas stream is mixed with a vapour saturated gas stream in order to achieve a defined vapour concentration in the carrier gas. This defined gas/vapour mixture is guided over the sample. Mass changes are recorded gravimetrically. Mostly, these DVS systems work at ambient pressures, but measurements at vacuum or pressures higher than atmospheric pressures can be conducted as well.

7 Evaluation of adsorption data

7.1 General

The amount of gas adsorbed n_a, preferably expressed in moles per gram, is plotted as ordinate against the respective relative pressure p/p_0 as abscissa to give the adsorption isotherm. The monolayer capacity n_m is calculated using the BET equation:

$$\frac{p/p_0}{n_a\left(1-p/p_0\right)} = \frac{1}{n_m C} + \frac{C-1}{n_m C} \cdot \frac{p}{p_0} \qquad (1)$$

NOTE   A modified formula includes, besides the BET parameter C, an additional parameter limiting the number of layers on the surface[5]. Although the two-parameter BET equation, as recommended by IUPAC, allows for an unlimited number of adsorbed layers[6], it gives comparable results for mesoporous material.

7.2 Multipoint determination

In the BET diagram, $(p/p_0) / [n_a(1 - p/p_0)]$ is plotted as ordinate against p/p_0 as abscissa (see Figure 9). The plot should give a straight line $y = a + bx$ within the relative pressure range 0,05 to 0,3. The intercept a must be positive. The slope $b = \Delta y/\Delta x = (C - 1)/(n_m C)$ and the intercept $a = 1/(n_m C)$ may be determined by linear regression. From this, the monolayer capacity

$$n_m = \frac{1}{a+b}$$

and the BET parameter

$$C = \frac{b}{a} + 1$$

can be derived.

The specific surface area per unit mass of the sample, a_s, is calculated from the monolayer capacity by assessing a value for the average area occupied by each molecule in the complete monolayer:

$$a_s = n_m a_m L \tag{2}$$

A molecular cross-sectional area, $a_m = 0,162$ nm^2, is often used for nitrogen at 77,3 K (see Annex A). Formula (2) then becomes

$$a_s = 9,76 \times 10^4 \, n_m$$

expressed in m^2 g^{-1}. n_m is hereby expressed in mol g^{-1}.

In the case of nonporous spheres of uniform radius r_s and density ρ, there is a relationship between the radius of the spheres and the specific surface area of the material:

