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Review

Porous materials: structure, properties and capillary phenomena

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The review covers the classification of porous materials, and the properties expected from the solid and the adsorbate within the pores. Rather than dealing, in what would inevitably be a seed-catalogue manner, with different solids, an attempt has been made to give a thorough introduction to the subject as a whole. The reader can then follow up particular avenues appropriate to his needs. Examples of porous carbons are used to illustrate the kinds of phenomena expected more generally with vapours adsorbed by porous solids. Capillary phenomena become evident when the adsorbate within the pores is liquid-like, and curvatures of fluid/fluid interfaces are important, e.g. with adsorption in macropores or the displacement of one liquid by another. Structural damage which can arise from vapour adsorption, or from phase changes of capillary fluids (e.g. frost damage to building materials) is surveyed. The literature cited covers main publications, or those providing a useful insight (with their own lists of references), especially from the past 30 years, but the subject is old, and some references cover the 19th Century. Flow of liquids is largely omitted except for general introductory references.

1. Introduction

The intending user of porous materials needs to know their various properties, and can often be faced with difficulties of specification. Porous materials present a wealth of challenging problems to the scientist, involving the solid and the fluid often present in the pores. It is intended in this review to show advances in the understanding of the behaviour of porous materials, in their widest sense. Emphasis will be largely on static systems, almost, but not entirely, avoiding transport phenomena associated with flow of fluids in the pores.

The need to be able to describe pore structure, and to be able to explain phenomena arising from the presence of pores, has produced many notable scientific meetings and subsequent proceedings. These publications often reveal much more than contemporary advances; they also demonstrate all too clearly the complexity of natural systems such as soils, certain minerals and wood, and they draw attention to persistent conceptual problems of understanding phenomena associated with pores. Monographs dealing with porous systems, but excepting those dealing with flow through pores (see Section 6), include those by Bond [1], Gregg and Sing [2], Linsen [3], and Breck [4]. Conference publications appearing in the past 30 years include a Faraday Society Discussion [5], certain papers from Industrial Carbons and Graphite meetings [6], and from Congresses on Surface Activity, especially the second [7], the Colston Symposium proceedings [8], a RILEM* meeting on Transfer of Water in Porous Media [9], an ACS Symposium on Porous Media [10], certain papers from the IUPAC/SCI meeting on surface Area Determination [11], the extensive RILEM/IUPAC Prague Symposium on Pore Structure and

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* Réunion Internationale des Laboratoires d'essais et de recherches sur les matériaux et les constructions (The International Union of Testing and Research Laboratories for Materials and Structures).

Properties of Materials [12], and the 48th ACS Colloid Symposium [13]. Recent reviews include those by Haynes [14], Dullien and Batra [15], Morrow [16], and Everett and Haynes [17]. Books dealing with complementary topics and providing background information, include those on physical adsorption [18–20], more general surface and colloid subjects [21–24], wetting and adhesion [25], and adsorption from solution [26]. It is also worth noting that papers on surface science are to be found throughout journals on physicochemical phenomena, and that relevant review series include *Advances in Colloid and Interface Science* [27], *Surface and Colloid Science* [28], *Progress in Surface and Membrane Science* [29], and *The Chemistry and Physics of Carbon* [30].

2. General classification of porous materials

It is difficult to give a consistent classification of porous substances like woods, cements, bricks, pellets of compressed powders, soils, some metals, and many carbons. A useful attempt at classification has been made by Haynes and Sneck [31], based on the performance concept. The porosity, pore-size distribution, and specific surface area of a brick can be determined by techniques well known to physical chemists, namely by pycnometry, mercury penetration, and gas (vapour) adsorption. The results of such measurements become more valuable if they can be related to features affecting performance, e.g. strength, weatherability, resistance to rain-water penetration, capillary action (suction or imbibition), and thermal conductivity. (Thermal, electrical, and acoustic properties will not feature in this review.)

Pores can be classified by their size and structure. Recent nomenclature [32] terms as micropores those of width (smallest dimension) less than 2 nm, as mesopores those ranging from 2 to 50 nm, and as macropores, those wider than 50 nm. Structure specification at a simple level involves answering such questions as, "are the pores approximated by terms based on model descriptions such as parallel-walled, cylindrical, open-ended, and inter-connected?" It may be with some systems that cavernous pores are connected by smaller diameter passages to the external surface of the solid; such "ink-bottle" pores are sometimes referred to as being saccate. In reality, pore structure, unless it is associated with crystallographic ordering as in zeolites [33, 34], is often complex and derives from the mode of solid and pore formation and from any subsequent modification, e.g. by heat-treatment. Much fundamental knowledge of porous media comes from theoretical and experimental studies on those systems best approximating to model behaviour, e.g. single right-circular capillaries, random packings of spheres, and pure carbons produced by thermally decomposing certain polymers.

In use, a porous material will usually be in contact with a fluid phase which is either a gas (vapour), or a liquid. While gas/solid systems are widely studied, less attention has been paid to adsorption phenomena involving liquids and porous, as opposed to non-porous, solids; slow attainment of equilibrium often makes immersional studies difficult. Pores are thus rarely empty; the characteristics of a particular adsorbate* within the pores will largely depend on temperature and pore size. A rough, but convenient demarkation can be made between adsorption phenomena where surface effects dominate the behaviour of the adsorbate, and capillary phenomena where the fluid within the pores is of sufficient extent (width) for both surface and bulk free energies to be important. The kind of intermolecular forces operating in any system will ultimately be responsible for its properties. In part, for instance, the stronger adsorption forces possible between a zeolite containing ions and adsorbate molecules which are polarized explains why they, and not microporous carbons, find extensive commercial applications as molecular sieves. The forces responsible for physical adsorption are similar to those giving the binding energy in a bulk liquid, and so physical adsorption is often likened to condensation. One characteristic feature of physical adsorption is that the amount adsorbed increases with decrease in temperature. Intermolecular forces of attraction are of the van der Waals (dispersion or London) type, they may arise from permanent or induced dipoles (or quadrupoles), and they may be electrostatic in origin [35]. Physical adsorption which is of gen-

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* *Adsorption* refers to the enhanced concentration of a species at an interface over that which would be present if bulk concentration existed up to a (suitably chosen) mathematical dividing surface in the interfacial region. The *adsorptive* is the substance being adsorbed from the bulk fluid phase; that which is actually in the adsorbed state is the *adsorbate* and the solid is the *adsorbent* [32].

eral occurrence and which may involve multilayers of adsorbate, is distinguished from chemical adsorption, such as that occurring in tarnishing reactions and in the initial stage of metal oxidation, which is limited to a single molecular layer.

Investigations of porous media can be broadly classified as being of two kinds: (i) those where techniques are employed to characterize the nature of the solid surface and the structure of the pore system, and (ii) studies of the properties of the solid plus adsorbate in conditions comparable to those encountered during use. Typical of the first kind is the use of vapour adsorption (e.g. of organics and water) to determine pore size and structures. Of the second kind would be studies of the effects upon the solid of phase transitions, e.g. freezing, of fluids within pores [14, 36]. Changes in external dimensions, and damage to internal structure, can arise from fluid within the pores. The thermal expansion of the solid, and the decrease in adsorption with increase in temperature can lead to combined coefficients of thermal expansion that are anomalous. In many situations, therefore, porous materials will behave as curious composites of solid plus adsorbate.

