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SUBCOMMITTEE ON REPORTING GAS ADSORPTION DATA*

REPORTING PHYSISORPTION DATA FOR GAS/SOLID SYSTEMS

with Special Reference to the Determination of Surface Area and Porosity

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SECTION 1. INTRODUCTION

Gas adsorption measurements are widely used for determining the surface area and pore size distribution of a variety of different solid materials, e.g. industrial adsorbents, catalysts, pigments, ceramics and building materials. The measurement of adsorption at the gas/solid interface also forms an essential part of most fundamental and applied investigations of the nature and behaviour of solid surfaces.

Although the role of gas adsorption in the characterisation of solid surfaces is firmly established, there is still a lack of general agreement on the evaluation, presentation and interpretation of adsorption data. Unfortunately, the complexity of most solid surfaces - especially those of industrial importance - makes it difficult to obtain any independent assessment of the physical significance of the derived quantities (e.g. the absolute magnitude of the surface area and pore size).

A number of attempts have been made (see Note a), at a national level, to establish standard procedures for the determination of surface area by the BET-nitrogen adsorption method. In addition, the results have been published (see Note b) of an SCI/IUPAC/NPL project on surface area standards. This project brought to light a number of potential sources of error in the determination of surface area by the gas adsorption method.

The purpose of the present Manual is two-fold: first to draw attention to the problems and ambiguities which have arisen in connection with the reporting of gas adsorption (physisorption) data and secondly to formulate tentative proposals for the standardisation of procedures and terminology which, through further discussion, will lead to a generally accepted code of practice. It is not the purpose of this Manual to provide detailed operational instructions or to give a comprehensive account of the theoretical aspects of physisorption. Determination of the surface area of supported metals is of special importance in the context of heterogeneous catalysis, but this topic is not dealt with in this Manual since chemisorption processes are necessarily involved.

The present proposals are based on, and are in general accordance with, the *Manual of Symbols and Terminology for Physicochemical Quantities and Units* (see Note c) and Parts I and II of Appendix II (see Note d). Although it has been necessary to extend the terminology, the principles are essentially those developed in Part I.

Note a. British Standard 4359: Part 1: 1969. Nitrogen adsorption (BET method).

Deutsche Normen DIN 66131, 1973. Bestimmung der spezifischen Oberfläche von Feststoffen durch Gasadsorption nach Brunauer, Emmett und Teller (BET).

Norme Française 11-621, 1975. Détermination de l'aire massique (surface spécifique) des poudres par adsorption de gaz.

American National Standard, ASTM D 3663-78. Standard test method for surface area of catalysts.

Note b. D.H. Everett, G.D. Parfitt, K.S.W. Sing and R. Wilson, *J. appl. Chem. Biotech.*, 24, 199 (1974).

Note c. *Manual of Symbols and Terminology for Physicochemical Quantities and Units* prepared for publication by D.H. Whiffen, *Pure Applied Chem.*, 51, 1-41 (1979).

Note d. *Part I of Appendix II, Definitions, Terminology and Symbols in Colloid and Surface Chemistry*, prepared by D.H. Everett, *Pure Applied Chem.*, 31, 579-638 (1972).

Part II of Appendix II, Terminology in Heterogeneous Catalysis, prepared for publication by R.L. Burwell, Jr., *Pure Applied Chem.*, 45, 71-90 (1976).

SECTION 2.   GENERAL DEFINITIONS AND TERMINOLOGY

The definitions given here are essentially those put forward in Appendix II, Part I, §1.1 and Part II, §1.2. Where a caveat is added, it is intended to draw attention to a conceptual difficulty or to a particular aspect which requires further consideration.

Adsorption (in the present context, positive adsorption at the gas/solid interface) is the enrichment of one or more components in an interfacial layer. *Physisorption* (as distinct from *chemisorption*) is a general phenomenon: it occurs whenever an adsorbable gas (the *adsorptive*) is brought into contact with the surface of a solid (the *adsorbent*). The intermolecular forces involved are of the same kind as those responsible for the imperfection of real gases and the condensation of vapours. With some adsorption systems, certain specific molecular interactions occur (e.g. polarisation, field-dipole, field gradient-quadrupole), arising from particular geometric and electronic properties of the adsorbent and adsorptive.

It is convenient to regard the interfacial layer as comprising two regions: the *surface layer* of the adsorbent (often simply called the *adsorbent surface*) and the *adsorption space* in which enrichment of the adsorptive can occur. The material in the adsorbed state is known as the *adsorbate*, i.e. as distinct from the adsorptive, the substance in the fluid phase which is capable of being adsorbed.

When the molecules of the adsorptive penetrate the surface layer and the structure of the bulk solid, the term *absorption* is used. It is sometimes difficult or impossible to distinguish between adsorption and absorption. In such cases it is convenient to use the wider term *sorption* which embraces both phenomena and to use the derived terms *sorbent*, *sorbate* and *sorptive*.

The term *adsorption* may also be used to denote the process in which adsorptive molecules are transferred to, and accumulate in, the interfacial layer. Its counterpart, *desorption*, denotes the converse process, i.e. the decrease in the amount of adsorbed substance. Adsorption and desorption are often used adjectivally to indicate the direction from which experimentally determined adsorption values have been approached, e.g. the adsorption curve (or point) and the desorption curve (or point). *Adsorption hysteresis* arises when the adsorption and desorption curves deviate from one another.

The relation, at constant temperature, between the quantity adsorbed (properly defined in Section 3.2) and the equilibrium pressure of the gas is known as the *adsorption isotherm*.

Many adsorbents of high surface area are porous and with such materials it is often useful to distinguish between the *external* and *internal* surface. The *external surface* is usually regarded as the geometrical envelope of discrete particles or agglomerates, but a difficulty arises in defining it because solid surfaces are rarely smooth on an atomic scale. A suggested convention is that the external surface be taken to include all the prominences and also the surface of those cracks which are wider than they are deep; the internal surface then comprises the walls of all cracks, pores and cavities which are deeper than they are wide and which are accessible to the adsorptive. In practice, the demarcation is likely to depend on the methods of assessment and the nature of the pore size distribution. Because the accessibility of pores may depend on the size and shape of the gas molecules, the area of, and the volume enclosed by, the internal surface as determined by gas adsorption may be controlled by the dimensions of the adsorptive molecules (*molecular sieve* effect). On a molecular scale the roughness of a solid surface may be characterized by a *roughness factor*, i.e. the ratio of the external surface to the chosen geometric surface.

It is expedient to classify pores according to their sizes:

(i)   pores with widths exceeding about 50 nm (0.05µm) are called *macropores;*

(ii)   pores with widths not exceeding about 2nm are called *micropores;*

(iii)   pores of intermediate size are called *mesopores.*

These limits are to some extent arbitrary since the pore filling mechanisms are dependent on the pore shape and are influenced by the properties of the adsorptive and the adsorbent-adsorbate interactions. The whole of the accessible volume in micropores may be regarded as adsorption space and the process of *micropore filling* thus occurs as distinct from coverage of the external surface and the walls of open macropores or mesopores. Micropore filling may be regarded as a primary physisorption process (see Section 8); on the other hand, physisorption in mesopores takes place in two more or less distinct stages (monolayer-multilayer adsorption and capillary condensation).

