11

Swelling

11.1 Introduction

11.1.1 Technical significance

When fibres absorb water, they change in dimensions, swelling transversely and axially. This has technical consequences in the dimensional stability of fabrics, the predominant transverse swelling usually resulting in a shrinkage of twisted or interlaced structures. It also means that the pores of closely woven fabrics will be completely blocked when the fibres are swollen, and they may then be impermeable to water. This principle is utilised in hosepipe materials and the *Ventile* fabrics, which were developed in the 1940s for showerproof garments. Swelling is also an important factor in crêpeing, due to the increased twist angle in a swollen yarn, and in drying and dyeing.

Swelling is akin to solution in that there is an interchange of position between fibre molecules and water molecules, but in swelling this occurs only to a limited extent, whereas in solution it continues until there is a uniform mixture of the two substances.

11.1.2 Definitions

The swelling may be expressed in terms of the increase in diameter, area, length or volume as illustrated in Fig. 11.1. This leads to the following quantities:

transverse diameter swelling = fractional increase in diameter

$$= S_D = \frac{\Delta D}{D} \tag{11.1}$$

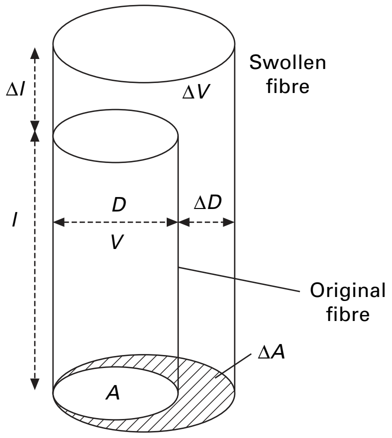
transverse area swelling = fractional increase in area of cross-section

$$= S_A = \frac{\Delta A}{A} \tag{11.2}$$

axial swelling = fractional increase in length $= S_l = \frac{\Delta l}{l}$ (11.3)

volume swelling = fractional increase in volume $= S_v = \frac{\Delta V}{V}$ (11.4)

In practice, these quantities are often expressed as percentages rather than fractions.



11.1 Changes in fibre dimensions on swelling.

Relations between them reduce the number of independent parameters to two, though these relations may be affected by the fibre shape. For instance, in a fibre that is uniform along its length, we have

$$V = Al \tag{11.5}$$

$$V + \Delta V = (A + \Delta A)\,(l + \Delta l) \tag{11.6}$$

$$S_{\mathrm{v}} = \frac{\Delta V}{V} = \left(\frac{A + \Delta Al}{Al}\right) = \frac{\Delta l}{l} + \frac{\Delta A}{A} + \frac{\Delta A \Delta l}{Al} = S_1 + S_{\mathrm{A}} + S_1 S_{\mathrm{A}} \tag{11.7}$$

where V = volume, A = area of cross-section and l = length.

It can be similarly shown that, for a fibre of circular cross-section

$$S_{\mathrm{A}} = 2S_{\mathrm{D}} + S_{\mathrm{D}}^2 \tag{11.8}$$

Another quantity that is a useful expression of the swelling behaviour is the swelling anisotropy = $K = S_{\mathrm{D}}/S_1$. This is related to the orientation of the molecules in the fibre, which cause it to range from infinity for a perfectly oriented arrangement, with no length swelling, to unity for a completely random one.

11.2 Measurement of swelling

11.2.1 Volume swelling

If we consider a specimen of mass 1 g when dry, we have

$$V = \frac{1}{\rho_0} \tag{11.9}$$

$$V + \Delta V = \frac{1 + m}{\rho_{\mathrm{s}}} = \frac{1 + r/100}{\rho_{\mathrm{s}}} \tag{11.10}$$

where ρ_0 = density when dry, ρ_{s} = density when swollen, m = mass of water absorbed, and r = regain %. Hence:

$$S_v = \frac{\Delta V}{V} = \frac{\left(\dfrac{1 + r/100}{\rho_s - 1/\rho_0}\right)}{1/\rho_0} = \frac{\rho_0}{\rho_s} \Big/ \left(\frac{1 + r}{100}\right) - 1 \tag{11.11}$$

Thus the volume swelling may be found from measurements of density (by using the methods described in Section 5.2) and regain.

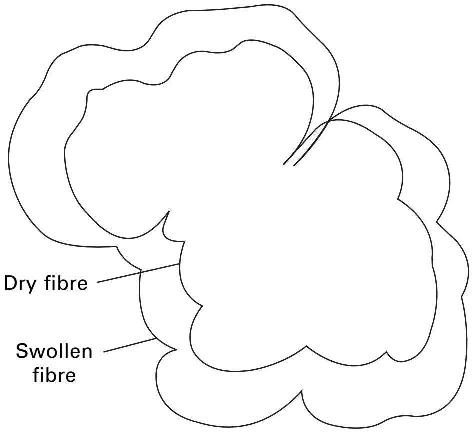
11.2.2 Axial swelling

The axial swelling of a continuous filament may be found by hanging up a length under a low tension and measuring the change in length with a cathetometer or some form of extension gauge. Observations of the change in length of short fibres may be made with a travelling microscope by using the procedure described by White and Stam [1].

11.2.3 Transverse swelling

Because fibres have such a small diameter, measurements of changes in transverse dimensions are not easy to make. The accuracy of a microscopical method is limited by the resolution of the microscope, which is of the order of magnitude of the wavelength of light used, say, 0.5 µm. If a fibre of 20 µm diameter is examined, it will be possible to distinguish detail down to one-fortieth of the fibre diameter, but, if the diameter swelling is 10%, it will be possible to measure this to an accuracy of only 0.5 in 2. This means that there may be an error of 25%.