3. Physical adsorption of gases and vapours

The amount of a gas or vapour adsorbed by a solid as a function of pressure, at constant temperature, is called the adsorption isotherm. There are no detailed accounts of the various pieces of apparatus which can be used to determine adsorption isotherms, although the basic methods have been outlined [37]. The two fundamental techniques of which there are many variations are gravimetry and volumetry. Direct weighing of the amount adsorbed can be carried out by using commercially available electromagnetic balances (the most sensitive can detect changes of $\sim 10^{-8}$ g), or by using spiral quartz spring balances. The system for handling the gas, and the spring suspension and enclosure, are usually constructed in the laboratory. Commercially available springs vary in sensitivity and in the maximum load they can withstand, e.g. 0.5 g maximum load with nominal sensitivity of $35\,\mathrm{cm\,g^{-1}}$, and 0.1 g load with sensitivity of about $180\,\mathrm{cm\,g^{-1}}$. Springs of tapered construction are more sensitive, e.g. about $450\,\mathrm{cm\,g^{-1}}$ for a maximum load of 0.1 g.

The apparatus for volumetric determinations is not usually purchased commercially. The technique involves compressions of the gas in contact with the thermostatted adsorbent and application of the gas laws to each stage giving a point on the isotherm.

3.1. Illustrations of principal features

Many features of general relevance to porous systems are shown by the adsorption isotherms for organic vapours on porous carbons prepared (below) by the thermal decomposition of certain polymers. (The isotherms were obtained gravimetrically using spiral springs.) Fig. 1 shows

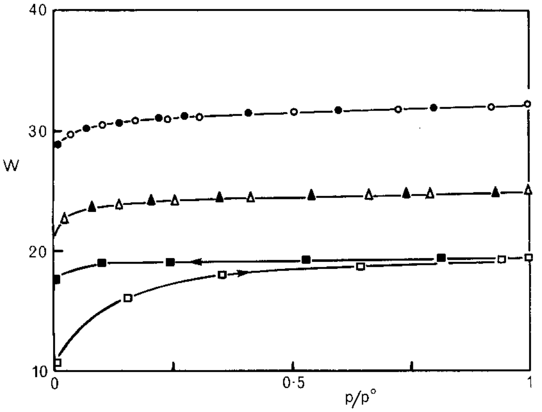

Figure 1 Isotherms showing the dependence of amount adsorbed, expressed as percentage weight increase *W*, on relative pressure p/p^0, for Saran carbon fibres at 25° C: (○) benzene, (△) cyclohexane, (□) 2,2-dimethylbutane. Filled-in symbols denote desorption.

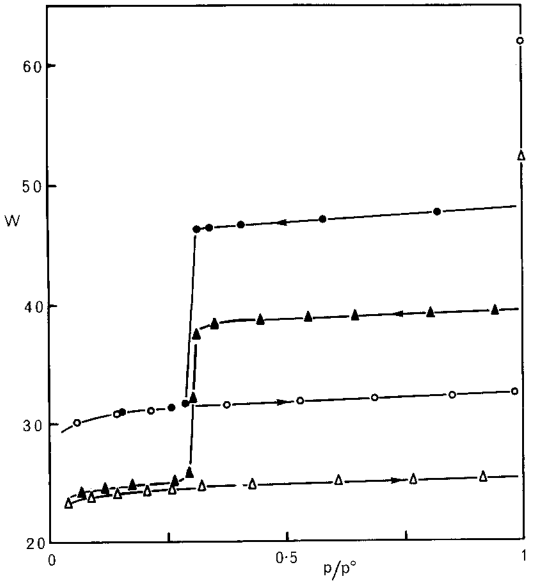

Figure 2 Adsorption isotherms showing high-pressure hysteresis for (○) benzene, and (△) cyclohexane on Saran carbon powder at 25° C. The cyclohexane isotherm also shows low-pressure hysteresis.

adsorption isotherms [38] for benzene, cyclohexane and 2,2-dimethylbutane (DMB) on Saran carbon fibres at 25° C. These fibres contain only micropores which are not much larger than the adsorbed molecules. When the relative pressure is about 0.2 the micropore space is virtually filled with adsorbate. The isotherm for DMB (the "largest" molecule) shows a hysteresis loop since desorption, indicated by the arrow, does not follow adsorption – the DMB molecules probably become intercalated in the solid structure (see Section 3.5).

Fig. 2 shows adsorption isotherms for benzene and cyclohexane vapours adsorbed on Saran carbon *powders* at 25° C. These vapours are readily adsorbed – the pore system increasing in weight by about 31 and 24% respectively at $p/p^0 = 0.2$, and the powders thus behave in this respect like the fibres of Fig. 1. They differ from the fibres by adsorbing in their macropores (present in powders but not in fibres) at $p/p^0 \simeq 1$. When the relative pressure is subsequently lowered in steps, separate desorption branches to the isotherms are found (high-pressure hysteresis). The isotherm for cyclohexane also shows low-pressure hysteresis which will be explained later.

The carbons used here as examples can be prepared [39, 40] by decomposing either poly(vinylidene chloride), $(\text{-}CH_2CCl_2\text{-})_n$, giving powders, or the co-polymer Saran, containing vinyl chloride as co-monomer, which can be obtained in powder and monofilament (melt extruded) forms. The polymers are initially heated at a temperature in the range 150 to 180° C for periods ranging from about 2 to 5 days, and then the temperature is raised to about 750° C over a period of at least 12 h to complete the carbonization. These carbons serve to illustrate the point made earlier about the characteristics of the porous system being derived from the condition of its preparation and subsequent modification. The most important factors are the morphology of the polymer to be carbonized, more specifically whether it is in the powder or monofilament form, and, with powders, the initial temperature of heating (which was 165° C for the carbon of Fig. 2) affects properties. The large pores in the carbon powders, within which capillary condensation occurs (Section 4.2), are produced by retention of the gaps between morphological units of the powder. These units are essentially crystalline platelets making up polymer particles [40, 41]. The size and shape of the residual gaps, i.e. of the mesopores and macropores, can be varied by "sintering" the polymer, and these pores can even be completely eliminated if the temperature of initial heating is about 180° C when the polymer is virtually melted. The micropores present in the carbon, regardless of the morphology of the polymer, are thought to form during the second heating stage (to 750° C) when cross-linking is occurring within the already brittle solid [39, 41].