In *monolayer adsorption* all the adsorbed molecules are in contact with the surface layer of
the adsorbent. In *multilayer adsorption* the adsorption space accommodates more than one
layer of molecules and not all adsorbed molecules are in contact with the surface layer of
the adsorbent. In *capillary condensation* the residual pore space which is left after
multilayer adsorption has occurred is filled with liquid-like material separated from the
gas phase by menisci. Capillary condensation is often accompanied by hysteresis. The term
capillary condensation should not be used to describe micropore filling.

For physisorption, the *monolayer capacity* (n_m) is usually defined as the amount of
adsorbate (expressed in appropriate units) needed to cover the surface with a complete
monolayer of molecules (Appendix II, Part I, §1.1.7). In some cases this may be a close-
packed array but in others the adsorbate may adopt a different structure. Quantities
relating to monolayer capacity may be denoted by the subscript m. The *surface coverage* (θ)
for both monolayer and multilayer adsorption is defined as the ratio of the amount of
adsorbed substance to the monolayer capacity.

The *surface area* (A_s) of the adsorbent may be calculated from the monolayer capacity (n_m in
moles), provided that the area effectively occupied by an adsorbed molecule in the
complete monolayer (a_m) is known.

Thus,

$$A_s = n_m . L . a_m$$

where L is the Avogadro constant. The *specific surface area* (a_s) refers to unit mass (m)
of adsorbent:

$$a_s = \frac{A_s}{m} .$$

Appendix II, Part I recommends the symbols A, A_s or S and a, a_s or s for area and specific
area, respectively, but A_s and a_s are preferred to avoid confusion with Helmholtz energy A
or entropy S.

In the case of micropore filling, the interpretation of the adsorption isotherm in terms of
surface coverage may lose its physical significance. In that event, it may be convenient to
define a *monolayer equivalent area* as the area, or specific area, respectively, which would
result if the amount of adsorbate required to fill the micropores were spread in a close-
packed monolayer of molecules (see Section 8).

          SECTION 3.   METHODOLOGY

3.1 Methods for the determination of adsorption isotherms
The many different procedures which have been devised for the determination of the amount of
gas adsorbed may be divided into two groups: (a) those which depend on the measurement of
the amount of gas leaving the gas phase (i.e. gas volumetric methods) and (b) those which
involve the measurement of the uptake of the gas by the adsorbent (e.g. direct
determination of increase in mass by gravimetric methods). Many other properties of the
adsorption system may be related to the amount adsorbed, but since they require calibration
they will not be discussed here. In practice, a static or a flow technique may be used in
the application of volumetric or gravimetric methods.

In the static volumetric determination a known quantity of gas is usually admitted to a
confined volume containing the adsorbent, maintained at constant temperature. As adsorption
takes place, the pressure in the confined volume falls until equilibrium is established.
The amount of gas adsorbed at the equilibrium pressure is given as the difference between
the amount of gas admitted and the amount of gas required to fill the space around the
adsorbent, i.e. the *dead space,* at the equilibrium pressure. The adsorption isotherm is
constructed point-by-point by the admission to the adsorbent of successive charges of gas
with the aid of a volumetric dosing technique and application of the gas laws. The volume
of the dead space must, of course, be known accurately: it is obtained (see Section 3.2)
either by pre-calibration of the confined volume and subtracting the volume of the
adsorbent (calculated from its density), or by the admission of a gas which is adsorbed to a
negligible extent (see Section 3.2). Nitrogen adsorption isotherms at the temperature of
the boiling point of nitrogen at ambient atmospheric pressure are generally determined by
the volumetric method and provide the basis for the various standard procedures which have
been proposed for the determination of surface area (see references in Section 1).

Volumetric measurements may be conducted with the aid of conventional gas chromatographic
equipment for the measurement of the change in composition of a flowing gas stream (a
mixture of carrier gas and adsorptive gas) to obtain the amount adsorbed at a given partial
pressure when the composition of the exit gas stream has returned to the inlet composition.

If the establishment of equilibrium is sufficiently fast and the adsorption of the carrier gas negligible, this method may be regarded as equivalent to a 'static' procedure. Other types of flow methods involve the introduction of the pure adsorptive, e.g. at a slow and constant rate under quasi-equilibrium conditions. The validity of flow techniques should be checked by changing the flow-rate.

Recent developments in vacuum microbalance techniques have revived the interest in gravimetric methods for the determination of adsorption isotherms. With the aid of an *adsorption balance* the change in weight of the adsorbent may be followed directly during the outgassing and adsorption stages. A gravimetric procedure is especially convenient for measurements with vapours at temperatures not too far removed from ambient. At both high and low temperatures, however, it becomes difficult to control and measure the exact temperature of the adsorbent, which is particularly important in the determination of mesopore size distribution.

3.2 Operational definitions of adsorption

To examine the fundamental basis on which experimental definitions depend, consider an adsorption experiment incorporating both volumetric and gravimetric measurements (see Fig. 1). A measured amount, n, of a specified gas (see Note e), is introduced into the system whose total volume, V, can be varied at constant temperature, T. Measurements are made of V, p (the equilibrium pressure) and w (the apparent weight of a mass, m, of adsorbent).
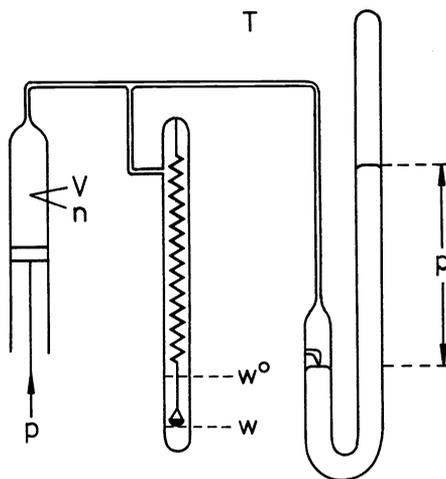

Fig. 1. Schematic arrangement of a simultaneous volumetric
         and gravimetric adsorption experiment.

In a calibration experiment the balance pan contains no adsorbent. The total volume, V^o, of the system is now simply related to the amount, n^o, of gas admitted:

$$V^o = n^o v^g(T,p) ,$$

where $v^g(T,p)$ is the molar volume of the gas at T and p, and is known from its equation of state. If the buoyancy effect arising from the balance itself is negligible, the apparent weight will remain constant. Since the gas concentration, $c^o = 1/v^g$, is constant throughout the volume V^o,

$$n^o = \int_{all\ V^o} c^o dV = c^o V^o = \frac{V^o}{v^g} .$$

A mass, m, of adsorbent (weighing w^o in vacuum) is now introduced and the experiment repeated using the same amount of gas. If adsorption is detectable at the given T, p, the volume V will usually be less than V^o and the apparent weight of the adsorbent will increase from w^o to w.