However, microscopy methods are used, either for examining the fibre profile and measuring the apparent diameter or for examining sections and measuring the diameter, or the area of cross-section, with a planimeter. Figure 11.2 shows the outlines of a viscose rayon fibre, swollen and unswollen, as observed by Morehead [2]. This



11.2 Outlines of cross-section of viscose rayon filament, dry and swollen in water. After Morehead [2].

makes clear the fact that diameter swelling is not a sound way of expressing the transverse swelling of a fibre with an irregular cross-section, since it will vary according to the position in which the 'diameter' is drawn. For irregular fibres, area swelling must be used.

Denton [3] has described an optical-interference method, and other workers have measured the change in air-flow along a tube containing a fibre [4] or the conductance in a tube with the fibre surrounded by a conducting liquid [5].

11.2.4 Digital imaging

The use of modern digital imaging, as described for fibre diameter and length measurements in Sections 3.7.1 and 4.11.2 would simplify the measurement of both axial and transverse swelling.

11.3 Results

11.3.1 The swelling of fibres in water

Table 11.1 gives a collection of values of swelling observed by several workers when fibres are immersed in water. It is immediately obvious that there are considerable discrepancies in the values of a given quantity obtained by different people. There are also several cases in which the relations between the results are widely different from equations (11.7) and (11.8). To some extent, these divergencies are a reflection of experimental difficulties, but there will also be real differences between different specimens of a given type of fibre.

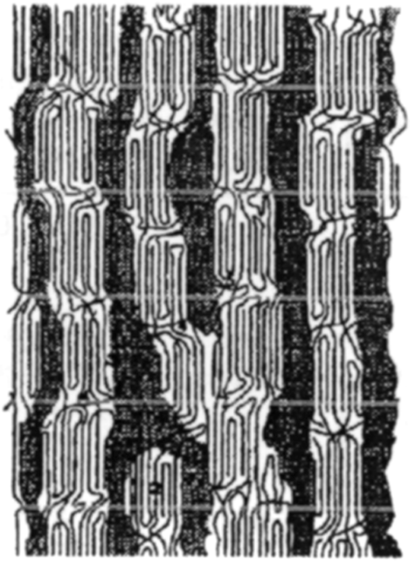
As would be expected, the values of volume swelling vary between different fibres in much the same way as values of regain: those fibres that absorb most water swell to the greatest extent.

Most moisture-absorbing fibres show a large transverse swelling, with a smaller axial swelling, so that the swelling anisotropy is high.

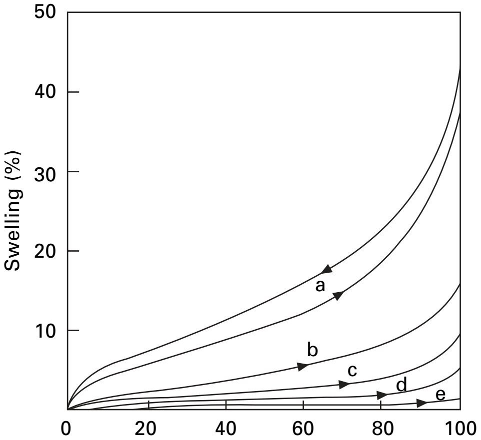
Table 11.1 Swelling of fibres in water. Values reported by various authors, collected by Preston and Nimkar [6]

Fibre	Transverse swelling (%)		Axial swelling (%)	Volume swelling (%)
	Diameter	Area		
Cotton	20, 23, 7	40, 42, 21		
Mercerised cotton	17	46, 24	0.1	
Flax		47	0.1, 0.2	
Jute	20, 21	40		
Viscose rayon	25, 35, 52	50, 65, 67, 66, 113, 114	3.7, 4.8	109, 117, 115, 119, 123,126, 74, 122, 127
Acetate	9, 11, 14	6, 8	0.1, 0.3	
Wool	14, 8, 17	25, 26		36, 37, 41
Silk	16.5, 16.3, 18.7	19	1.6, 1.3	30, 32
Nylon	1.9, 2.6	1.6, 3.2	2.7, 2.9	8.1, 11.0

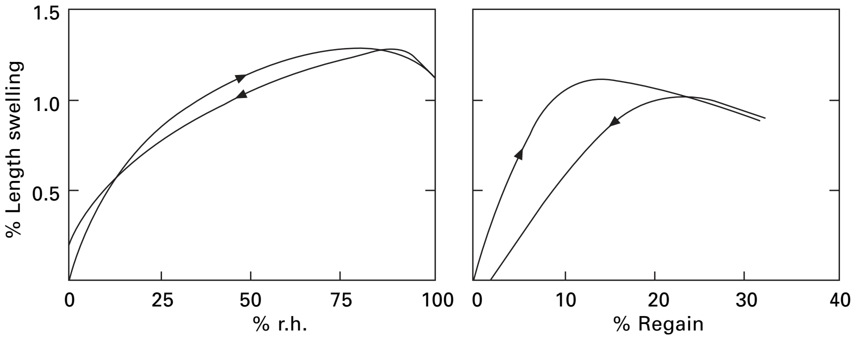
Nylon is exceptional in having a value of the anisotropy that is close to or less than unity. There has been some controversy about the cause of this; it has been suggested that the nylon fibre is surrounded by a skin or sheath, which restricts the transverse swelling. However, it is more likely that it results from the micellar form shown in Fig. 11.3. The swelling of amorphous regions between crystallites in the quasi-fibrils will have a larger effect than the swelling between the fibrils. An interesting consequence of the axial swelling is that carpet tiles expand when humidity increases and this leads to buckling [8].



11.3 Micellar structure of nylon, as proposed by Murthy *et al.* [7].



11.4 Swelling of fibres between dryness and saturation: a, cotton, area swelling in absorption and desorption [9]; b, wool, diameter swelling [4]; c, nylon, area swelling [10]; d, nylon, diameter swelling [10]; e cotton, length swelling [9].



11.5 Length changes in merino wool fibres, observed by Mackay and Downes [11]; (a) variation of length in absorption and desorption; (b) hysteresis between length change and regain.