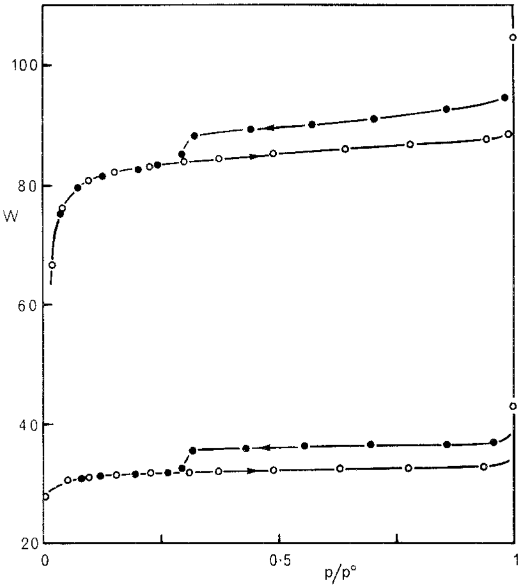

Figure 3 The lower isotherm is for benzene on a Saran carbon powder sample, and the upper isotherm is for benzene adsorption on a sample made by burning off 52.5% by weight of carbon with carbon dioxide at 900° C. Both isotherms are for 25° C.

Large changes in the pore size and the adsorption capacity of these carbons (Fig. 3) can be brought about by partial oxidation, e.g. by carbon dioxide at 900° C which is more controllable than the exothermic reaction of carbon with oxygen.

With the examples given above it is possible to deal with selected topics which commonly arise when attempting to study porous media by physical adsorption.

3.2. Surface areas and the capacity of solids to adsorb

The surface area of a non-porous solid can be used as a specific quantity pertaining to its capacity to adsorb. The essence of obtaining surface areas by gas adsorption is usually to determine experimentally the amount of adsorptive required to form a unimolecular layer on the solid, and to directly obtain the area which that layer occupies from knowledge of the area σ occupied by a single adsorbate molecule – this is usually itself related to the molar volume v of the bulk liquid phase of the adsorptive species [2, 42] (see examples in Table I). In some cases where sitewise adsorption occurs, the geometrical arrangement of the sites may influence the effective mean area of the surface occupied by an adsorbate molecule. Guidelines to the use of standard comparison surfaces have recently been published [43].

With porous solids, the quantity similarly obtained, which is often called the surface area, although the term monolayer equivalent area is preferable, is useful but its significance is less well understood. It might be excusable to think that the pores have walls whose total area, no matter how irregular the pores are, provide a good measure of the adsorptive capacity of the entire porous medium. With macropores this is probably true, but in broad terms porous media differ from non-porous ones for two reasons: (a) the presence of pores enables the solid to hold fluid, i.e. topologically, plane solid surfaces and curved continuous surfaces are able to constrain fluids in basically different interfacial configurations; (b) in many cases "opposite" walls of pores are sufficiently close, or a wall may be sufficiently re-entrant, that the forces of attraction with adsorbate are greatly enhanced compared to the case of a plane surface. The topological attributes may not pose a severe problem, but consideration of the magnitudes of the force field and its dependence on the pore space (distance apart of the walls) leads to the conclusion that any single quantity, e.g. monolayer equivalent area, may be inadequate to characterize the adsorptive† capacity: it is still a good compromise.

Fig. 4 shows highly schematically how the potential energy ϵ of a single molecule of adsorptive varies with its distance r from a plane surface, and with its position between parallel walls of model pores. The minimum in the potential energy curve occurs for the single plane surface case where $r = r^*$ and $\epsilon = \epsilon^*$. The concentration of molecules at distance r can be obtained from Boltzmann's law and the ideal gas law,

$$n_r = n^0 \exp(-\epsilon/kT); n^0 = p/kT. \qquad (1)$$

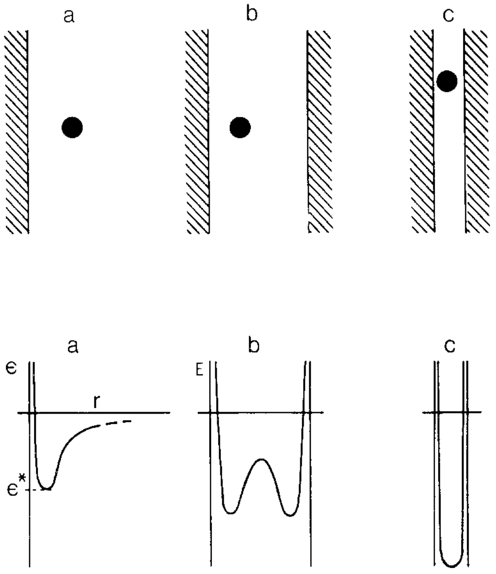

Figure 4 Schematic representation of the dependence of the potential energy of a molecule on (a) its distance from a plane wall; (b) and (c) on its position within pores whose walls are at two different separations.

The amount adsorbed per unit area is proportional to the gas pressure, the proportionality constant (Henry's law constant) k_H depending on the magnitude of the adsorption potential energy, and so on ϵ^*,

$$N^{ad} = pk_H; k_H = \frac{1}{kT}\int_0^\infty [\exp(-\epsilon/kT) - 1]\, dr. \qquad (2)$$

On the assumption that for the pores the contributions to the potential energy E from the walls are additive, then E increases in magnitude with decrease in wall separation, but the geometrical volume of space between the walls also decreases. Generally these effects combine to increase the amount adsorbed, and they certainly increase the concentration of adsorbate. Much work on adsorption is not in the regime of low pressure and high temperature where the model will hold even approximately, and for adsorption below the critical temperature of the adsorptive, the description of physical adsorption presents problems which are even more complex than those for a liquid in contact with a solid providing a force field.

Adsorption isotherms for gases and vapours on non-porous solids often have a "knee" in the

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† Note that *adsorptive* can be the noun (the adsorbed substance) as well as the adjective meaning ability to adsorb (cf. a sponge is absorptive [*sic*]).

vicinity of the range of relative pressure 0.1 to 0.3. The top of the knee corresponds approximately to unimolecular coverage. For microporous adsorbents the sharp knee, as shown in Fig. 1, roughly corresponds to complete filling of micropores, but the walls of any meso- or macropores which may be present will probably also be covered by adsorbate. For example, the adsorption of benzene vapour by the Saran-carbon powder shown in Fig. 2 gives a monolayer equivalent area for the solid of about $10^3 \mathrm{m}^2 \mathrm{g}^{-1}$. There are many empirical or theoretical isotherm equations with which experimental data can be used to give the amount adsorbed corresponding to monolayer, or its equivalent, coverage. Commonly used, apart from the simple Henry's law model, are those of Langmuir [44] and of Brunauer *et al.* [45]. These equations and the techniques of plotting experimental data are explained more fully in textbooks [2, 19]. To avoid misleading over-simplification it is emphasized that there are many theories pertaining to, and much controversy about, micropore filling [46, 47]. It is sufficient here to note that adsorption data often fit reasonably will the Dubinin–Kaganer equations [48, 49].