Note e. for simplicity, adsorption of a single gas is considered here (cf. Appendix II, Part 1, §1.1.11).

V/v^g is the amount of gas which would be contained in the volume V if the gas concentration were uniform throughout the volume. That the amount actually present is n^o means that local variations in gas concentration must occur: the gas concentration within the bulk of the solid is zero, but is greater than c^o in the interfacial layer. The difference between n^o and V/v^g may be called the *apparent adsorption*

$$n^a \text{ (app)} = n^o - V/v^g \ ,$$

and is a directly observable quantity. The precision with which it can be measured is controlled only by the experimental precision in T, p and V, and by the reliability with which v^g (and c^o) can be calculated from the equation of state of the gas.

The apparent adsorption may, alternatively, be defined by measuring the amount of gas which has to be added to the system at constant T, p to increase the volume V back to V^o. The apparent adsorption is then equal to the extra amount of gas which can be accommodated in a volume V^o at a given T, p when the solid is introduced. It can, therefore, be expressed in terms of the local deviations of the concentration, c, of adsorptive molecules, from the bulk concentration c^o:

$$n^a(\text{app}) = \int_{V^o} (c-c^o)\,dV.$$

If the gas does not penetrate into the bulk solid (i.e. is not *ab*sorbed), the above integral consists of two parts, that over the volume occupied by the solid (V^s) within which c = o, and that over the adsorption space plus the gas phase volume, which taken together is denoted by V^g:

$$n^a(\text{app}) = -c^o v^s + \int_{V^g} (c-c^o)\,dV.$$

The first term represents the amount of gas excluded by the solid, while the second is the extra amount of gas accommodated because of the accummulation of gas on the neighbourhood of the solid surface. If the adsorption is very weak the first term may exceed the second and the apparent adsorption may be negative (V > V^o).

The quantity

$$n^a = n^a(\text{app}) + c^o v^s = \int_{V^g} (c-c^o)\,dV$$

is thus equal to the *Gibbs adsorption* (see note f) (surface excess amount of adsorbed substance – see Part I, §1.1.8) when the surface of the solid is taken as the Gibbs dividing surface: it is the difference between the amount of substance actually present in the interfacial layer and that which would be present at the same equilibrium gas pressure in a reference system in which the gas phase composition is constant up to the Gibbs surface, and in which no adsorptive penetrates into the surface layer or the bulk of the solid.

The operational definition of n^a is thus

$$n^a = \int_{V^g} (c-c^o)\ dV = n - c^o v^g \ ,$$

where n is the total amount of gas admitted.

The precision with which n^a can be determined depends, not only on the precision of T, p, V and v^g but also on the precision with which V^s (and hence v^g) is known.

The volume of the solid (i.e. the volume enclosed by the Gibbs surface) is often defined experimentally as that volume which is not accessible to a non-sorbable gas (e.g. helium – leading to the *helium dead-space*). In making this identification it is assumed that the volume available to He atoms is the same as that for molecules of the gas under investigation (which is not true, for example, if the solid acts as a molecular sieve, or if the molecules of the gas are significantly larger than the He atom), and that the solid does not swell under the influence of the adsorbate. Helium adsorption may occur if the solid contains very fine pores (or pore entrances) and the only proof that the adsorption is zero is that the apparent value of V^s is independent of temperature. It is usual to take the high temperature limit of V^s as being the correct value, but if V^s is determined at a

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Note f. n_i^σ was used to denote the Gibbs adsorption in Part I, §1.1.8.

temperature widely different from that used in an adsorption experiment, a correction for the thermal expansion of the solid may be required.

Alternatively, v^s may be estimated from the known density of the bulk solid with the implied assumption that this is the same as that of the material of the adsorbent.

The above discussion in terms of the volumetric technique when applied to gravimetric measurements gives for the apparent change in weight

$$\Delta w = w - w_o = \left[n^a - \frac{v^s}{v^g} \right] M$$

where M is the molar mass of the adsorptive.

Thus
$$n^a = \frac{\Delta w}{M} + \frac{v^s}{v^g} \quad .$$

The second term on the right-hand-side is the buoyancy correction which has the same origin as the dead-space correction in a volumetric determination.

An alternative but less useful definition of adsorption is

$$n^s = \int_{V_a} c\, dV \quad ,$$

where $V_a = \tau A_s$ is the volume of the interfacial layer (see Note g) and c is the local concentraction. V_a has to be defined on the basis of some appropriate model of gas adsorption which gives a value of τ the layer thickness. Provided that the equilibrium pressure is sufficiently low and the adsorption not too weak, then

$$n^s \approx n^a \quad ;$$

the surface excess amount (n^a) and total amount (n^s) of substance in the adsorbed layer become indistinguishable and the general term *amount adsorbed* is applicable to both quantities.

SECTION 4. EXPERIMENTAL PROCEDURES

4.1 Outgassing the adsorbent
Prior to the determination of an adsorption isotherm most if not all of the physisorbed species must be removed from the surface of the adsorbent. This may be achieved by outgassing, i.e. exposure of the surface to a high vacuum - usually at elevated temperature. The outgassing conditions (temperature programme, change in pressure over the adsorbent and the residual pressure) required to attain reproducible isotherms must be controlled to within limits which are dependent on the adsorption system. Instead of exposing the adsorbent to a high vacuum, it is sometimes expedient to achieve adequate cleanliness of the surface by flushing the adsorbent with an inert gas (which may be the adsorptive) at elevated temperature. With certain microporous solids reproducible isotherms are only obtained after one or more adsorption-desorption cycles. This problem can be overcome by flushing with the adsorptive and subsequent heating in vacuum.

Contrary to chemisorption studies where more rigorous surface cleanliness is required, outgassing to a residual pressure of ~ 10 mPa is usually considered sufficient if physisorption measurements are to be employed for the determination of surface area and/or porosity. Such conditions are readily achieved with the aid of conventional vacuum equipment - usually a combination of a rotary and diffusion pump. The rate of desorption is strongly temperature dependent and to minimize the outgassing time, the temperature should be the maximum consistent with the avoidance of changes in the nature of the adsorbent and with the achievement of reproducible isotherms. Outgassing at too high a temperature or under high vacuum conditions (residual pressure < 1 μPa), as well as flushing with certain gases may lead to changes in the surface composition, e.g. decomposition of hydroxides or carbonates, formation of surface defects or irreversible changes in texture.

For most purposes the outgassing temperature may be conveniently selected as within the range over which the thermal gravimetric curve obtained in vacuo exhibits a minimum slope.