11.3.2 Swelling at various humidities

The variation of swelling with humidity usually follows the change of regain, with hysteresis showing between swelling and humidity. Typical curves are shown in Fig. 11.4.

However, Mackay and Downes [11] found that single wool fibres can show a maximum length between 75 and 85% r.h., as in Fig. 11.5(a). This was not observed in other studies by Speakman [12], Haly [13] and Watt [14]. Mackay and Downes also found hysteresis between length swelling and regain, as shown in Figure 11.4(b); Treloar [15] found a similar result for horsehair.

11.4 References

1. H. J. White and P. B. Stam. *Text. Res. J.*, 1949, **19**, 136.
2. F. F. Morehead. *Text. Res. J.*, 1947, **17**, 96; 1952, **22**, 535.
3. P. Denton. *J. Sci. Instrum.*, 1952, **29**, 55.
4. F. L. Warburton. *J. Text. Inst.*, 1947, **38**, T65.
5. J. M. Preston. *Trans. Faraday Soc.*, 1946, **42B**, 131.
6. J. M. Preston and M. V. Nimkar. *J. Text. Inst.*, 1949, **40**, P674.
7. N. S. Murthy, A. C. Reimschussel and V. J. Kramer, *J. Appl. Polymer Sci.*, 1990, **40** 249.
8. E Tan. PhD thesis, University of Manchester, 1970.
9. G. E. Collins. *J. Text. Inst.*, 1930, **21**, T311.
10. J. B. Speakman and A. K. Saville. *J. Text. Inst.*, 1946, **37**, P271.
11. B. H. Mackay and J. G. Downes. *J. Text. Inst.*, 1969, **60**, 378.
12. J. B. Speakman. *Trans. Faraday Soc.*, 1929, **25**, 92.
13. A. R. Haly. *Text. Res. J.*, 1961, **31**, 189.
14. I. C. Watt. *Text. Res. J.*, 1965, **35**, 1072.
15. L. R. G. Treloar. *Trans. Faraday Soc.*, 1952, **48**, 567.

12

Theories of moisture sorption

12.1 The general view

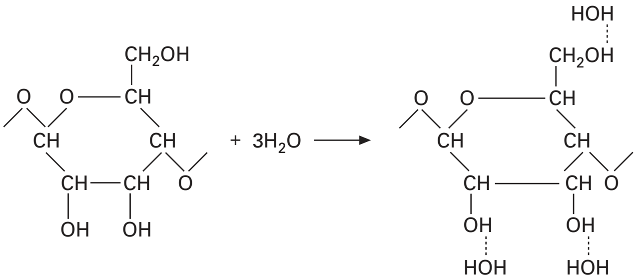
12.1.1 Introduction

Adsorption in a non-swelling medium, for example, the adsorption of gases on charcoal, is a comparatively simple process, and so is the solution of one substance in another, for example the solution of sugar in water, but the absorption of water by fibres is an example of a process that comes midway between these two and partakes of some features of each. It encompasses not only the relation between regain and humidity but also associated phenomena, such as hysteresis, heat effects, the variation of regain with temperature, the influence of moisture on physical properties, and all the complicated factors arising from the interaction of moisture and mechanical effects owing to the limited swelling of fibres. All this cannot be explained by a single theory. A general qualitative view of the whole subject shows the action of several mechanisms of absorption, and there are quantitative theories associated with every possible mechanism. These theories shed light on the subject from a variety of points of view, and a quantitative understanding of the whole process must be built up from them. Although some of the ideas are conflicting, they are mainly complementary to one another.

In this chapter, we shall first give a broad description of the way in which water is absorbed and then go on to discuss some particular theories. For convenience, the theories will usually be discussed in terms of the particular type of fibre for which they were first proposed, but the ideas will usually be applicable to other fibres as well.

12.1.2 The effect of hydrophilic groups

In considering absorption, we must take account of the interaction between the water molecules and the molecules of the fibre substance. All the natural animal and vegetable fibres (and the fibres regenerated from natural materials) have groups in their molecules that attract water: indeed, this is probably a necessary result of the fact that the molecules were first formed in the presence of water. For example, the cellulose molecule contains three hydroxyl groups for each glucose residue, and hydrogen bonds can be formed between water molecules and the hydroxyl groups (see Fig. 12.1).



12.1 Absorption of water by hydrogen bonding to hydroxyl groups in a cellulose molecule.

The molecular weight of water is 18, and that of the glucose residue is 162, so that if one water molecule were attached to each hydroxyl group the regain would be 33.1%. In fact, as is discussed in later sections, not all the hydroxyl groups are involved, and there may be more than one water molecule per hydroxyl group.

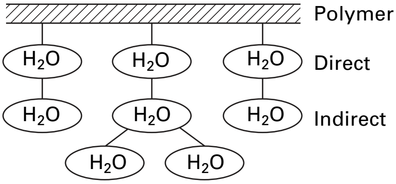
In cellulose acetate, all or most of the hydroxyl groups have been replaced by the comparatively inert acetyl ($CH_3 \cdot COO$—) groups. These groups do not attract water strongly, so the absorption of water by acetate is low. In particular, there is no rapid rise at low humidities owing to the initial absorption on strongly attractive groups.

The protein fibres contain amide groups (—NH—) in the main chain, to which water can be hydrogen bonded, and other water-attracting groups such as —OH, —NH_3^+, —COO^-, —$CO \cdot NH_2$, in the side chains. Wool contains many active groups in the side chains, but silk contains only a few. By blocking off certain groups, Watt and Leeder [1] have attempted to divide up the water absorbed by wool according to the various amino-acid residues responsible.