3.3. Micropore capacity and micropore sizes

If one makes the tacit assumption that the adsorbate in filled micropores is liquid-like, then the volumes of the various adsorbates can be obtained from adsorption isotherms and the molar volumes v (readily obtained from tabulated densities [50]). It has been found that the micropore capacity, expressed as the volume of adsorbate, assumed to be liquid, is virtually constant for a variety of adsorbates on a particular adsorbent, for numerous kinds of microporous solid. The constancy of adsorbate volume is referred to as Gurvitsch's rule [51]. A particularly illuminating theoretical study of pore filling has recently been carried out by Nicholson [52]. It should be noted that fluids in pores cannot be expected to have properties which are identical to those of their bulk counterparts. When bulk thermodynamic quantities are used, as they often are with considerable success in making comparisons between fluids, it is usually because the precise nature of capillary fluids is not known.

One basis for determining the actual sizes of micropores is to associate the "minimum dimension" l_{min}, of a molecule which is adsorbed with the minimum mean width of pore present (this is not stating that they are equal). For cases where comparisons have been made [38, 53], it was found that l_{min} is given approximately by v/σ as shown in Table I.

TABLE I Comparison of adsorbates[*]

Adsorbate	σ[†] (nm^2)	v/σ (nm)	l_{min} (nm)
Nitrogen (– 196 C)	0.162	0.355	–
Benzene	0.41	0.362	0.37[‡]
n-hexane	0.515	0.424	0.4 – 0.43[§]
Cyclohexane	0.38	0.48	0.48[‡]
2,2-dimethyl butane	0.46	0.484	0.56[§]
i-octane	0.545	0.506	0.59[§]

[*] Based on [38].
[†] Based on [42].
[‡] From [53].
[§] Estimated from molecular scale models.

Again referring to the Saran carbons, it was found [38] that there was a fall off in ease of adsorption (reflected in decreases in amount and rate) with adsorbates with $l_{\mathrm{min}} \gtrsim 0.45\,\mathrm{nm}$, and that in particular *i*-octane was adsorbed with considerable difficulty by the fibres. The majority of pores in these carbons are probably less than about 0.5 nm in their minimum dimension: it has been suggested that they are slot-shaped [38, 54].

Not all solids where micropores are important are highly porous like these carbons. Pores may be merely cracks near the surface of solid particles. Two related methods have been developed called the t-method and the α_s-method for analysing isotherm data so as to detect the presence of micropores, and to assess the amounts of internal and external surface of a solid [55, 56]. The essential premise of the methods is that there should be a universal isotherm for certain adsorbates on certain adsorbents. Adsorption on the "unknown" solid is compared to that, expressed as the thickness t of the adsorbed layer, on a standard adsorbent of the same kind. Controversy surrounds the choice of standard and the attribution of departures from ideal behaviour to the presence of micropores. The reader is referred to detailed reviews of this topic, such as that by Sing [56] and to the references therein. The α_s-method is a variant of the t-method involving a change in the defined standard adsorption conditions.

3.4. Hysteresis in physical adsorption

The occurrence of hysteresis in adsorption iso-

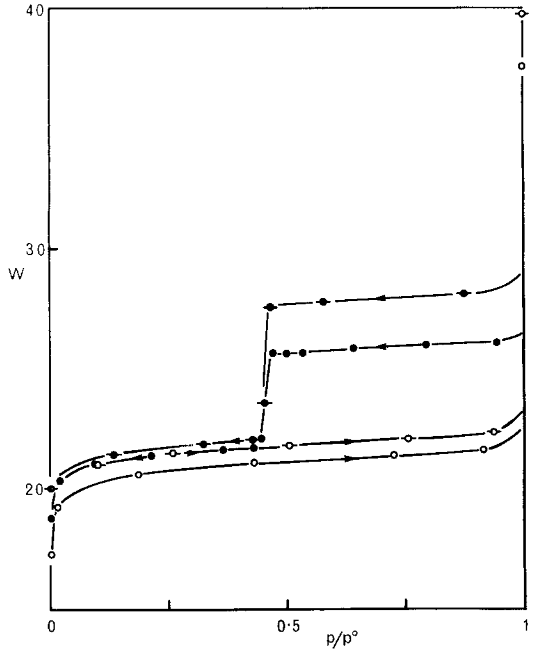

Figure 5 Isotherms for 2,2-dimethylbutane at 25° C on a Saran carbon powder sample. Two adsorption – desorption cycles, without intervening out-gassing, are shown: (○) first adsorption, (●) first desorption, (–○–) second adsorption, and (–●–) second desorption.

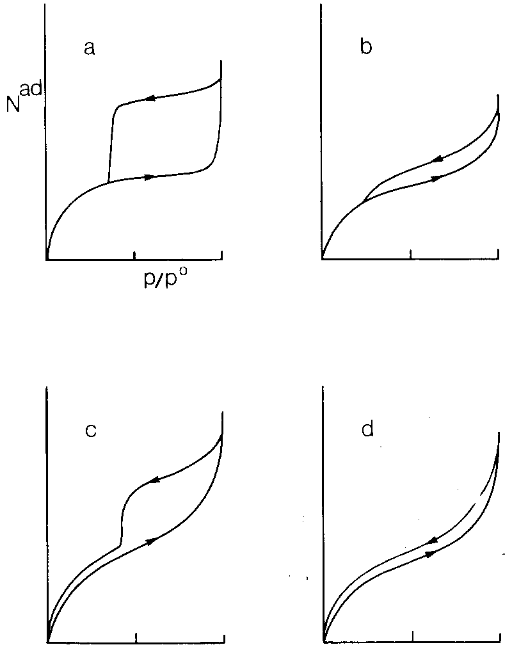

Figure 6 Four types of adsorption isotherm showing hysteresis loops (see text).

therms* at $p/p^0 \gtrsim 0.3$, referred to here as "high-pressure hysteresis", is a good indicator, but not proof, of the presence of meso- or macropores. Recently, several cases have been reported in detail [36, 38, 57–59], where complete closure of the hysteresis loop does not occur, i.e. there is "low-pressure hysteresis" (see Figs. 2 and 5 and Section 3.5), which is not thought to be associated with the larger pores. There are no easy guides for relating pore size and structure to characteristics of high-pressure hysteresis loops, although the hysteresis behaviour found with many different systems has been reviewed [60]. Fig. 6 shows schematically four types of isotherm with hysteresis loops. The large rather square-shaped high-pressure hysteresis loop in (a) is typified by the Saran–carbon powders and other macroporous solids. In (b) the behaviour is that to be expected from compacted particles of powder, or solids where the total macropore volume is relatively small. With type (c) a loop smaller than that in (a) is combined with a low-pressure hysteresis loop. Current theoretical explanations treat these two features quite distinctly: they may have a common origin due to the mode of pore formation. Type (d) is a case where low-pressure hysteresis dominates. A simple model capable of explaining many features of high-pressure hysteresis involves capillary condensation which is dealt with in Section 4.2.

3.5. Low-pressure hysteresis and dimensional changes.

A distinction is made, as far as possible, between dimensional changes occurring in the region of capillary condensation where phase transitions (e.g. freezing of adsorbate) might occur, and those changes occurring at lower adsorptive pressure ($p/p^0 \lesssim 0.3$). It has been established [61–63], that dimensional changes accompany gas and vapour adsorption, and early papers are briefly reviewed by Dacey and Evans [64]. It has only recently been established that certain aspects of dimensional changes may be associated with low-pressure hysteresis (Fig. 5), and that this hysteresis may be related to stress–strain hysteresis observed with application and release of a tensile load [57, 59].