Note g. In part I, §1.1.11, the volume of the interfacial layer was denoted by v^s

To monitor the progress of outgassing it is useful to follow the change in gas pressure by means of suitable vacuum gauges and, if the experimental technique permits, the change in weight of the adsorbent. Further information on the effect of outgassing may be obtained by the application of temperature programmed desorption (thermal desorption spectroscopy) in association with mass spectrometric analysis.

4.2 Determination of the adsorption isotherm
It is essential to take into account a number of potential sources of experimental error in the determination of an adsorption isotherm. In the application of a volumetric technique involving a dosing procedure it must be kept in mind that any errors in the measured doses of gas are cumulative and that the amount remaining unadsorbed in the dead space becomes increasingly important as the pressure increases. In particular, the accuracy of nitrogen adsorption measurements at temperatures of about 77K will depend on the control of the following factors:-

(i)   Gas burettes and other parts of the apparatus containing appreciable volumes of gas must be thermostatted, preferably to $\pm$ 0.1°C. If possible the whole apparatus should be maintained at reasonably constant temperature.

(ii)   The pressure must be measured accurately (to $\pm$ 10 Pa). If a mercury manometer is used the tubes should be sufficiently wide - preferably ~1 cm in diameter.

(iii)   The level of liquid nitrogen in the cryostat bath must be kept constant to within a few millimetres, preferably by means of an automatic device.

(iv)   The sample bulb must be immersed to a depth of at least 5cm below the liquid nitrogen level.

(v)   The temperature of the liquid nitrogen must be monitored, e.g. by using a suitably calibrated nitrogen or oxygen vapour pressure manometer or a suitable electrical device.

(vi)   The nitrogen used as adsorptive must be of purity not less than 99.9%.

(vii)   The conditions chosen for pretreatment of the adsorbent must be carefully controlled and monitored (i.e. the outgassing time and temperature and the residual pressure, or conditions of flushing with adsorptive).

(viii) It is recommended that the *outgassed weight* of the adsorbent should be determined either before or after the adsorption measurements. In routine work it may be convenient to admit dry air or nitrogen to the sample after a final evacuation under the same conditions as those used for the pretreatment.

SECTION 5. EVALUATION OF ADSORPTION DATA

5.1 Presentation of primary data
The quantity of gas adsorbed may be measured in any convenient units: moles, grams and cubic centimetres at s.t.p. have all been used. For the presentation of the data it is recommended that the amount adsorbed should be expressed in moles per gram of the *outgassed* adsorbent. The mode of outgassing and if possible the composition of the adsorbent should be specified and its surface characterised. To facilitate the comparison of adsorption data it is recommended that adsorption isotherms be displayed in graphical form with the amount adsorbed (n^a in mol g^{-1}) plotted against the equilibrium relative pressure (p/p^o), where p^o is the saturation pressure of the pure adsorptive at the temperature of the measurement, or against p when the temperature is above the critical temperature of the adsorptive. If the surface area of the adsorbent is known the amount adsorbed may be expressed as number of molecules, or moles per unit area, (i.e. N^a molecules m^{-2} or n^a mol m^{-2}). Adsorption data obtained on well-defined surfaces or in model pore systems should be given in tabular form.

5.2 Classification of adsorption isotherms
The majority of physisorption isotherms may be grouped into the six types shown in Figure 2. In most cases at sufficiently low surface coverage the isotherm reduces to a linear form (i.e. $n^a \propto p$), which is often referred to as the Henry's Law region (see Note h).

Note h.   On heterogeneous surfaces this linear region may fall below the lowest experimentally measurable pressure.
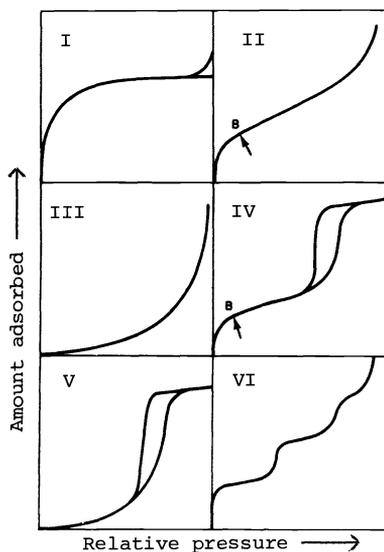
Fig. 2. Types of physisorption isotherms.

The reversible *Type I* isotherm (see Note i) is concave to the p/p^o axis and n^a approaches a limiting value as $p/p^o \longrightarrow 1$. Type I isotherms are given by microporous solids having relatively small external surfaces (e.g. activated carbons, molecular sieve zeolites and certain porous oxides), the limiting uptake being governed by the accessible micropore volume rather than by the internal surface area.

The reversible *Type II* isotherm is the normal form of isotherm obtained with a non-porous or macroporous adsorbent. The Type II isotherm represents unrestricted monolayer-multilayer adsorption. Point B, the beginning of the almost linear middle section of the isotherm, is often taken to indicate the stage at which monolayer coverage is complete and multilayer adsorption about to begin.

The reversible *Type III* isotherm is convex to the p/p^o axis over its entire range and therefore does not exhibit a Point B. Isotherms of this type are not common; the best known examples are found with water vapour adsorption on pure non-porous carbons. However, there are a number of systems (e.g. nitrogen on polyethylene) which give isotherms with gradual curvature and an indistinct Point B. In such cases, the adsorbent-adsorbate interaction is weak as compared with the adsorbate-adsorbate interactions.

Characteristic features of the *Type IV* isotherm are its hysteresis loop, which is associated with capillary condensation taking place in mesopores, and the limiting uptake over a range of high p/p^o. The initial part of the Type IV isotherm is attributed to monolayer-multilayer adsorption since it follows the same path as the corresponding part of a Type II isotherm obtained with the given adsorptive on the same surface area of the adsorbent in a non-porous form. Type IV isotherms are given by many mesoporous industrial adsorbents.

The *Type V* isotherm is uncommon; it is related to the Type III isotherm in that the adsorbent-adsorbate interaction is weak, but is obtained with certain porous adsorbents.

The *Type VI* isotherm represents stepwise multilayer adsorption on a uniform non-porous surface. The step-height now represents the monolayer capacity for each adsorbed layer and, in the simplest case, remains nearly constant for two or three adsorbed layers. Amongst the best examples of Type VI isotherms are those obtained with argon or krypton on graphitised carbon blacks at liquid nitrogen temperature.

Note i. Type I isotherms are sometimes referred to as *Langmuir isotherms*, but this nomenclature is not recommended.