All the synthetic fibres so far produced contain few if any water-attractive groups, and this accounts for their low moisture absorption. The polyamide fibres, nylon 6.6 and 6 and aramids, contain one amide (—NH—) group for every six carbon atoms in the chain, which would give a regain of 16% of each amide group held one water molecule. The polyester fibres, polyethylene terephthalate, are composed only of benzene rings, —CH_2— groups, and —CO·O— groups, none of which attracts water strongly. Polyethylene is simply a -CH_2-chain, polypropylene has additional –CH_3 side groups, and the vinyl fibres are similar except for the substitution of —Cl, —$O \cdot CO \cdot CH_3$, or other comparatively inert groups for some of the hydrogen atoms, and consequently these fibres absorb little water. Acrylic fibres, containing —CN groups and other groups from the minor components, absorb slightly more than the other vinyl fibres, and polyvinyl alcohol, containing some —OH groups, absorbs still more. Inorganic fibres, including carbon, do not attract water absorption.

12.1.3 Directly and indirectly attached water

The first water molecules must be absorbed directly onto the hydrophilic groups, but, there is a choice for those absorbed after the first. They may be attracted to other hydrophilic groups, or they may form further layers on top of the water molecules already absorbed. The resulting effect is illustrated in Fig. 12.2.



12.2 Direct and indirect absorption of water molecules by a polymer molecule.

The directly attached water molecules will be firmly fixed, fitting closely to the structure of the molecules. They will be limited in their movement. The indirectly attached water molecules will be more loosely held. Their arrangement is uncertain, but the dielectric properties of fibres (see Section 21.5) suggest that they are not as free as the molecules in liquid water and are probably restrained to about the same extent as the water molecules in ice. This is not incompatible with values of the heat of sorption (see Section 8.3), which for most fibres at 50% r.h. are of the order of magnitude of the latent heat of freezing of water (330 J/g). At high humidities, the heat of sorption falls to about half the value of the latent heat. It may also be noted that Kolkmeyer and Heyn [2] observed lines characteristic of ice in the X-ray diffraction pattern of cellulose. Nuclear magnetic resonance (NMR) studies on keratin by Lynch and Marsden [3] suggest a more complicated situation, with relaxation times one-thousandth of those for water molecules in ice, but 100 times as long as those in the liquid state.

Quantitative estimates of the division between the two types of absorbed water are given in Section 12.2. Boesen [4] reviewed the evidence on the amount of directly bound water in cellulose.

12.1.4 Absorption in crystalline and non-crystalline regions

In crystalline regions, the fibre molecules are closely packed together in a regular pattern. The active groups form crosslinks between the molecules, for example by hydrogen bonding in cellulose and keratin. Thus it will not be easy for water molecules to penetrate into a crystalline region, and, for absorption to take place, the active groups would have to be freed by the breaking of crosslinks.

In native cellulose, with the crystalline arrangement known as cellulose I, the X-ray diffraction pattern is unchanged during the absorption of water by the fibre, which indicates that no water is absorbed in the crystalline regions. In regenerated cellulose, with a slightly less compact crystal structure known as cellulose II, there is a change of crystal structure on absorption. This is due to the formation of a hydrate, which probably contains one water molecule to every three glucose residues. This would correspond to a regain of about 3.7% in the crystalline region (about 1% regain in the whole fibre). When the regenerated cellulose is wet, there is a further modification of the crystal structure owing to the formation of a hydrate with about three water molecules to every two glucose residues.

The material easily accessible to moisture will be either the non-crystalline regions or the surfaces of crystalline regions. As was stated in Chapter 1, it is very difficult to separate the disorder in a fibre that is due to extensive disordered regions from that which is due to the imperfect packing of small crystallites or crystalline fibrils. It is therefore simplest, for the present discussion, to lump both categories of accessible material together as effectively non-crystalline.

It would then be expected that the regain at any particular relative humidity would be proportional to the amount of this effectively non-crystalline material. Consequently, the ratios of regain at the same relative humidity for any two cellulosic fibres should be independent of the relative humidity, that is, the curves of regain against relative humidity should be the same shape and differ only in scale. This has been proved experimentally (see Section 7.4.2). In addition, the differential heat of sorption should be the same for all cellulosic fibres at the same relative humidity, since it must be the heat evolved when 1 g of water reacts with non-crystalline cellulose. This has also been demonstrated experimentally (see Section 8.3). On the other hand, other fibres, having different absorbing substances, give curves of different shapes and have different heats of sorption.

The moisture absorption thus offers one way of estimating the effective crystalline/non-crystalline ratio in cellulosic fibres. Marsden [5] gives values of approximately 60% crystalline material for native cellulose and 25% for regenerated cellulose. Results by different methods do not agree exactly, probably because the distinction between non-crystalline and crystalline regions is not precise and different methods would have different limits. Jeffries *et al.* [6], collecting data from the literature, have values for percentage of disordered material ranging from 8 to 42% for cotton and from 20 to 77% for regenerated cellulose.

In nylon, the amount of crystalline material has been estimated to be 50–60% of the whole.

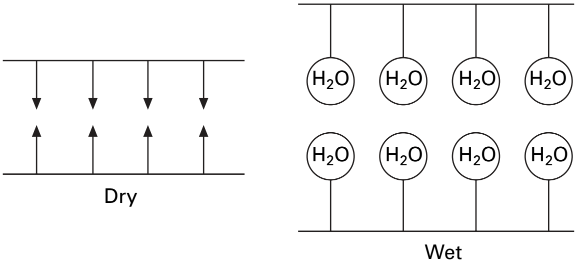
12.1.5 Hysteresis: a molecular explanation

Urquhart [7] put forward a theory of hysteresis based on molecular effects, and this has been restated, in the light of later views of cellulose structure, by Hermans [8]. In non-crystalline cellulose, there are some crosslinks, formed where molecules pass near to one another, and these crosslinks reduce the amount of absorption, both by providing mechanical restraint (the influence of which is discussed in Section 12.3) and by reducing the number of available hydroxyl groups. As absorption increases, the crosslinks will tend to be broken and replaced by water absorption on the hydroxyl groups. Thus there is the following change:

$$\begin{array}{c}\text{DRY}\\ \text{structure with}\\ \text{many crosslinks}\end{array}\quad \underset{\begin{array}{c}\scriptstyle\text{Water coming off}\\ \scriptstyle\text{crosslinks forming}\end{array}}{\overset{\begin{array}{c}\scriptstyle\text{Crosslinks breaking}\\ \scriptstyle\text{water attaching}\end{array}}{\rightleftarrows}}\quad \begin{array}{c}\text{WET}\\ \text{structure with}\\ \text{few crosslinks}\end{array}$$

Owing to the tendency of the structure to remain unchanged, there will be a hysteresis in the breaking and re-forming of crosslinks, and consequently in the moisture absorption.