$$a_s = 3/(\rho r_s)$$
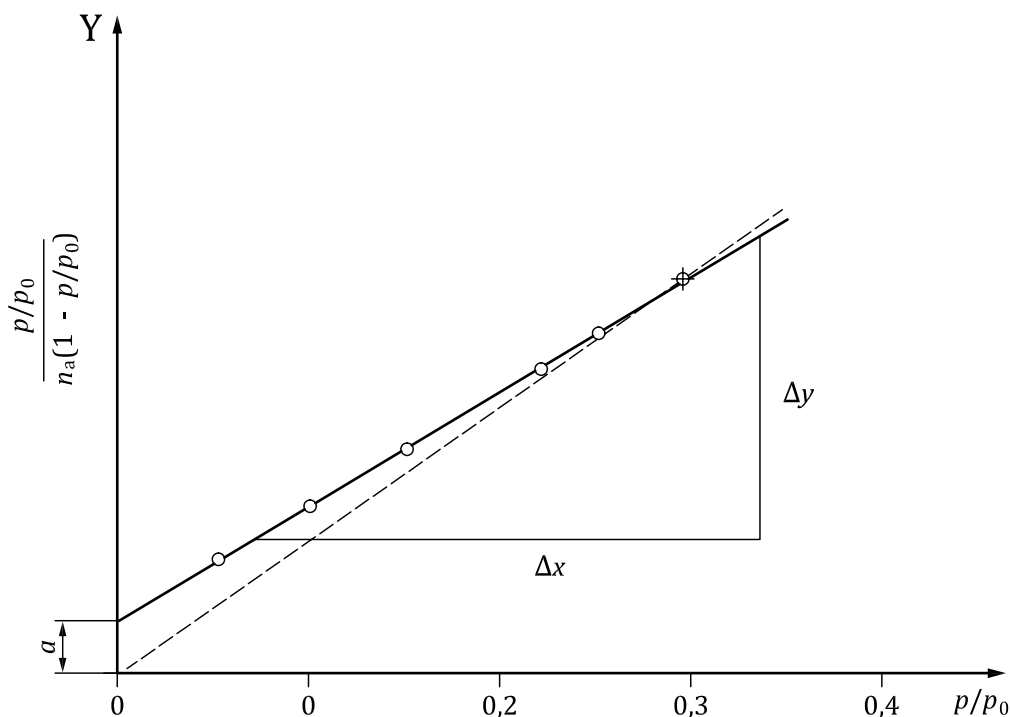
Key

────	multipoint BET fit
─ ─ ─ ─	single-point BET line
○	experimental data points
+	data point selected for single-point calculation

Figure 9 — BET plot

Values for the molecular cross-sectional area of other adsorbates can be found in References [7], [8], [9], [10] and [11]. Generally, accepted values for the molecular cross-sectional area are shown in Annex A.

For microporous adsorbents, which gives rise to Type I adsorption isotherms, the application of the BET method is problematic because it can be impossible to separate the processes of mono-multilayer adsorption and micropore filling. Here, it is often difficult to locate the linear range of the BET plot. As described in detail in Annex B, a useful procedure can here be applied to determine the range of linearity by reducing any subjectivity in evaluating the BET monolayer capacity. The BET method is not applicable if a straight line is not obtained or if there is a negative intercept. In any case, the BET area derived from a Type I adsorption isotherm does not reflect a realistic probe accessible surface area, but only an apparent surface area, which however may serve as useful adsorbent "fingerprint"[3].

In the range $100 < C < 200$, completion of the monolayer becomes clearly evidenced by the appearance of a bend in the vicinity of $p/p_0 \approx 0,1$ and the BET method fits well. C values above 200 may be indicative of the presence of micropores. The C value gives an indication of the force of the adsorbent-adsorbate interaction but cannot be used to calculate quantitatively the adsorption enthalpy. An estimation of the errors resulting from uncertainties in the measured values or in the linear regression does not include all the fundamental sources of error. Rather, the reproducibility of the results should be verified by repeated measurements using fresh samples for each run and the mean value with standard deviations reported.

7.3 Single-point determination

Having established that the BET plot for the particular type of material gives a straight line, it is possible to use a simplified procedure requiring only the determination of a single point on the isotherm in the

range of relative pressures between 0,2 and 0,3. For $C \gg 1$, the ordinate intercept $1 / (n_m C)$ of the BET plot is small and Formula (1) simplifies to:

$$n_{m,sp} = n_a \left(1 - \frac{p}{p_0} \right)$$

The monolayer capacity $n_{m,sp}$ is less than or equal to $n_{m,mp}$ derived from a multipoint determination. For measurements on samples of similar materials the error in the single-point method can be corrected for by performing a multipoint analysis first to determine:

— either the appropriate value of the intercept, which can then be used in subsequent single-point analyses;

— or the appropriate value of the BET parameter C, which can then be used to correct the single-point $n_{m,sp}$ values using Formula (3):

$$\frac{n_{m,mp} - n_{m,sp}}{n_{m,mp}} = \frac{1-(p/p_0)}{1+(p/p_0) \cdot (C-1)} \tag{3}$$