5.3 Adsorption hysteresis

Hysteresis appearing in the multilayer range of physisorption isotherms is usually
associated with capillary condensation in mesopore structures. Such hysteresis loops may
exhibit a wide variety of shapes. Two extreme types are shown as *H1* (formerly Type A) and
H4 in Figure 3. In the former the two branches are almost vertical and nearly parallel over
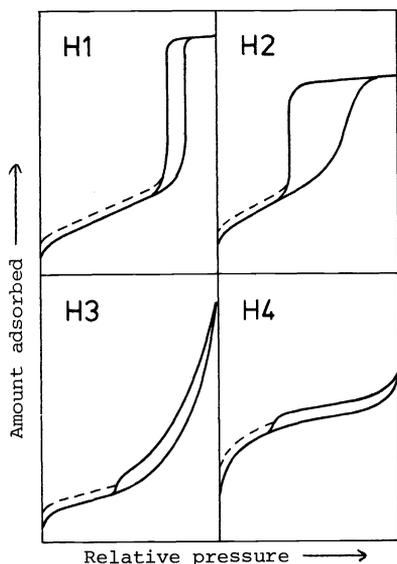

Fig. 3. Types of hysteresis loops.

an appreciable range of gas uptake, whereas in the latter they remain nearly horizontal and
parallel over a wide range of p/p^o. In certain respects *Types H2* and *H3* (formerly termed
Types E and B, respectively) may be regarded as intermediate between these two extremes.
A feature common to many hysteresis loops is that the steep region of the desorption branch
leading to the lower closure point occurs (for a given adsorptive at a given temperature)
at a relative pressure which is almost independent of the nature of the porous adsorbent
(e.g. for nitrogen at its boiling point at p/p^o ~0.42 and for benzene at $25^{\circ}C$ at p/p^o ~0.28).

The shapes of hysteresis loops have often been identified with specific pore structures.
Thus, *Type H1* is often associated with porous materials known, from other evidence, to
consist of agglomerates or compacts of approximately uniform spheres in fairly regular
array, and hence to have narrow distributions of pore size. Some corpuscular systems
(e.g. silica gels) tend to give Type H2 loops, but in these cases the distribution of pore
size and shape is not well-defined. Indeed, the H2 loop is especially difficult to
interpret: in the past it was attributed to a difference in mechanism between condensation
and evaporation processes occurring in pores with narrow necks and wide bodies (often
referred to as 'ink bottle' pores), but it is now recognised that this provides an
over-simplified picture.

The Type H3 loop, which does not exhibit any limiting adsorption at high p/p^o, is observed
with aggregates of plate-like particles giving rise to slit-shaped pores. Similarly, the
Type H4 loop appears to be associated with narrow slit-like pores, but in this case the
Type I isotherm character is indicative of microporosity.

With many systems, especially those containing micropores, *low pressure hysteresis*
(indicated by the dashed lines in Figure 3), may be observed extending to the lowest
attainable pressures. Removal of the residual adsorbed material is then possible only if
the adsorbent is outgassed at higher temperatures. This phenomenon is thought to be
associated with the swelling of a non-rigid porous structure or with the irreversible
uptake of molecules in pores (or through pore entrances) of about the same width as that of
the adsorbate molecule.

SECTION 6.   DETERMINATION OF SURFACE AREA

6.1 Application of the BET method

The Brunauer-Emmett-Teller (BET) gas adsorption method has become the most widely used standard procedure for the determination of the surface area of finely-divided and porous materials, in spite of the oversimplification of the model on which the theory is based.

It is customary to apply the BET equation in the linear form

$$\frac{p}{n^a.(p^o-p)} = \frac{1}{n_m^a.C} + \frac{(C-1)}{n_m^a.C}.\frac{p}{p^o}$$

where n^a is the amount adsorbed at the relative pressure p/p^o and n_m^a is the monolayer capacity.

According to the BET theory C is related exponentially to the enthalpy (heat) of adsorption in the first adsorbed layer. It is now generally recognised, however, that although the value of C may be used to characterise the shape of the isotherm in the BET range it does not provide a quantitative measure of enthalpy of adsorption but merely gives an indication of the order of magnitude of the adsorbent-adsorbate interaction energy. Thus, in reporting BET data it is recommended that C values are stated, but not converted to enthalpies of adsorption.

A high value of C (~100) is associated with a sharp knee in the isotherm, thus making it possible to obtain by visual inspection the uptake at Point B, which usually agrees with n_m^a derived from the above equation to within a few per cent. On the other hand, if C is low (<20) Point B cannot be identified as a single point on the isotherm. Unfortunately Point B is not itself amenable to any precise mathematical description and the theoretical significance of the amount adsorbed at Point B is therefore questionable.

The BET equation requires a linear relation between $p/n^a(p^o-p)$ and p/p^o (i.e. the *BET* plot). The range of linearity is, however, restricted to a limited part of the isotherm – usually not outside the p/p^o range of 0.05-0.30. This range is shifted to lower relative pressures in cases of the energetically more homogeneous surfaces, e.g. for nitrogen or argon adsorption on graphitised carbon or xenon on clean metal films under ultra high vacuum conditions.

The second stage in the application of the BET method is the calculation of the surface area (often termed *BET area*). This requires a knowledge of the average area, a_m *(molecular cross-sectional area)*, occupied by the adsorbate molecule in the complete monolayer. Thus

$$A_s(BET) = n_m^a.L.a_m$$

and $$a_s(BET) = A_s(BET)/m$$

where $A_s(BET)$ and $a_s(BET)$ are the total and specific surface areas, respectively, of the adsorbent (of mass m) and L is the Avogadro constant.

For the close-packed nitrogen monolayer at 77K, $a_m(N_2) = 0.162$ nm^2, as calculated from the density of liquid nitrogen at 77K by assuming hexagonal close packing. This value appears to be satisfactory to within about ± 10% for the adsorption of nitrogen on a wide number of different surfaces. With other adsorptives, arbitrary adjustments of the a_m value is generally required to bring the BET area into agreement with the nitrogen value. The adjusted values of a_m for a particular adsorptive are dependent on temperature and the adsorbent surface. They may also differ appreciably from the value calculated for the close-packed monolayer on the basis of the density of the liquid or solid adsorptive. In view of this situation and the fact that full nitrogen isotherms may be conveniently measured at temperatures ~77K, it is recommended that nitrogen should continue to be used for the determination of both surface area and mesopore size distribution (Section 7.3).

The standard BET procedure requires the measurement of at least three and preferably five or more points in the appropriate pressure range on the N_2 adsorption isotherm at the normal boiling point of liquid nitrogen.

For routine measurements of surface areas, e.g. of finely divided or porous industrial products, a simplified procedure may be applied using only a single point on the adsorption isotherm, lying within the linear range of the BET plot. For N_2, the C value is usually sufficiently large ($\geqslant 100$) to warrant the assumption that the BET straight line passes through the origin of the coordinate system. Thus

$$n_m^a = n^a(1 - p/p^o) \; .$$

The validity of the simplifying assumption is usually within the variance of surface area determinations (about ± 10%) for different materials and may be checked by calibration against the standard BET procedure or by using surface area reference samples (see Section 6.2).

It is strongly recommended that in reporting a_s(BET) values, the conditions of outgassing (see Section 4.1), the temperature of the measurements, the range of linearity of the BET plot, the values of n_m^a and C and the value taken for the cross-sectional area a_m should all be stated.