In the more highly ordered, fibrillar, natural cellulose fibres, the crosslinks and



12.3 Schematic view of dry and wet structures.

water attachment will be between and on the surfaces of the fibrils. Figure 12.3 can thus be regarded as showing a small part of these surfaces.

The structure in extensive non-crystalline regions is a three-dimensional network and is more difficult to visualise. However, the two-dimensional analogy (which must not be taken too literally) shown in Fig. 12.3 may be used to lead to an understanding of what happens. The figure shows a dry structure with crosslinks and a wet structure with water absorption. Suppose that the two structures are both put in the same atmosphere. Owing to the natural energy of the system, causing the continual motion of atoms and molecules, active groups will at intervals become free because of the breaking of crosslinks or the evaporation of water. A free active group will not remain free indefinitely, since either a water molecule will be absorbed on it or a crosslink will form. If these two possibilities are considered independently, the chance of water absorption depends on the number and velocity of the water molecules present in the atmosphere, and this is the same in both cases. The chance of a crosslink forming depends on the nearness of another active group. It is thus more likely to occur in the dry structure, where the other crosslinks are holding the molecules close together, than in the wet structure, where the molecules are far apart. Consequently, when the two possibilities are in competition, the net chance of water absorption is greater in the wet structure, so there will be hysteresis in the moisture absorption.

Translating the above ideas into three-dimensional terms, we may say that the presence of other crosslinks in a dry structure tends to hold the molecules together in the network and makes crosslink formation easier than in a structure with few crosslinks. Thus an initially dry specimen will always retain a higher number of crosslinks and less water absorption than an initially wet specimen in the same atmosphere. Similar arguments apply to the fibrillar network in the natural fibres.

When cellulose is first formed in the cotton plant, it is laid down in the presence of water. This favours the absorption of water, and the resulting structure has few crosslinks, giving rise to the high primary desorption curve (see Section 7.4.2). Once it has been dried below a certain humidity, crosslinks will form. Some of these will remain permanently and prevent such high regains from being obtained again. Heating a fibre wet is also a process that favours moisture absorption, destroys crosslinks, and gives rise to a high primary-desorption curve. On the other hand, heating a substance dry increases the number of crosslinks and lowers the curve of regain against relative humidity.

12.1.6 Limited swelling

Although glucose and cellulose are chemically very similar, they behave differently when placed in water. Glucose dissolves, but cellulose swells to only a limited extent. The limited swelling is due to the penetration of water into the non-crystalline regions or between fibrils and its failure to penetrate into crystalline regions. The non-crystalline regions tend to dissolve as glucose does, the cellulose molecules moving apart and so giving room for the water to enter, but the cellulose molecules cannot break away completely, since they are held firmly in the crystalline regions. The fibrils in natural cellulose fibres must also be molecularly interconnected in a way that prevents complete solution or alternatively held together in a state of dynamic equilibrium, which prevents any fibre from becoming completely free at any instant.

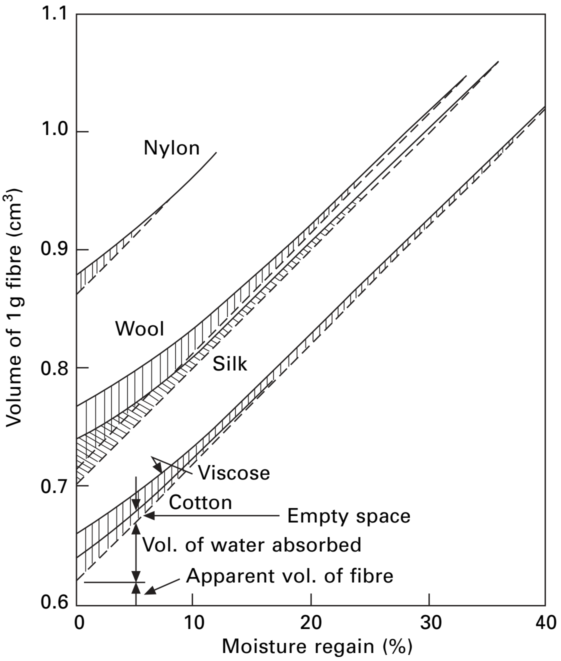
Since it is a necessary condition for the stability of fibres in water, the reason why the crystalline regions do not dissolve is worth a closer study. It is due to the cumulative action of all the active groups in forming crosslinks. Whereas in glucose, or non-crystalline cellulose, one active group can be attacked by water at a time, in order to penetrate the crystalline regions of cellulose it would be necessary to attack a large number of active groups at the same time. This is inherently unlikely to occur, since the water molecules act at random and not together. The situation may be compared to a war between irregular forces and a large army. If the army is spread out, the irregular forces can harry and destroy it by isolated raids, although they could not organise and win a single pitched battle with the army in close formation.

Swelling occurs because the fibre molecules are pushed apart by the absorbed water molecules. The resulting distortion of the fibre sets up internal stresses, which influence the moisture absorption. This aspect of the subject, which can be treated mathematically by thermodynamics, has been particularly studied by Barkas and is discussed in Section 12.3. It leads to an alternative explanation of hysteresis, for if there is mechanical hysteresis in the fibres, it must necessarily cause moisture hysteresis.