8 Test report

A report of the determination of the specific surface area of a solid by gas adsorption using the BET method shall include the following information:

a) a reference to this International Standard (i.e. ISO 9277:2022);

b) laboratory, type of equipment, operator, date of determination;

c) sample identification (characterization of the sample), for example, source, chemical class of the material, purity, method of sampling, sample division;

d) pretreatment and degassing conditions, for example, degassing in a vacuum or in inert gas flow, temperature and duration of degassing;

e) mass of degassed sample;

f) experimental procedure for adsorption isotherm determination, for example, volumetric, gravimetric, static or continuous gas admission, single-point determination, calibration of dead volume or buoyancy;

g) adsorptive (chemical nature, purity);

h) adsorption isotherm (n_a, plotted against relative pressure, p/p_0), measurement temperature;

i) evaluation parameters: multipoint or single-point determination, BET plot or range of linearity, monolayer capacity n_m, BET parameter C, molecular cross-sectional area used;

j) specific surface area;

k) certified or local reference material(s) used for performance testing of the instrument and validation of results.

9 Use of reference materials

To ensure proper working conditions and correct data evaluation, the apparatus performance should be monitored periodically using a certified reference material or a quality control material.[12] The quality control material, which can be an in-house produced secondary reference material, should be verified against a certified reference material. A number of national or international institutes or organizations offer certified surface area reference materials can be found in Reference [20].

Annex A
(informative)

Cross-sectional areas of some frequently used adsorptives

Table A.1 — Cross sectional areas

Adsorptive	Temperature K	Recommended value nm^2
Nitrogen	77,4	0,162 [a]
Argon	77,4	0,138 [b]
Argon	87,3	0,142
Krypton	77,4	0,202
n-Butane	273,15	0,444
n-Heptane	298,15	0,631
n-Octane	298,15	0,646
Benzene	293,15	0,430

[a]   The orientation of the nitrogen quadrupole is dependent on the surface chemistry, such as for instance the density of hydroxyl groups because, i.e. here the nitrogen molecules tend to interact vertically with surface hydroxyl groups. This leads to a reduced value for the cross-sectional area of nitrogen. This uncertainty in the nitrogen cross-sectional area can contribute to errors in BET area determination in the order of approximately 20 % for some surfaces.[3] Hence, it is recommended to use Ar at the temperature of liquid Ar (87,3 K) for the determination of the BET area of such surfaces.

[b]   Contrary to argon adsorption at 87,3 K, the use of argon at 77,3 K (which is approximately 6,5 K below the triple point of bulk argon) is considered to be less reliable than the adsorption of nitrogen. At 77,3 K, all nitrogen isotherms on nonporous adsorbents are Type II, whereas some argon 77,3 K isotherms are Type II and others are Type VI. These and other differences indicate that at 77,3 K, the structure of the argon monolayer may be highly dependent on the surface chemistry of the adsorbent.[3] The cross-sectional area for argon at 77,3 K is not well defined. The value of 0,138 nm^2, as given in the table is based on the assumption of a closed-packed liquid monolayer and can also be considered to be the customary value. However, one can also find the use of 0,166 nm^2 in the literature.

Annex B
(informative)

BET area of microporous materials

Specific surface area is a crucial parameter for optimizing the use of not only meso- and macroporous but also of microporous materials in many applications. However, due to the complex nature of porous materials no single experimental technique can be expected to provide an evaluation of the "absolute" surface area. Surface area values are procedurally defined and should always be related to the method, conditions and probe molecules used in the experimental work. Despite the well-known limitations, the BET method continues to be widely used for the evaluation of specific surface areas of porous materials.

As pointed out in Clause 7, usually two stages are involved in the evaluation of the BET specific surface area. First, it is necessary to transform a physisorption isotherm into the 'BET plot' and from it to derive the value of the BET monolayer capacity n_m. The second stage is the calculation of the specific surface area a_s, which requires knowledge of the molecular cross-sectional area.

In the original work of Brunauer, Emmett and Teller (1938),[1] it was found that Type II nitrogen isotherms on various adsorbents gave linear BET plots over the approximate p/p_0 range from 0,05 to 0,35.