It is thought, for example, that the failure of the high-pressure hysteresis loop in Fig. 5 to com-

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* Note that hysteresis often only occurs on desorption after a high relative pressure has been reached on adsorption, and that it may not be sufficient to go just past the p/p^0 value where closure of the loop would occur.

pletely close on desorption is due to the intercalation of adsorbate molecules in cracks (fissures) produced during adsorption. With these carbons, it is possible that morphological entities of the original polymer from which they were produced lead to carbon structures (roughly pseudomorphs) which are weakly joined. Low-pressure hysteresis has also been found with Saran carbon *fibres* [38]. The necessary conditions for observing low-pressure hysteresis are not yet clear, but its occurrence depends on the nature of the solid (most studied have been carbons (e.g. [57, 59]), porous glasses [36] and minerals such as montmorillonites [65–67]), the nature of the adsorbate, and the temperature of adsorption.

Extension isotherms can be obtained by relating dimensional changes at a particular temperature to the adsorption isotherm. They are usually given in the form of fractional extension $\Delta L/L$ or volume change $\Delta V/V$ as a function of amount adsorbed. The reported behaviour found in this manner has not always been consistent among different workers, but a broad picture is emerging. There is sometimes an initial decrease in a linear dimension or in volume as shown for water on a carbon in Fig. 7 [64]. The decrease is invariably followed by a much larger increase in size as the adsorptive pressure is increased. With water on porous glass [36], a broad maximum in length change occurred at $p/p^0 \simeq 0.45$, i.e. in the neighbourhood of the near-closure of the high-pressure hysteresis loop associated with this system. The length increased even more with p/p^0 near unity, reaching a fractional extension of the order of 0.2%. Extension isotherms also exhibit hysteresis – $\Delta L/L$ for desorption is less than its value on adsorption, down to $p/p^0 \simeq 0.45$, and including a minimum in $\Delta L/L$, with the value of $\Delta L/L$ at this minimum even becoming negative, as shown schematically in Fig. 8. Furthermore, in the region where low-pressure hysteresis occurs with the vapour adsorption isotherm, adsorption and desorption branches of the *extension* isotherm cross over, i.e. the extension at low p/p^0 on desorption is greater than on adsorption.

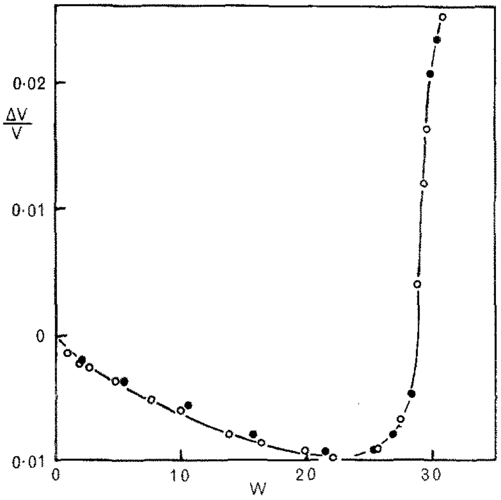

Figure 7 Dependence of percentage volume change, $\Delta V/V$, on amount adsorbed W, for water on a Saran carbon at 25° C. (Based on data used in [64].)

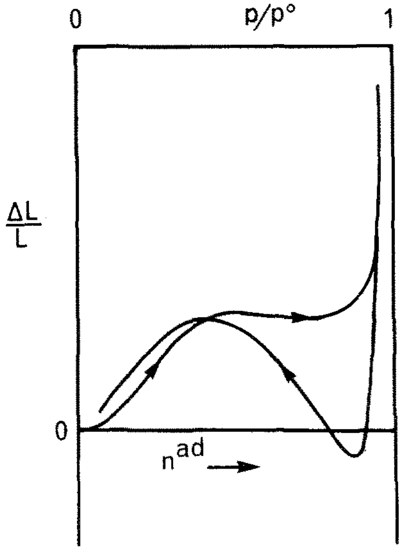

Figure 8 Schematic representation of linear dimension changes for water vapour adsorbed on porous glass. See text and [36] for explanation.

These findings are in accord with observations with montmorillonites [65], that polar but not non-polar adsorbates become irreversibly intercalated between layers in crystallites of these solids, and that even so a threshold value of p/p^0 must be exceeded before intercalation can occur. With the Saran carbons [38] it has been found that thermal annealing under vacuum is necessary before they return to their original state. When such annealing is not carried out, a second adsorption isotherm begins by following the desorption branch of the previous one, as shown in Fig. 5. Such behaviour is similar to stress–strain hysteresis when conditions (e.g. time, temperature) between cycles do not permit recovery from the irreversible dissipation of free energy accompanying the first hysteresis loop.

A distinction can be drawn between intercalation involving essentially physical forces, and the more extreme kinds of chemical intercalation which are possible with many solids including clay minerals and graphite [68, 69]. The effects of the presence of pores on the chemical reactions of solids, which are particularly studied in connection with heterogeneous catalysis, do not feature in this review. The Proceedings of International Symposia on the Reactivity of Solids (e.g. [70]), provide a useful introduction to these aspects.

4. Capillary phenomena

4.1. Basic considerations

Quite generally, systems where curved interfaces between two fluid phases are important can be termed capillary systems. Often a solid, which partially determines the geometrical configuration of the fluid/fluid interface, is also present, and of particular interest here are cases where the interface is within the pores of the solid. The fluids are generally considered to have properties approximating those of their bulk counterparts, but additionally, several thermodynamic quantities arise which are not of interest in bulk systems. The fluid α/fluid β interface will be in tension, and will be characterized by a measurable quantity, the interfacial tension $\gamma^{\alpha\beta}$. The interfacial tension can be regarded as the force acting on a line of unit length within the interface, or as the change in Helmholtz free energy F of the system accompanying a change in the interfacial area $A^{\alpha\beta}$:

$$\gamma^{\alpha\beta} = (\partial F/\partial A^{\alpha\beta})_{T,V,n_j}, \qquad (3)$$

at constant temperature, volume and composition.

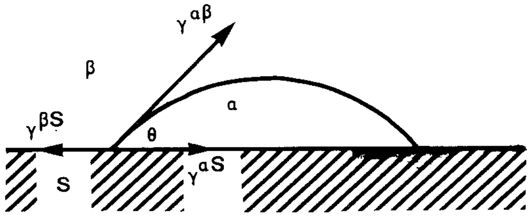

Figure 9 Sessile drop of liquid α on a plane solid surface, showing the contact angle θ and indicating interfacial tensions.