The density changes during swelling (see Section 6.3) are also of interest. Initially, as shown in Fig. 12.4, the change is such that the increase in volume is less than the volume of the added water. Apart from the improbable suggestion that the absorbed water is compressed, this must mean that the water molecules are fitted closely into the structure, with a more complete use of the space available. This is analogous to filling the spaces between tennis balls in a box with marbles. The close fitting is in accord with the view that the first water molecules are directly attached to the active groups in the fibre molecule. As absorption proceeds, the increase in volume becomes equal to the volume of water added, which indicates that the water is packed in much the same way as in liquid water or ice and is merely spreading out the polymer structure. A change in moisture content with little change in volume will again occur at high moisture contents if void spaces are filled with water by capillary sorption.

12.1.7 Capillary water

At very high humidities, liquid water may be held by the forces of surface tension in capillary spaces between fibres or in crevices in the fibre surface. The equilibrium vapour pressure, p_a over a concave curved surface of radius a is lower than that over



12.4 Change in fibre specific volume with regain. From Meredith [9].

a plane surface p_∞, owing to the surface tension of the water. This is given by Kelvin's equation:

$$\log_e \frac{p_a}{p_\infty} = -\frac{2\sigma M}{\rho R T a} \tag{12.1}$$

where σ = surface tension, M = molecular weight of water, i.e. 18, ρ = density of water, R = gas constant, and T = absolute temperature.

Now, p_∞ is equal to the saturation vapour pressure, and thus the relative humidity over the curved surface will be given by:

$$\text{relative humidity} = H = 100\left(\frac{p_a}{p_\infty}\right)\% \tag{12.2}$$

$$\log_e \frac{H}{100} = -\frac{2\sigma M}{\rho R T a} \tag{12.3}$$

For water at 20 °C,

$$a = \frac{0.47}{2 - \log_{10} H}\ \text{nm} \tag{12.4}$$

Consequently, for a specimen in an atmosphere of given relative humidity, there will be no tendency for water to evaporate from capillaries in which the radius of the water meniscus is less than that given by the above equation. At higher relative humidities, water will remain in larger capillaries, and so the regain will increase.

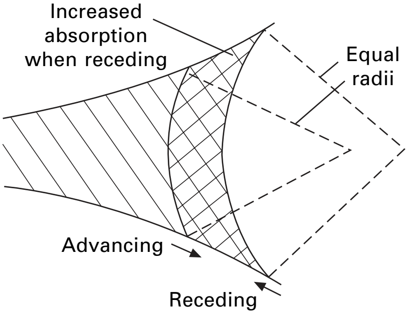
Hysteresis may be explained as being due to a change of contact angle, depending on whether the meniscus is advancing or receding. Thus a given radius of meniscus (i.e. a given relative humidity) will occur at a wider portion of the capillary when it is receding, and there will be a greater amount of water present, as shown in Fig. 12.5.

The capillary theory was, indeed, first proposed as a general explanation of moisture absorption over a wide range of humidities. It is worth examining why it is not valid in this way, apart from the fact that capillary spaces within the fibre are purely hypothetical.

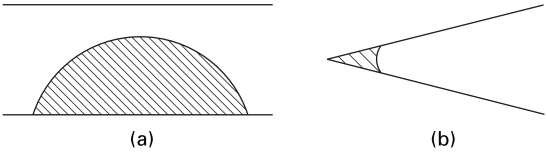
The first difficulty with the theory is that it does not explain how condensation could occur initially in an open capillary. As is shown in Fig. 12.6(a), this would have to pass through a phase in which the surface is convex and would thus be formed only in a supersaturated atmosphere. A possible answer to this difficulty is that the condensation starts at the end of a wedge-shaped capillary (Fig. 12.6(b)), where the radius would be very small and the surface concave.

The second difficulty is more important. Table 12.1 shows the radii of the menisci at various humidities, given by Equation (12.4). The diameter of a water molecule is 0.4 nm, which enables us to calculate the number of water molecules that would fit across a capillary. At 60% r.h., this is only ten, or fewer if the contact angle is greater than zero. Surface tension is, however, an average property based on summation over a large number of molecules, and thus it is not a concept that can be applied to capillaries that are only a few molecules wide. Indeed, unless there is a large number of molecules in the surface, it is not possible to define a radius of curvature.

This means that the capillary water can play a part only at very high humidities. In fact, the experimental results, discussed in Section 10.3.3, suggest that there is a



12.5 Hysteresis in capillaries.



12.6 Initial condensation in capillaries: (a) open capillary; (b) wedge-shaped capillary.

Table 12.1 Meniscus dimensions

r.h. (%)	Radius of meniscus (nm) from equation (12.4)	Diameter of meniscus / Diameter of water molecule
50	1.6	5
60	2.1	10
70	3.0	15
80	4.8	24
90	10	50
95	21	104
99	110	500
99.9	1200 (1.2 μm)	5000

significant amount of capillary water present only at relative humidities greater than 99%.

12.2 Quantitative theories of absorption

12.2.1 Mechanistic molecular theories

The calculation of the division between directly and indirectly attached water, and its relation to relative humidity, have been the subject of much theoretical speculation. These theories have been reviewed by McLaren and Rowen [10] and subjected to critical comment by various other authors [11, 12]. Some of them will be described here, but others will be mentioned only briefly. More recent reviews [13–15] relate to moisture absorption in foods.