In addition, to problems arising from the chemical and geometrical heterogeneity of the surface, the kind of porosity (i.e. existence of macro-, meso- or micropores) plays an important role for the applicability of the BET equation. The BET equation is applicable to specific surface area analysis of nonporous, macro- and mesoporous materials consisting of pores of wide pore diameter, but is in a strict sense not applicable in the case of microporous adsorbents (a critical appraisal of the BET method is given in various textbooks on porosity measurements[8],[9],[10],[11]). It is difficult to separate the processes of mono-multilayer adsorption from micropore filling and micropore filling is usually completed at relative pressures below 0,1. It appears that in presence of micropores, the linear (BET) range is significantly shifted to lower relative pressures. The application of the BET method is also problematic for estimating the specific surface area of mesoporous molecular sieves of pore widths less than approximately 4 nm, because pore condensation is observed at pressures very close to the pressure range where monolayer-multilayer formation on the pore walls occur. This can lead to a significant overestimation of the monolayer capacity in case of BET analysis. Another problem is associated with the size and shape of adsorptive molecule, i.e. the effective yardstick used to assess the surface area. In case of adsorbents with very narrow cylindrical micropores (approximately 0,5 nm to 0,7 nm pore channels), the area covered by the adsorptive (usually nitrogen or argon) is significantly smaller than the total area available. This is due to the extreme curvature of the pore channels and the relatively large size of the probe molecule (problems related with the correct assessment of the specific surface area of zeolite particles is discussed in Reference [14]). However, in broader super-micropores (>0,7 nm), a number of molecules located in the centre of the pores do not touch the surface, i.e. this leads to an overestimation of the specific surface area.

Therefore, the specific surface area obtained by applying the BET method on adsorption isotherms from microporous solids does not reflect the true internal surface area, but should be considered as a kind of "characteristic or apparent BET area". In this case, it is of course obligatory to report the range of linearity for the BET plot. There is of course the question how to find the linear range of the BET plot for microporous materials in a way that it reduces any subjectivity in the assessment of the monolayer capacity. Reference [15] suggests a procedure, which is mainly based on two criteria:

a) the quantity of C must be positive (i.e. any negative intercept on the ordinate of the BET plot is an indication that one is outside the valid range of the BET equation),

b) the application of the BET equation should be limited to the pressure range where the term $n_a(p_0 - p)$ or alternatively $n_a(1 - p/p_0)$ continuously increases with p/p_0, and

c)   the p/p_0 value corresponding to n_m should be within the selected BET range.