If the standard BET procedure is to be used, it should be established that monolayer-multilayer formation is operative and is not accompanied by micropore filling (Section 8.3), which is usually associated with an increase in the value of C (>200, say). It should be appreciated that the BET analysis does not take into account the possibility of micropore filling or penetration into cavities of molecular size. These effects can thus falsify the BET surface areas and in case of doubt their absence should be checked by means of an empirical method of isotherm analysis or by using surface area reference samples (see Section 6.2).

For the determination of *small specific surface areas* (<5m²g⁻¹, say) adsorptives with relatively low vapour pressure are used in order to minimise the dead space correction, preferably krypton or xenon at liquid nitrogen temperature. In the case of krypton, use of the extrapolated p^o value for the supercooled liquid tends to lead to a wider range of the linear BET plot and larger monolayer capacities (the difference being <10%) as compared with p^o for the solid. Evaluation of surface areas is further complicated by the choice of the a_m value which is found to vary from solid to solid if compared with the BET nitrogen areas (a_m(Kr) = 0.17–0.23 nm²; a_m(Xe) = 0.17–0.27 nm²). Since no generally valid recommendations can be made, it is essential to state the chosen p^o and a_m values.

Ultrahigh vacuum techniques (basic pressure ~10² μPa) enable adsorption studies to be made on stringently *clean solid surfaces* whereas degassing under moderate vacuum conditions, as normally applied in surface area determinations, leave the adsorbent covered with a preadsorbed layer of impurities and/or the adsorbate. On subsequent adsorption (e.g. N_2 or noble gases) the complete physisorbed monolayer is usually reached at $p/p^o \sim 0.1$ while with clean surfaces this state occurs at p/p^o values which are smaller by orders of magnitude. In the latter case it is found that straight line BET plots may be obtained in various ranges of p/p^o, leading to larger monolayer capacities as the relative pressure increases. It should, however, be realised that it is not the range of p/p^o which is the determining factor for the relevant BET plot, but rather the region of θ around θ = 1.

Noble gas adsorption is often assumed to be the least complicated form of physisorption. However, on clean solid surfaces additional Coulombic forces may contribute to the adsorption bond, e.g. Xe on clean metal surfaces. Such specific interactions may lead to ordered structures of the adsorbate in registry with the substrate lattice and thus affect the molecular cross sectional area (e.g. a_m(Xe) = 0.172 nm² on Pd(110)).

6.2 Empirical procedures for isotherm analysis

In view of the complexity of real solid/gas interfaces and the different mechanisms which may contribute to physisorption, it is hardly surprising to find that none of the current theories of adsorption is capable of providing a mathematical description of an experimental isotherm over its entire range of relative pressure. In practice, two different procedures have been used to overcome this problem. The first, and older, approach involves the application of various semi-empirical equations (e.g. the Langmuir, Dubinin-Radushkevich, Frenkel-Halsey-Hill equations), the particular mathematical form depending on the range of the isotherm to be fitted and also on the nature of the system. The second procedure (e.g. the t-method, $α_s$-method, comparison plot) makes use of standard adsorption isotherms obtained with selected non-porous reference materials and attempts to explain differences in the isotherm shape in terms of the three different mechanisms of physisorption, i.e. monolayer-multilayer coverage, capillary condensation and micropore filling. Much discussion has surrounded the choice of the standard isotherm, but it now seems generally accepted that it should be one obtained on a chemically similar adsorbent rather than one having the same value of C as the isotherm to be analysed. In favourable cases, this approach can provide an independent assessment of the *total* surface area (for mesoporous, macroporous or non-porous solids) and an assessment of the *external* area for microporous solids (see Section 8.3).

SECTION 7.   ASSESSMENT OF MESOPOROSITY

7.1   Properties of porous materials

Most solids of high surface area are to some extent porous. The *texture* of such
materials is defined by the detailed geometry of the void and pore space. Porosity, ε, is
a concept related to texture and refers to the pore space in a material. An *open pore* is a
cavity or channel communicating with the surface of a particle, as opposed to a *closed pore*.
Void is the space or interstice between particles. In the context of adsorption and fluid
penetration *powder porosity* is the ratio of the volume of voids plus the volume of open
pores to the total volume occupied by the powder. Similarly, *particle porosity* is the ratio
of the volume of open pores to the total volume of the particle. It should be noted that
these definitions place the emphasis on the accessibility of pore space to the adsorptive.

The *total pore volume*, V_p, is often derived from the amount of vapour adsorbed at a
relative pressure close to unity – by assuming that the pores are then filled with liquid
adsorptive.

If the solid contains no macropores, the isotherm remains nearly horizontal over a range of
p/p^o approaching unity and the total pore volume is well-defined. In the presence of
macropores the isotherm rises rapidly near $p/p^o = 1$ and in the limit of large macropores
may exhibit an essentially vertical rise. In this case the limiting adsorption at the top
of the vertical rise can be identified reliably with the total pore volume only if the
temperature on the sample is very carefully controlled and there are no 'cold spots' in the
apparatus (which lead to bulk condensation of the gas and a false measure of adsorption in
the volumetric method).

The *mean hydraulic radius*, r_h , is defined as

$$r_h = \left(\frac{V}{A_s}\right)_p \qquad ,$$

where $(V/A_s)_p$ is the ratio of the volume to the area of walls of a group of mesopores.

If the pores have a well-defined shape there is a simple relationship between r_h and the
mean pore radius, r_p. Thus, in the case of non-intersecting cylindrical capillaries

$$r_p = 2\, r_h \quad .$$

For a parallel-sided slit-shaped pore, r_h is half the slit width.

The *pore size distribution* is the distribution of pore volume with respect to pore size.
The computation of pore size distribution involves a number of assumptions (pore shape,
mechanism of pore filling, validity of Kelvin equation etc).

7.2   Application of the Kelvin equation

Mesopore size calculations are usually made with the aid of the Kelvin equation in the form

$$\frac{1}{r_1} + \frac{1}{r_2} = - \frac{RT}{\sigma^{lg} v^l} \, \ln\left(\frac{p}{p^o}\right)$$

which relates the principal radii, r_1 and r_2, of curvature of the liquid meniscus in the
pore to the relative pressure, p/p^o, at which condensation occurs. Hence σ^{lg} is the surface
tension of the liquid condensate and v^l is its molar volume. It is generally assumed that
this equation can be applied locally to each element of liquid surface.

In using this approach to obtain the *pore radius* or *pore width*, it is necessary to assume:
(i) a model for the pore shape and (ii) that the curvature of the meniscus is directly
related to the pore width. The pore shape is generally assumed to be either cylindrical or
slit-shaped: in the former case, the meniscus is hemispherical and $r_1 = r_2$; in the latter
case, the meniscus is hemicylindrical and $r_2 = \infty$.

Rearrangement of the Kelvin equation and replacement of the principal radii of curvature
terms by $2/r_K$ gives

$$r_K = \frac{2\sigma^{lg} v^l}{RT \ln (p^o/p)}$$

(r_K is often termed the *Kelvin radius*).