Likewise, but not readily measurable, there are interfacial tensions $\gamma^{\alpha s}$ and $\gamma^{\beta s}$ for the solid and the two fluids [71]. The phases α, β, and solid s meet at a three-phase line. The equilibrium conditions for a drop of, say, fluid α on a plane solid with contact angle θ, shown in Fig. 9, is given by Young's equation

$$\gamma^{\beta s} = \gamma^{\alpha s} + \gamma^{\alpha\beta}\cos\theta. \qquad (4)$$

The contact angle can show hysteresis behaviour, by giving two extreme values θ_a and θ_r (as well as intermediate values) depending on whether it has arisen from an interface which is advancing or receding over the solid surface [72]. There are two other major features to note about curved interfaces between fluids. There will be a difference, $\Delta p = p^\alpha - p^\beta$, in hydrostatic pressures across an interface between phases α and β, given by the Laplace equation:

$$\Delta p = J\gamma^{\alpha\beta}, \qquad (5)$$

where J is the mean curvature of the interface. With fluids within pores, neglect of gravitational effects is often quite justified, and fluid interfaces will have constant mean curvatures. A slight digression explains these terms.

The mean curvature J at a point on an interface can be defined [73] as:

$$J = \frac{1}{R_1} + \frac{1}{R_2}, \qquad (6)$$

where R_1 and R_2 are the principal radii of curvature at that point. Broadly three situations are encountered in practice when dealing with capillary surfaces: (a) is that largely discussed in this paper where interfaces are assumed to have simple configurations, e.g. spherical or cylindrical; (b) is where analytical mathematical expressions can be found involving elliptic integrals to describe the configurations of surfaces where J is everywhere constant*; and in case (c) where gravity is important, numerical computation or approximate expressions must be used [73]. The gravity-free condition can be met by having fluids α and β of comparable densities, or by having interfaces of small extent.

It is seen that the mean curvature occurs in the Laplace equation and in the Kelvin equation (below). The spherical-capped interface in the cylindrical pore of Fig. 10a leads to Equation 7, and the cylindrical situation in Fig. 10b, where one radius is now infinite, leads to Equation 9.

To be carefully distinguished from hydrostatic

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* There is a class of axially symmetrical figures of revolution on each of whose surfaces J is constant. They are the circle, the cylinder, the unduloid, the nodoid and the catenoid.

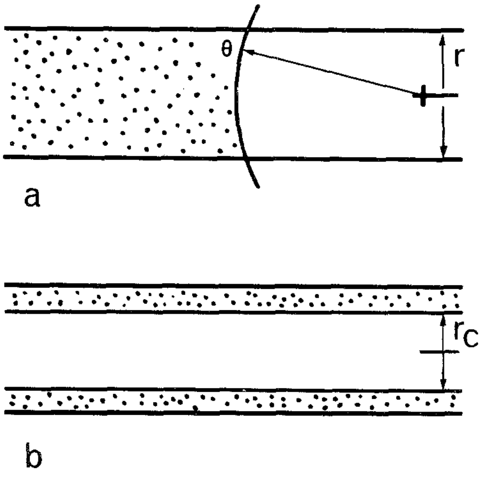

Figure 10 The mean interfacial curvature J occurring in the Laplace and the Kelvin equations is given by: (a) $J = (2/r)\cos\theta$ and (b) $J = r_c^{-1}$.

pressure effects, are effects of curvature on vapour pressures above liquid surfaces. The vapour pressure of a liquid will be increased relative to that above a plane surface at the same temperature if the surface is convex towards the vapour phase, and it will be decreased if the surface is concave towards the vapour. The appropriate equation is that of Kelvin,

$$RT\ln(p/p^0) = \frac{2v\gamma^{lg}}{r}\cos\theta, \qquad (7)$$

where $(2\cos\theta)/r$ is the mean interfacial curvature. According to this equation, for constant γ^{lg} and θ, a value of p/p^0 will have a value of r associated with it.

It is not possible here to survey the field of capillarity, but it may help the reader to realize that studies can be broadly organized so as to recognize the following factors. It may be possible to focus attention separately, in a thermodynamic sense, on Laplace-related phenomena, and on Kelvin-related phenomena. Then in either case, to concern oneself firstly with conditions for equilibrium in the system, and then with the stability of that equilibrium.

Invariably analyses of capillary-related phenomena involve interfacial areas, and in this connection, a development concerns what has become known as the effective area, defined as:

$$A^{eff} = A^{lg} - A^{sl}\cos\theta, \qquad (8)$$

with previous superscripts for fluids replaced: $\alpha = $ g(gas), $\beta = $ l(liquid). Recent interest in A^{eff} arises from several studies [73–77], but it appears to owe its origin to Gauss [78]. Its capabilities have yet to be fully explored, although it should find increasing useage. For a change dA^{eff} in the effective area with increase in volume dV, the contribution of the surface to the free energy of the system will change by $\gamma^{lg}dA^{eff}$.

The Laplace and Kelvin equations are used to interpret physical adsorption behaviour in the region of high relative pressures, and they form bases of methods for obtaining pore-size distributions.

The study of capillarity has been stimulated by studies of the drainage of fluids from model packings of particles, e.g. random spheres [79] relevant to soils, and by attempts to find the conditions under which one fluid can be displaced by another, e.g. in secondary oil recovery [16, 80–82]. Capillary forces also play a role when compacts of particles are dried, which includes the formation of a continuous film from polymer particles during the drying of emulsion paints [83]. In addition to the direct effect of surface tension in drawing the particles together, as drying proceeds and the vapour/liquid interface becomes more curved, the pressure within the liquid decreases compared to the total gas pressure (Laplace effect) and the force tending to coalesce the particles increases.

4.2. Capillary condensation and high-pressure hysteresis

It is well established that high-pressure hysteresis (shortened to hysteresis in this section) is associated with the presence of pores in the adsorbent, and that these pores are larger than the micropores already discussed. The logicality of examining micropores and larger pores separately is strengthened by analyses [84, 85] supporting the view that the, often steep, approach to closure or near closure of the desorption branch of a hysteresis loop is a consequence of the tensile strength of the liquid-like adsorbate within the pores. By the Laplace relation, Equation 5, the pressure in the liquid will be less than that of the vapour and this difference increases as the meniscus passes to pores of decreasing radius with decrease in p/p^0. The value of p/p^0 at loop closure (in the absence of low-pressure hysteresis) will therefore largely depend on the adsorbate species, being about 0.3 for benzene.

Fig. 11a to d shows highly schematically, four

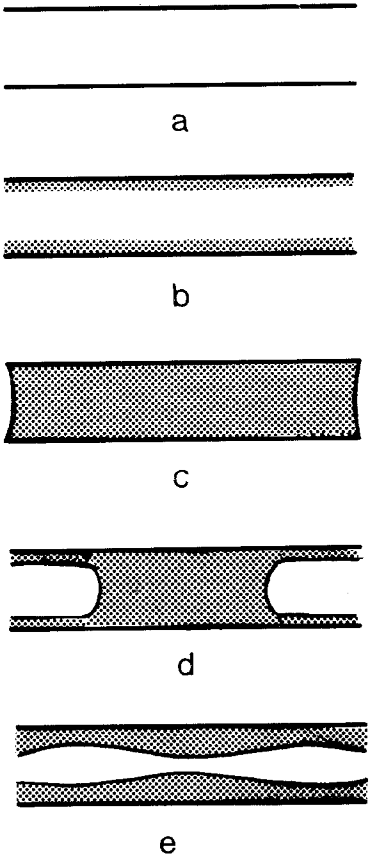

Figure 11 Schematic representation of stages of adsorption and desorption in cylindrical pores showing capillary condensation.