An example where this procedure was applied in order to determine the linear BET range for the argon adsorption isotherm at 87,3 K on a faujasite zeolite (adsorption isotherm data from Figure B.1) is shown in Figure B.2. It is clearly visible that based on this criterion all data points above a relative pressure of 0,053 have to be eliminated for application of the BET calculation. The resulting plot is shown in Figure B.3, i.e. the BET equation is applied for relative pressures below about 0,053 down to 0,01, and a linear plot with positive C constant is obtained.
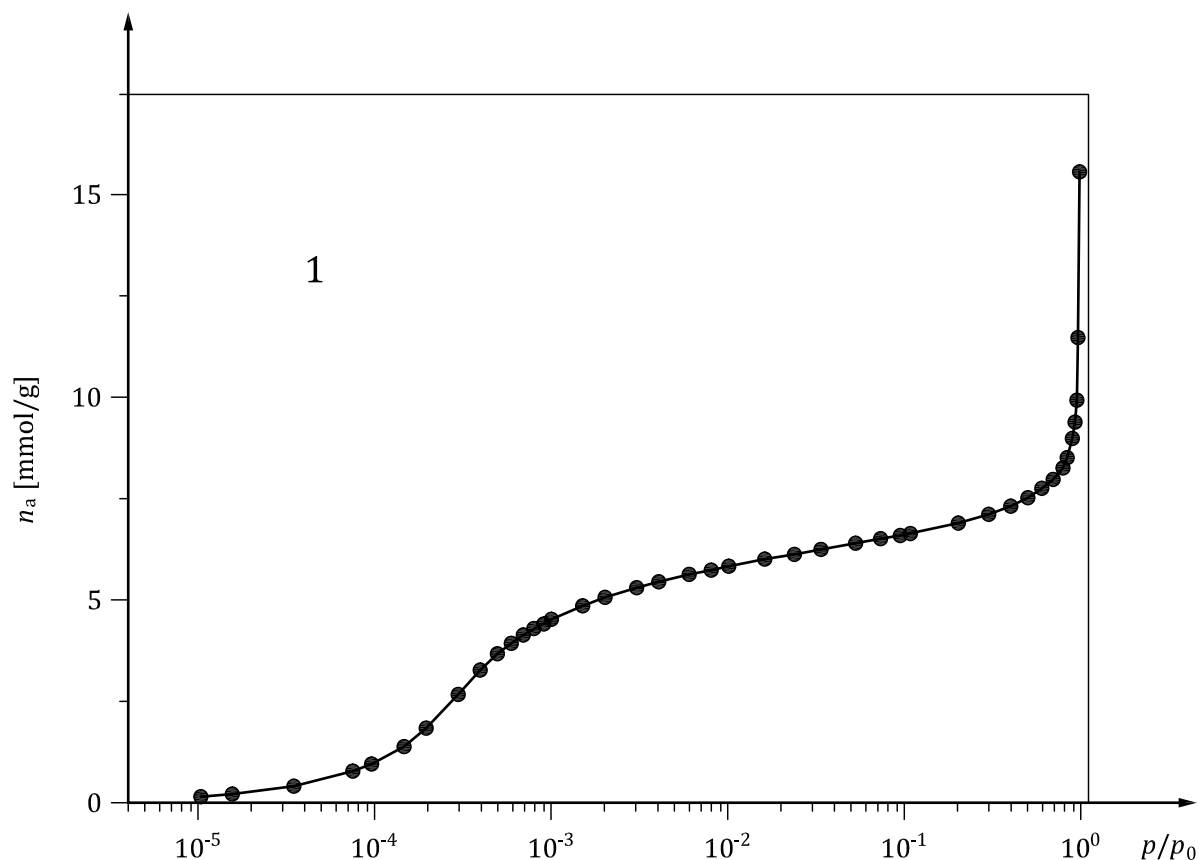
Key