In 1929, Peirce [16] put forward a theory which, despite arbitrary assumptions, still bears comparison with the more sophisticated theories proposed later. He first developed an argument for calculating the division between directly and indirectly attached water molecules, as follows. Let C = total number of water molecules/absorption site, C_a = number of directly absorbed water molecules/absorption site, C_b = number of indirectly absorbed water molecules/absorption site, so that

$$C = C_a + C_b \tag{12.5}$$

If C increases by dC, then the fraction of molecules directly absorbed will be proportional to the number of unoccupied sites $(1 - C_a)$:

$$\frac{\mathrm{d}C_a}{\mathrm{d}C} = q(1 - C_a) \tag{12.6}$$

where q is a factor of proportionality. Integrating, we obtain

$$-\log_e (1 - C_a) = qC \tag{12.7}$$

$$C_a = 1 - e^{-qC} \tag{12.8}$$

Peirce assumes that the constant q is equal to 1 and puts forward some arguments in support of this. It must, however, be regarded as an arbitrary assumption, which is open to criticism on the grounds that it does not correctly represent the different attractions of the vacant and covered sites. With this assumption, we have

$$C_a = 1 - e^{-C} \tag{12.9}$$

and, from equation (12.5):

$$C_b = C - 1 + e^{-C} \tag{12.10}$$

We can express C in terms of the regain of the material r since we have:

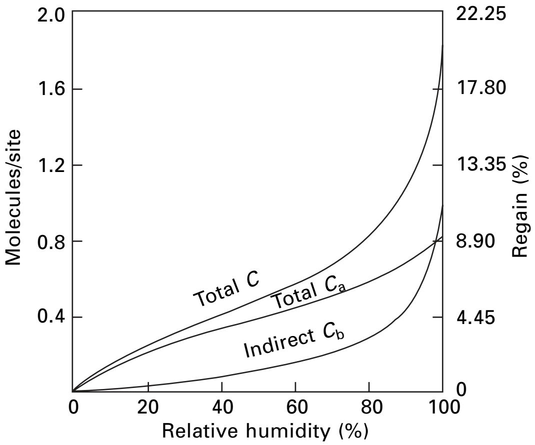
$$r = 100\left(\frac{\text{mass of absorbed water}}{\text{mass of material}}\right)\% = 100\,\frac{M_W C}{\gamma M_0} \tag{12.11}$$

where M_W = molecular weight of water = 18; M_0 = molecular weight per absorption site = 1/3 molecular weight of glucose residue = 54; γ = total mass of material/mass of absorbing (non-crystalline) material[1]. Hence

$$C = \frac{3\gamma r}{100} \tag{12.12}$$

Figure 12.7 shows the division of the experimental curve for regain against relative humidity into the two phases. This shows the combination of two curves of different shapes to give a resultant sigmoidal curve. Most of the initial absorption is directly attached, whereas the absorption at higher humidities is mainly indirectly attached.

It is the directly attached water that changes the forces between molecules and breaks crosslinks, so that it should have a greater effect than the indirectly attached



12.7 Division of regain of cotton between two phases on Peirce's theory.

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[1] In his original argument for cotton, Peirce assumed that all the material was accessible but that only one hydroxyl group per glucose residue was effective in absorption, but Hearle [17] has pointed out that, since only about one-third of the material in cotton is effectively non-crystalline and so accessible to water molecules, the same numerical result would be obtained by assuming that all the hydroxyl groups in the non-crystalline regions, but none in the crystalline regions, are effective in absorption. This also enables the analysis to be applied to other cellulosic fibres.

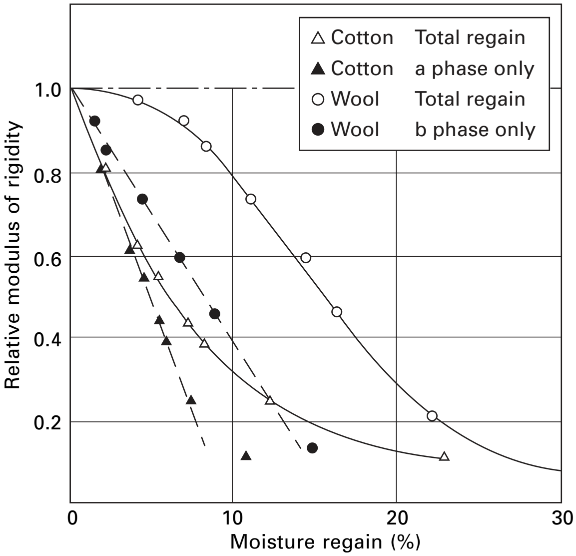
water on the physical properties of the fibre. Figure 12.8 shows a plot of relative torsional rigidity against moisture absorption that confirms this view. There is a linear relation between rigidity and C_a.

On the other hand, it will be the indirectly attached water molecules that will be the first to evaporate, so these would be expected to have the greatest effect on the vapour pressure. This enables a relation between regain and relative humidity to be calculated. Peirce assumes that only a fraction 1/β of the sites is effective in indirect absorption and that when these are filled there is saturation. The reason given for assuming that not all sites are effective is that one indirectly attached water molecule can seal off a number of sites, as in Fig. 12.9.

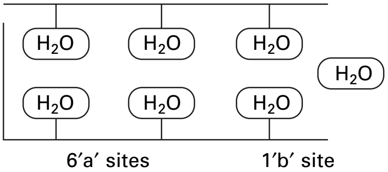
We then have:

$$\text{vapour pressure} = p = \text{saturation vapour pressure } p_0$$
$$\times \text{ fraction of these sites occupied}$$

Thus the fraction of sites occupied by one or more water molecules equals p/p_0.