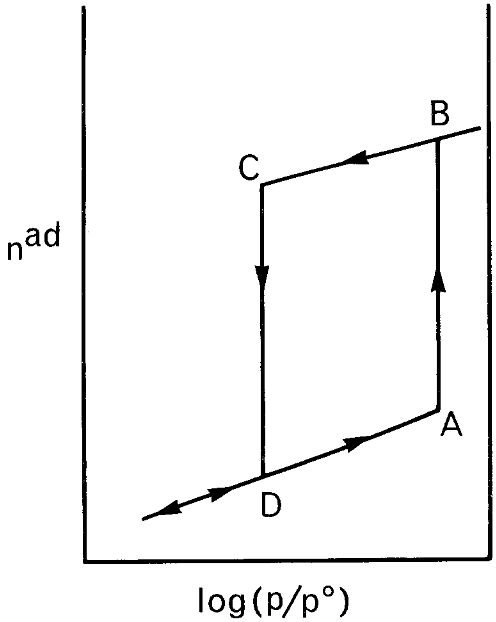

Figure 12 Idealized isotherm with high-pressure hysteresis – see text and Fig. 11.

stages which might occur during adsorption and subsequent desorption with a cylindrical pore. In (a) the pore is in equilibrium with vapour at low p/p^0, and there are adsorbed molecules on the pore walls. In (b) is shown a situation where the adsorbed layer has become liquid-like. However, by Kelvin's relation (Equation 7), if an attempt is made to keep p/p^0 constant, the system is unstable since the mean *curvature* of the cylindircal interface within the pore increases as the amount adsorbed increases, i.e. the pore will spontaneously fill as depicted by the line AB in Fig. 12. Filling will continue from the onset of instability until a situation as shown in Fig. 11c is reached where the fluid with spherically-shaped interfaces is in stable equilibrium with the vapour phase. On reducing p/p^0, desorption will become spontaneous (CD in Fig. 12) as soon as the radius of the interface equals that of the pore, as is shown to be so in the emptying pore in Fig. 11d. Fig. 11e shows that the adsorbate might undulate in the pores [86]; the pattern of events remains broadly that described, but more sophisticated treatments [74] recognize the roles of both Laplace and Kelvin instabilities in capillary condensation.

Cohan [87, 88] used what was essentially a proposal by Foster [89, 90] to explain hysteresis in simple fashion, with a cylindrical interface on adsorption and a hemispherical interface on desorption. For the cylindrical interface of radius r, the other radius of curvature is infinite, so Kelvin's general relation (Equation 7), can be written in a form known as Cohan's equation,

$$RT \ln (p/p^0) = \frac{v\gamma^{lg}}{r_c}. \qquad (9)$$

In the case of saccate or ink-bottle pores, Kraemer [91] and McBain [92] suggested a capillary condensation scheme whereby adsorption took place in the large part of the pore, but with desorption controlled by the interface of adsorbate in the narrow entry passage into this type of pore. Other theories of hysteresis have been proposed, including Zsigmondy's theory [93] of capillary condensation with contact angle hysteresis, and explanations involving phase changes and deformation of the porous medium [94, 95].

Several conceptual problems arise in attempting to apply capillary equations to fluids in pore systems with the intention of both providing a theory of capillary condensation, and of using experimental data to gain information about pore structure. The major problems are: (a) that it is often necessary to start a theoretical analysis by assuming that a simple model pore structure is acceptable (see Nicholson and Petropoulos [96] for recent work); (b) that it is necessary to assume that thermodynamic quantities, e.g. interfacial tensions, can be assigned to interfaces of small extent (even if acceptable, $\gamma^{\alpha\beta}$ may depend on curvature and on fluid densities); and (c) that "films" of adsorbate on pore walls can be expected to be present in addition to capillary fluid bridging the walls.

In spite of these difficulties, the importance of which should not be minimized, and some of which will succumb to continued efforts, analyses of data for capillary condensation can yield useful information on pore structures, particularly when comparisons between samples are required. See the work of Cross and Haynes [97] for various analyses carried out on porous glasses subjected to several leaching procedures, and that of Scholten and co-workers [98–100] for pore structure determinations of chrysotile, garnirite [$M_3(OH)_4Si_2O_5$, M = Mg and Ni respectively] and zirconia, which demonstrate the use of a variety of techniques. The materials scientist may well be in a position of having to find an acceptable compromise between carrying out experiments and analysing the data according to a crude "working model", and the more lengthy procedure of choosing and applying refinements to techniques and analyses for the kind of solid being investigated.

4.3. Mercury porosimetry and pore-size distributions

Mercury porosimetry is a technique for pore distribution measurement involving the determination of the amount of penetration of liquid mercury into pores as a function of applied pressure. The basis for determining pore-size distributions is Laplace's relation, Equation 5. For cylindrical capillaries of radius r, the pressure difference for non-wetting mercury (assumed to have a hemispherical-cap meniscus, of radius r, which is convex towards the vapour in the initially evacuated pores) will be about $2\gamma/r$. The surface tension of mercury is about $475\,\mathrm{mN\,m^{-1}}$, so the applied pressure needed to force mercury into a pore of radius $1\,\mu\mathrm{m}$ will be of the order of $1\,\mathrm{mN\,m^{-2}}$. Experimentally, it is possible to cover the nominal radius range $100\mu\mathrm{m}$ down to 5 nm. The contact angle for mercury is usually taken as about 140° – a value seemingly appropriate for carbon. Although usually employed, the model of independent cylindrical pores is a great simplification of real systems of interconnected pores. Recent reviews [15, 17, 101] cover papers dealing with attempts to surmount problems associated with porosimetry, which is usually employed to give pore-size distributions.

It will be realized that many aspects of capillarity briefly surveyed here will be relevant to impregnation treatments of porous materials by fluids (e.g. bulking of wood by *in situ* polymerization) aimed at decreasing their susceptibility to ambient changes and at modifying their physical properties. The rather complex subject of the wetting and flow of liquids into porous media is not covered here. A recent treatment [102] includes many key references, and the present author [103] has given a general review of associated topics of wetting and adhesion.

4.4. Phase changes of adsorbates in porous media

It is generally agreed on theoretical and experimental grounds that, in as far as the term is appropriate, freezing of adsorbate will occur at a temperature lower than that for the bulk liquid → solid transition. Of interest in connection with the freezing of adsorbates has been the effects of frost on porous media containing water, particularly in cements and concrete, in the biological cells of plants and freezing foodstuffs, in natural rocks (e.g. Portland stone), and in soils and road aggregates. Several extensive papers have recently been presented on cement and concrete [104–106], and it is at least clear that many factors determine susceptibility to frost damage, including transport phenomena, and the expansion of water on freezing. It is interesting to note that the pressure build up in porous media having a distribution of pore sizes can be explained thermodynamically without the need for the absorbate to increase in molar volume on freezing [14, 107, 108]. Curiously, it is known [104] that with cements, the introduction of relatively large air bubbles when the mix is still wet, affords some protection from frost damage. Porous materials can also be damaged by crystallization of dissolved solids.