If the pore radius of a cylindrical pore is r_p and a correction is made for the thickness of a layer already adsorbed on the pore walls, i.e. the *multilayer thickness*, t,

$$r_p = r_K + 2t.$$

Correspondingly, for a parallel-sided slit, the slit width, d_p, is given by

$$d_p = r_K + t.$$

7.3 Computation of mesopore size distribution

Many attempts have been made to calculate the mesopore size distribution from physisorption isotherms. In such calculations it is generally assumed (often tacitly): (a) that the pores are rigid and of a regular shape (e.g. cylindrical capillaries or parallel-sided slits), (b) that micropores are absent, and (c) that the size distribution does not extend *continuously* from the mesopore into the macropore range. Furthermore, to obtain the pore size distribution, which is usually expressed in the graphical form $\Delta V_p/\Delta r_p$ vs. r_p, allowance must be made for the effect of multilayer adsorption in progressively reducing the dimensions of the free pore space available for capillary condensation.

The location and shape of the distribution curve is, of course, dependent on which branch of the hysteresis loop is used to compute the pore size. In spite of the considerable attention given to this problem, it is still not possible to provide unequivocal general recommendations. In principle, the regions of metastability and instability should be established for the liquid/vapour meniscus in the various parts of a given pore structure, but in practice this would be extremely difficult to undertake in any but the simplest types of pore systems.

Recent work has drawn attention to the complexity of capillary condensation in pore networks and has indicated that a pore size distribution curve derived from the desorption branch of the loop is likely to be unreliable if pore blocking effects occur. It is significant that a very steep desorption branch is usually found if the lower closure point of the loop is located at the limiting p/p^o (see Section 5.3). In particular, the desorption branch of a Type H2 loop is one that should not be used for the computation of pore size distribution.

It is evident from the above considerations that the use of the physisorption method for the determination of mesopore size distribution is subject to a number of uncertainties arising from the assumptions made and the complexities of most real pore structures. It should be recognised that derived pore size distribution curves may often give a misleading picture of the pore structure. On the other hand, there are certain features of physisorption isotherms (and hence of the derived pore distribution curves) which are highly characteristic of particular types of pore structures. Physisorption is one of the few non-destructive methods available for investigating mesoporosity, but it is to be hoped that future work will lead to refinements in the application of the method – especially through the study of model pore systems and the application of modern computer techniques.

SECTION 8. ASSESSMENT OF MICROPOROSITY

8.1 Terminology

It is generally recognised that the mechanism of physisorption is modified in very fine pores (i.e. pores of molecular dimensions) since the close proximity of the pore walls gives rise to an increase in the strength of the adsorbent-adsorbate interactions. As a result of the enhanced adsorption energy, the pores are filled with physisorbed molecules at low p/p^o. Adsorbents with such fine pores are usually referred to as *microporous*.

The limiting dimensions of micropores are difficult to specify exactly, but the concept of *micropore filling* is especially useful when it is applied to the primary filling of pore space as distinct from the secondary process of capillary condensation in mesopores.

The terminology of pore size has become somewhat confused because of the attempts made to designate the different categories of pores in terms of exact dimensions rather than by reference to the gas-solid system (the size, shape and electronic nature of the adsorptive molecules and the surface structure of the adsorbent) as well as to the pore size and shape.

The upper limit of 2.0 nm for the micropore width was put forward as part of the IUPAC classification of pore size (see Appendix II, Part I). It now seems likely that there are two different micropore filling mechanisms, which may take place at p/p^o below the onset of capillary condensation: the first, occurring at low p/p^o, involves the entry of isolated adsorbate molecules into very narrow pores; the second, at a somewhat higher p/p^o, is a *cooperative* process in that the interaction between adsorbate molecules is involved.

It is recommended that, on the basis of this approach, attention should be directed towards the *mechanism* of pore filling rather than to the specification of the necessarily rather arbitrary limits of pore size. Until further progress has been made it is undesirable to modify the original IUPAC classification or to introduce any new terms (e.g. ultrapores or ultramicropores).

8.2 Concept of surface area

In recent years a radical change has been taking place in the interpretation of the Type I isotherm. According to the classical Langmuir theory, the limiting adsorption n_p^a (at the plateau) represents completion of the monolayer and may therefore be used for the calculation of the surface area. The alternative view, which is now widely accepted, is that the initial (steep) part of the Type I isotherm represents micropore filling (rather than surface coverage) and that the low slope at the plateau is due to multilayer adsorption being confined to a small external area.

If the latter explanation is correct, it follows that the value of A_s (as derived by either BET or Langmuir analysis (see Note j)) cannot be accepted as the true surface area of a microporous adsorbent. On the other hand, if the slope of the isotherm is not too low at higher p/p^o and provided that capillary condensation is absent, it should (in principle) be possible to assess the *external* surface area from the multilayer region.

In view of the above difficulties, it has been suggested that the term *monolayer equivalent area* should be applied to microporous solids. However, the exact meaning of this term may not always be clear and it is recommended that the terms *Langmuir area* or *BET area* be used where appropriate, with a clear indication of the range of linearity of the Langmuir, or BET, plot, the magnitude of C etc. (see Section 6.1).

8.3 Assessment of micropore volume

No current theory is capable of providing a general mathematical description of micropore filling and caution should be exercised in the interpretation of derived quantities (e.g. micropore volume) obtained by the application of a relatively simple equation (e.g. the Dubinin-Radushkevich equation) to adsorption isotherm data over a limited range of p/p^o and at a single temperature. The fact that a particular equation gives a reasonably good fit over a certain range of an isotherm does not in itself provide sufficient evidence for a particular mechanism of adsorption.

The t-method and its extensions provide a simple means of comparing the shape of a given isotherm with that of a standard on a non-porous solid. In the original t-method, the amount adsorbed is plotted against t, the corresponding multilayer thickness calculated from the standard isotherm obtained with a non-porous reference solid. Any deviation in shape of the given isotherm from that of the standard is detected as a departure of the 't-plot' from linearity. For the assessment of microporosity, the thickness of the multilayer is irrelevant and it is preferable to replace t by the 'reduced' adsorption, α_s, defined as $\left(n^a/n_s^a\right)_{ref}$ where n_s^a is the amount adsorbed by the reference solid at a fixed relative pressure, $p/p^o = s$. An advantage of this method is that it can be used even when the standard isotherm does not exhibit a well-defined Point B, i.e. when the value of C is low. Once the standard α_s-curve has been obtained for the adsorption system at the given temperature, the α_s-method can be applied in an analogous manner to the t-method. It should be recognised that such methods can only be expected to give an understanding of the true nature of the micropore filling process (and hence of the micropore structure) if the standard isotherms (or t-curves) are obtained with non-porous reference solids of known surface structure. It is strongly recommended that the appropriate standard isotherm is selected for the given adsorption *system* and not by arbitrarily choosing a Type II isotherm having the same C value as the isotherm on a particular microporous solid.