1   Ar on faujasite at 87,3 K

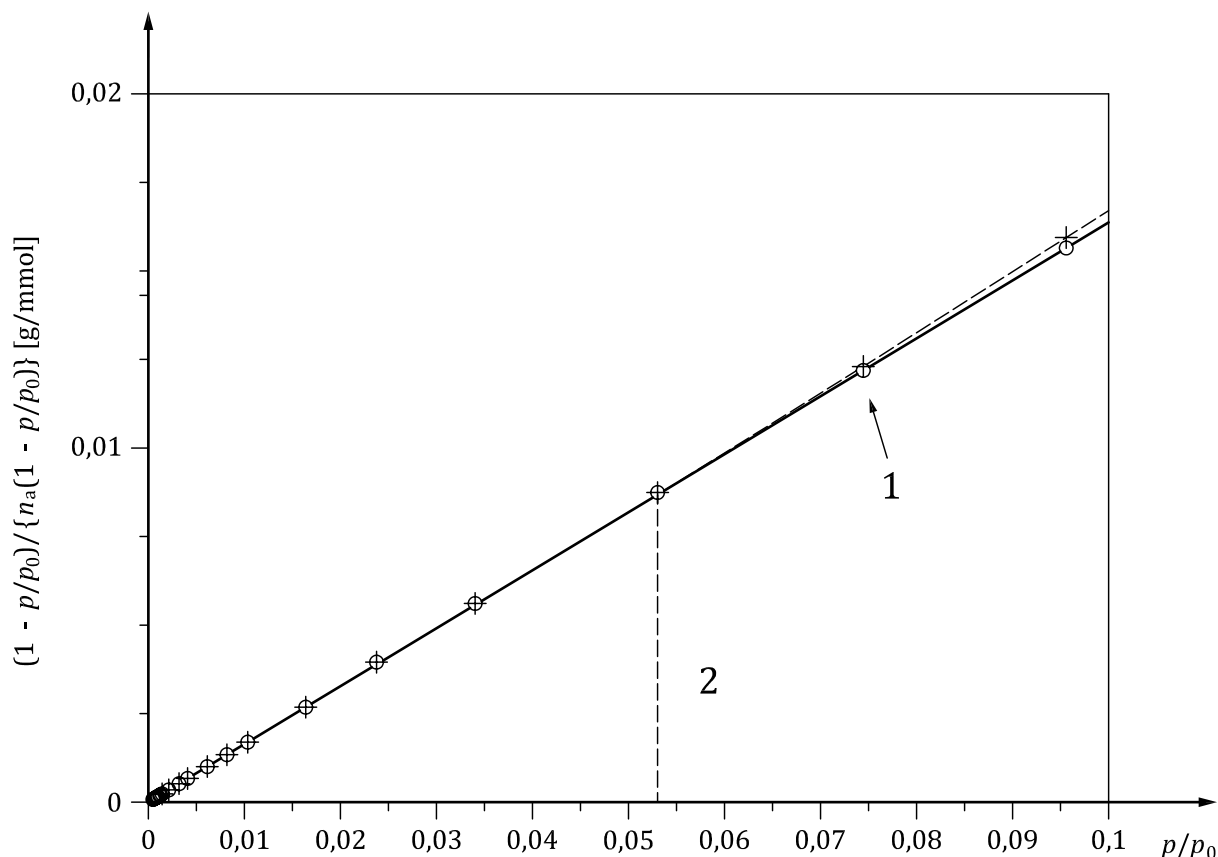**Figure B.1 — Semilogarithmic plot of the argon adsorption isotherm at 87,3 K on a faujasite-type zeolite**
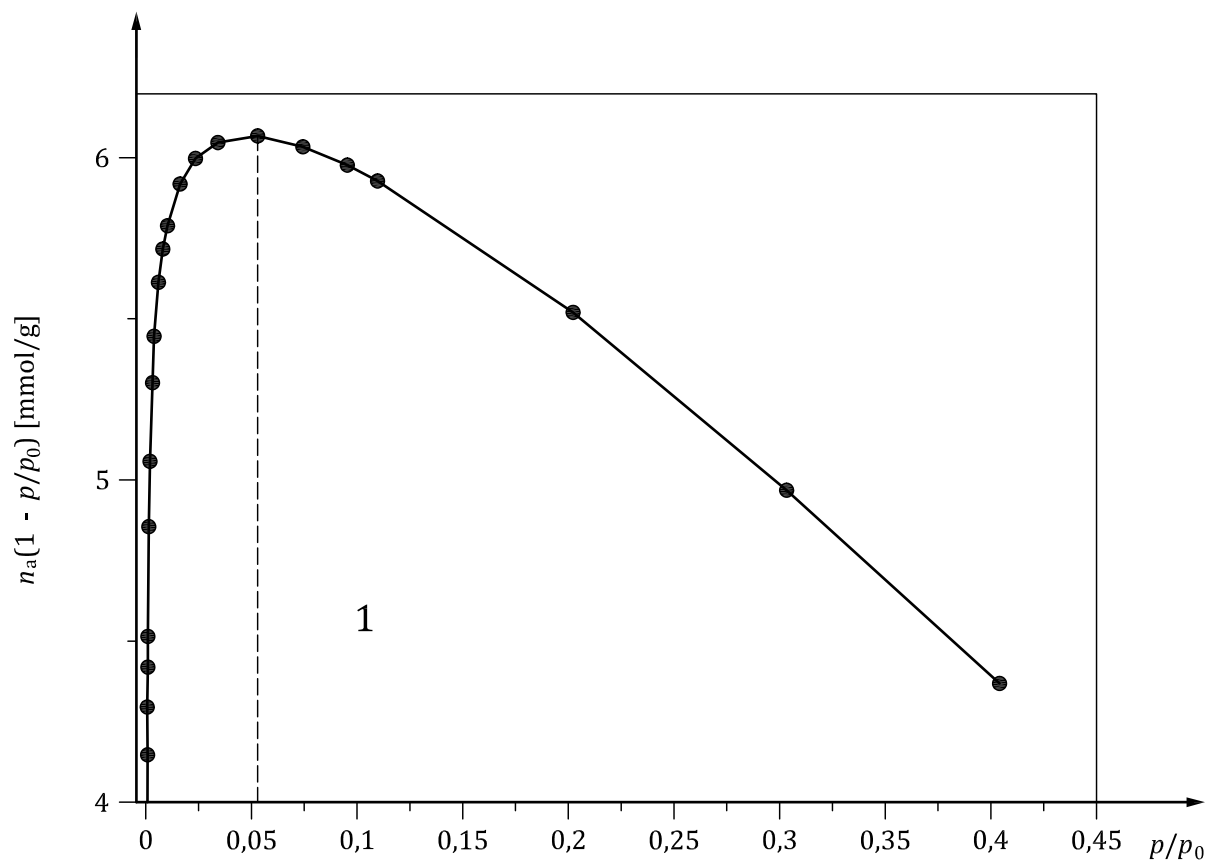
Key
1   BET range limit