In addition to the study of the nature of adsorbates by the more conventional surface chemistry techniques, their properties can be determined by heat capacity measurement [109], infra-red absorption [110] and nuclear magnetic resonance spectroscopy [111], dielectric relaxation [112], neutron scattering [113], and ultrasonic propagation [114]. There is generally much scope for the continued systematic development of the application of these techniques to problems in surface chemistry, especially with porous systems.

5. Polymeric solids

Solid polymers are briefly discussed separately because certain features of their nature have led to their having a separate literature. Indeed, compared to the amount of effort spent on non-polymeric solids, they are rarely studied by the more conventional surface chemistry techniques described earlier. Polymers as prepared in powdered form by emulsion, heterogeneous or suspension polymerization, or as precipitated from solution, can have appreciable surface areas. Examples include polyacrylonitrile, and poly(vinylidene chloride) or Saran [41]. The pore structure of these polymers is associated with gaps between basic morphological units (e.g. "platelets") of which the particles are composed. Hall and Stoeckli [115], have reported studies of gases and vapours on polymers (see citations also). Polymers have low-energy surfaces [25], and are not readily wetted, so their behaviour in the presence of liquids and even vapours can be expected to differ from that of inorganic solids (oxides or minerals).

The permeability to gases, vapours and liquids of solid polymers often arises from activated diffusion [116, 117], i.e. in the usual sense, pore structure is absent, but, depending on the species of polymer and small molecule, penetration of the polymer may occur. The temperature of the polymer, and especially whether it is above or below its glass-transition temperature, also greatly affects permeability which has certain features in common with solubility. In addition, permeability of a polymer may greatly depend on whether it contains additives, e.g. plasticizers. The importance of the penetration of polymers by small molecules should not be overlooked. It plays a role in plasticization and dyeing, and can lead to swelling. Small species, e.g. stabilizers and lubricants, can also bleed out or be leached out during polymer useage, and it should be feasible to effect controlled lubrication of moving parts by bleeding from a polymeric component. The degree of control of polymer properties makes it possible to use them as permeable, semi-permeable or permeoselective membranes. It is not at all clear whether in any cases the lubricant or plasticizer in a polymeric solid can be regarded as capillary-held fluid, susceptible to movement (thermodynamic instability) if interfacial tensions change during useage, e.g. on contact with an external fluid. Phenomena associated with polymeric membranes, such as reverse osmosis, have yet to be satisfactorily explained.

6. Miscellaneous topics

It is intended that readers will find an introduction to areas of science with which they might not otherwise easily become acquainted. Many aspects have been omitted, and to redress the balance, some of these are briefly mentioned.

Little mention has been made of electron microscopy which can be used to study pore structure, since the technique at least will no doubt be familiar to the reader. Much more systematic work, rather than *ad hoc* efforts, is highly desirable on porous solids. Note that Saran carbon fibres would provide a good test of technique, since the pores occupy about 30% of the visible solid, yet they are mostly less than 1 nm in width, and the mean thickness of the carbon walls is of this order. Use can also be made of impregnation (e.g. by molten silver) followed by sectioning and microscopic or radiographic examination of the specimen [118, 119]. Quantitative stereology [120, 121] – the study of two-phase three-dimensional objects from sections using statistical correlations – might receive more attention than at present.

Sintering is usually associated with inorganic solids and metals, but it (or an analogous process) can occur with polymers [40, 41]. Aspects of the surface chemistry of sintering have been reviewed by Gregg [22]. In addition to surface forces playing a role in sintering, it is noted that techniques previously described can be used to monitor structural (morphological) changes, including changes in surface area and pore sizes and shapes, at various stages during sintering. The scope of the subject can be judged from the Proceedings of International Congresses on Sintering (e.g. [122, 123]), and from *Powder Metallurgy*.

The flow of gases, vapours and liquids through porous media is outside the scope of this article. Among standard works are those of Barrer [124], Carman [125], Collins [126], and Scheidegger [127]. A review symposium has recently been held [10], and Barrer [128] has reviewed certain aspects.

The flow of liquids over electrically charged surfaces which would generally be found with aqueous media, since charge can be acquired by preferential dissolution of ions, by adsorption, or by ionization, gives rise to electrokinetic phenomena [129]. When the liquid is forced to flow over the solid, an electrical potential, the streaming potential, develops, and if the liquid movement is due to an applied field, electro-osmosis occurs. With rising damp it is possible that capillary forces are responsible for part of the liquid rise, but that the presence of dissolved salts in the water plays a role and may lead to electrokinetic effects [130, 131]. The deposition of salts carried in the capillary fluid is termed efflorescence (the results are often seen on exterior brick surfaces). It is noted that the properties of capillary fluids containing solute, although not thoroughly studied, may be significantly different from those of pure liquids, as can be judged from the thermodynamics of solution droplets in clouds [132].

In an introductory review of this kind, it is necessary to leave the reader with the view that many of the problems one encounters with a particular solid are likely to recur in connection with others. It is very difficult to be explicit about any porous solid – see detailed review of recent work [133]. The reader must decide if the present state of knowledge as he finds it is at a level sufficient for his purposes. That increased understanding can come from further efforts is evident in the publications of the Prague RILEM/IUPAC meeting [12].

For simplicity at the expense of scholarly accuracy (but at the risk of ultimately being confusing), equations have been attributed to one person. A case has been made that the Laplace relation (Equation 5), should be the Young and Laplace equation [134]. It would perhaps be more accurate to ascribe the equation to Laplace, and the principle to both Young and Laplace, since it is not clear to what extent each was aware of the others work at the time. Interestingly the National Biography [135] emphasizes Young's work on the notion of a definite contact angle, usually referred to as Laplace's second law of capillarity. Young's relation (Equation 4), might well be called the Young and Dupré equation [136]. The Lord Kelvin responsible for Equation 7, (see history of the equation by Skinner and Sambles [137], was originally William Thomson, and with respect to a liquid droplet, the relation

$$RT \ln (p/p^0) = \frac{2\gamma^{\alpha\beta} v^\alpha}{r}, \qquad (10)$$

is usually called the Gibbs–Thomson equation, since it was derived by Gibbs [138]. It should not be confused with the modification by J.J. Thomson for the melting point T_r of a small crystal compared to that, T_∞, of a large one

$$\frac{T_\infty - T_r}{T_\infty} = \frac{2\gamma^{\alpha\beta} v^\alpha}{r \Delta_f h}, \qquad (11)$$

where v^α is now the molar volume of the crystalline substance, and $\Delta_f h$ is the enthalpy of fusion (see Dunning [139]).

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