Another procedure which may be used for the assessment of microporosity is the *pre-adsorption method*. In this approach the micropores are filled with large molecules (e.g. nonane), which are not removed by pumping the adsorbent at ambient temperature. In the most straightforward case, this procedure can provide an effective way of isolating the micropores and leaving the external surface available for the adsorption of nitrogen, or some other adsorptive.

Note j.   In fact, many microporous solids do not give linear BET plots although their
          Langmuir plots may be linear over an appreciable range of p/p^o.

SECTION 9.   GENERAL CONCLUSIONS AND RECOMMENDATIONS

9.1   For evaluation of both the surface area and the pore size distribution from a single adsorption isotherm, nitrogen (at ~77K) is the recommended adsorptive. If the surface area is relatively low (a_s <5 $m^2 g^{-1}$, say), krypton or xenon, also at ~77K, offer the possibility of higher precision in the actual measurement of the adsorption, but not necessarily higher accuracy than could be obtained with nitrogen in the resultant value of the surface area.

9.2   For a given system at a given temperature, the adsorption isotherm should be reproducible, but the possibility of ageing of the adsorbent - e.g. through the addition or removal of water - must always be borne in mind. The reproducibility of the adsorption should be checked whenever possible by measurement of an isotherm on a second sample (of different mass) of the given adsorbent.

9.3   The first stage in the interpretation of a physisorption isotherm is to identify the isotherm type and hence the nature of the adsorption process(es):   monolayer-multilayer adsorption, capillary condensation or micropore filling. If the isotherm exhibits low pressure hysteresis (i.e. at p/p^o < 0.4, with nitrogen at 77K) the technique should be checked to establish the degree of accuracy and reproducibility of the measurements.

9.4   The BET method is unlikely to yield a value of the actual surface area if the isotherm is of either Type I or Type III; on the other hand both Type II and Type IV isotherms are, in general, amenable to the BET analysis, provided that the value of C is not too high and that the BET plot is linear for the region of the isotherm containing Point B. It is recommended that both the value of C and the range of linearity of the BET plot be recorded. If the value of C is found to be higher than normal for the particular gas-solid system, the presence of microporosity is to be suspected even if the isotherm is of Type II or Type IV; the validity of the BET area then needs checking, e.g. by the α_s-method, in order to ascertain how closely the shape of the isotherm conforms to that of the standard isotherm in the monolayer range.

9.5   The computation of mesopore size distribution is valid only if the isotherm is of Type IV. In view of the uncertainties inherent in the application of the Kelvin equation and the complexity of most pore systems, little is to be gained by recourse to an elaborate method of computation. The decision as to which branch of the hysteresis loop to use in the calculation remains largely arbitrary. If the desorption branch is adopted (as appears to be favoured by most workers), it should be appreciated that neither a Type H2 nor a Type H3 hysteresis loop is likely to yield a reliable estimate of pore size distribution, even for comparative purposes.

9.6   If a Type I isotherm exhibits a nearly constant adsorption at high relative pressure, the micropore volume is given by the amount adsorbed (converted to a *liquid* volume) in the plateau region, since the mesopore volume and the external surface are both relatively small. In the more usual case where the Type I isotherm has a finite slope at high relative pressures, both the external area and the micropore volume can be evaluated provided that a standard isotherm on a suitable non-porous reference solid is available. At present, however, there is no reliable procedure for the computation of micropore size *distribution* from a single isotherm; but if the size extends down to micropores of molecular dimensions, adsorptive molecules of selected size can be employed as molecular probes.

9.7   The following *check list* is recommended to assist authors in the measurement of adsorption isotherms and the presentation of the data in the primary literature. The reporting of results along generally accepted lines would considerably facilitate the compilation of data in the secondary literature and would thus promote interdisciplinary scientific cooperation (see Note k).

It is suggested that the following items be checked and the relevant experimental conditions and results reported:-

(i)   Characterisation of the sample (e.g. source, chemical composition, purity, physical state).

(ii)   Pretreatment and outgassing conditions (e.g. temperature, residual pressure/ partial pressures, duration of outgassing, flushing with adsorptive).

Note k.   see "Guide for the Presentation in the Primary Literature of Numerical Data Derived from Experiments". Report of the CODATA Task Group on Presentation of Data in the Primary Literature, CODATA Bulletin No. 9 (1973).

(iii)   Mass of outgassed sample (m in g).

(iv)   Adsorptive (e.g. chemical nature, purity, drying).

(v)   Experimental procedure for isotherm determination: method (e.g. static volumetric, adsorption balance, chromatographic; calibration of dead space or buoyancy). Measurement and accuracy of pressure (p in Pa (or mbar) or p/p^o), equilibration times.

(vi)   Reproducibility (a) second run, (b) with fresh sample of adsorbent.

(vii)   Adsorption isotherm: plot of amount adsorbed (n^a in mol g^{-1} or N^a in molecules m^{-2}) versus pressure (p in Pa (or mbar) or p/p^o), statement of measured/calculated p^o value at T.

(viii)   Type of isotherm, type of hysteresis, nature of adsorption (monolayer-multilayer adsorption, capillary condensation, micropore filling).

(ix)   BET data: adsorptive, temperature (T in K), region of p/p^o and θ in linear BET plot, single point method, monolayer capacity (n_m^a in mol g^{-1} or N_m^a in molecules m^{-2}), C value, molecular cross-sectional area (a_m in nm^2 per molecule), specific surface area (a_s in m^2 g^{-1}).

(x)   Porosity (ϵ with reference to powder porosity or particle porosity indicating in the latter case whether open pores or open plus closed pores are considered).

(xi)   Assessment of mesoporosity (pore width ~ 2-50 nm), method of computation, choice of ad- or desorption branch, p^o value at T and region of p/p^o used, surface tension of liquid adsorptive (σ^{lg} in Nm^{-1} at T), model for pore shape. Correction for multilayer thickness, t-curve: plot of t in nm vs p/p^o (indication whether a standard curve is assumed or an adsorption isotherm determined on a non-porous sample of the adsorbent). Pore size distribution: plot of $\Delta V_p/\Delta r_p$ vs r_p (pore volume V_p per unit mass of adsorbent in cm^3 g^{-1} as calculated with the density ρ in g cm^{-3} of the liquid adsorptive, mean pore radius r_p in nm), total pore volume at saturation.

(xii)   Assessment of microporosity (pore width < ca 2 nm), method of evaluation, t-plot: amount adsorbed n^a in mol g^{-1} vs multilayer thickness t in nm, α_s-plot: n^a vs $(n^a/n_s^a)_{ref}$, where the index refers to a chosen value s = p/p^o, Dubinin-Radushkevich plot or pre-adsorption method. Micropore volume per unit mass of adsorbent in cm^3 g^{-1} as calculated with the density ρ^ℓ of the liquid adsorptive, monolayer equivalent area of microporous solid, external surface area.