Figure B.2 — Plot of the term $n_a(1 - p/p_0)$ versus p/p_0 for the argon isotherm shown in **Figure B.1**

Key

——o—— BET regression line

——|—— measured data points

1   deviation of measured data points initiates

2   BET range limit

Figure B.3 — BET plot for the argon isotherm shown in Figure B.1

In order to address problems associated with applying the BET equation on isotherm data obtained from microporous materials, Reference [16] suggests to treat the adsorption data of physical adsorption of nitrogen by a modified BET-equation, which includes the micropore volume, $V_{p,micro}$.[16] The approach in Reference [16] allows to extract the $V_{p,micro}$ value from adsorption data and consequently to determine the value of C and specific surface area of the non-microporous part of solid materials.

As already pointed out, an additional problem is the heterogeneous nature of many surfaces, which, of course, include supported and other multicomponent catalysts. It is known that the quadrupole moment of the nitrogen molecule leads for instance to specific interactions with the hydroxyl groups on the surface, causing an orientating effect on the adsorbed nitrogen molecule.[17],[18],[19] Consequently, the effective cross-sectional area is smaller than the customary value of $0,162 \text{ nm}^2$. For a completely hydroxylated surface, a cross-sectional area of $0,135 \text{ nm}^2$ for the nitrogen molecule was proposed, which was obtained by measuring the volume of N_2 adsorbed on silica spheres of known diameter.[17] Hence, argon adsorption (at 87,3 K) may seem to be an alternative adsorptive for a reliable specific surface area determination because the argon molecule is monatomic and much less reactive than the diatomic nitrogen molecule with its quadrupole moment. Because of the absence of a quadrupole moment and the higher temperature, the cross-sectional area of argon ($0,142 \text{ nm}^2$ at 87,3 K) is less sensitive to differences in structure of the adsorbent surface. As already indicated in Annex A, the uncertainty concerning the effective cross-sectional area of the nitrogen molecule can contribute to errors in BET area determination in the order of approximately 20 % for some materials. Other methods to obtain a specific surface area from gas adsorption are based on the application of the standard isotherm concept,

for example, t-plot and α_s-plot methods (see ISO 15901-2), which allows one to obtain in particular the external (i.e. the non-microporous) specific surface area. By subtracting the external surface area from the apparent BET (total specific) surface area, one can determine an apparent micropore surface area (details are given in ISO 15901-2).

The application of non-local density functional theory (NLDFT, see ISO 15901-2) and of methods based on molecular simulation allow to obtain the specific surface area of porous solids and to differentiate between micropore, mesopore and external surface area. However, the application of these advanced methods leads to accurate results only if the given experimental adsorptive/adsorbent system is compatible with the available kernel of theoretical adsorption isotherms.

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