12.8 Modulus of rigidity (relative to value when dry) plotted against regain.



12.9 Suggested mechanism for limitation of number of sites for indirect absorption.

If C_b increases by dC_b, the added water molecules divide between previously occupied and unoccupied sites, and we have:

$$\begin{aligned}\text{increase in fraction of occupied sites} &= d(p/p_0)\\ &= (1/p_0)\,dp\\ &= \frac{\text{fraction of previously unoccupied sites} \times \text{number of molecules added}}{\text{total number of sites}}\\ &= \frac{(1 - p/p_0)\,dC_b}{1/\beta} \qquad (12.13)\end{aligned}$$

Thus,

$$\frac{dp}{1 - p/p_0} = \beta p_0\,dC_0 \qquad (12.14)$$

which on integration gives:

$$\frac{p}{p_0} = 1 - \exp(-\beta C_b) \qquad (12.15)$$

This gives a relation between relative humidity and moisture absorption, but a correction term should be added for evaporation from sites with directly absorbed water that is not covered by indirectly absorbed water. The number of these is $(1 - p/p_0)C_a$, which equals $C_a\exp(-\beta C_b)$. Assuming that they have K times the effect of indirectly attached water molecules, we get:

$$\frac{p}{p_0} = 1 - \exp(-\beta C_b) + K\,C_a\exp(-\beta C_b) \qquad (12.16)$$

which gives

$$1 - \frac{p}{p_0} = (1 - K\,C_a)\exp(-\beta C_b) \qquad (12.17)$$

or, substituting from equations (12.9), (12.10) and (12.12)

$$1 - \frac{p}{p_0} = \{1 - K(1 - e^{-3\gamma r/100})\}\,e^{-\beta(e^{(-3\gamma r/100} - 1 + 3\gamma r/100)} \qquad (12.18)$$

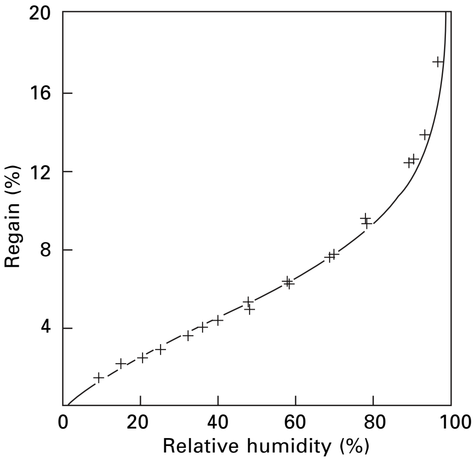
This is the equation for the curve of regain against relative humidity. A comparison with experiment is shown in Fig. 12.10.

Cooper [18] has shown that, at very low humidities, Peirce's equation reduces to the form

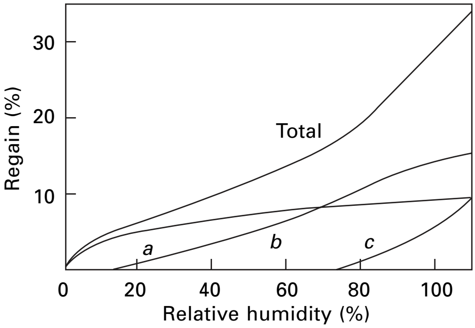
$$-\log_e(1 - p/P) = b_1 r + b_2 r^2 \qquad (12.19)$$

where b_1 and b_2 are constants. This equation fits experimental results for cellulosic fibres reasonably well.

Speakman [19] developed for wool a theory similar to Peirce's. He divided the water up into three phases, as shown in Fig. 12.11. The first phase to be absorbed is



12.10 Comparison of Peirce's equation with experimental data for soda-boiled cotton at 110 °C [12]. Equation for curve is: $1 - p/P = (1 - 0.40\ C_a)\ e^{-5.4C_b}$.



12.11 Division of water into three phases on Speakman's theory for wool [19].

tightly bound to hydrophilic groups in the side chains of the keratin molecule, and has little effect on the rigidity of the structure. Hearle [20] has pointed out that it has little effect on the permittivity and electrical resistance of wool. The second phase is attached to groups in the main chain and replaces crosslinks between molecules. It thus has the main effect on the rigidity, as shown in Fig. 12.8. The third phase is more loosely attached and is appreciable only at high humidities. Speakman suggested that it is due to capillary condensation, though it would probably be more correct to regard it as similar to Peirce's indirectly attached water.

12.2.2 Multilayer adsorption: the Brunauer, Emmett and Teller (BET) equation

Another theory derives from Langmuir's [21] classical adsorption isotherm for gases and vapours adsorbed in a monomolecular layer on the surface of a material.

This was extended by Brunauer Emmett, and Teller [22] to cover multilayer adsorption[2].

The analysis is based on the equilibrium between the rate of evaporation and the rate of condensation on the surface. The analyis involves two constants: r_1, the regain corresponding to a monomolecular layer, and α, which is approximately equal to $\exp[(E_1 - E_L)/RT]$, where E_1 is the heat of absorption on the first and E_L that on the succeeding layers. It yields an equation that may be written in the following forms:

$$\frac{r}{r_1} = \frac{\alpha p}{(p_0 - p)\,[1 + (\alpha - 1)\,p/p_0]} \tag{12.20}$$

$$\frac{p}{r(p_0 - p)} = \frac{1}{\alpha r_1} + \frac{\alpha - 1}{\alpha r_1}\,\frac{p}{p_0} \tag{12.21}$$

The latter is a convenient form for testing the relation, since it means that a plot of $p/r(p_0 - p)$ against p/p_0 should give a straight line from which the values α and r_1 can be determined.

The BET equation gives a sigmoidal isotherm, which shows a good fit with several practical examples of absorption. However, its application to absorption by fibres may be criticised on several grounds: (1) that the idea of adsorption on a surface, even an internal surface, is not valid for the mixing of fibre molecules and water molecules that actually occurs; (2) that it neglects the interaction between neighbouring molecules in a layer; (3) that it takes no account of effects due to swelling and mechanical restraint. The first objection does not apply to the derivations of the same equation on the basis of modern theories of statistical thermodynamics that have been put forward by Cassie[3] [23] and by Hill [24]. In this method, it is necessary to assume that the adsorption takes place on localised sites, but these may be either spread throughout the volume of the material or concentrated on a surface.

The BET equation fits the experimental results for cotton, viscose rayon, secondary acetate, wool, silk and nylon between about 5 and 50% r.h. It breaks down at high humidities, as would be expected, since it assumes that the regain tends to infinity at saturation. Bull [25] gives values of α, r_1 and $(E_1 - E_L)$ for these fibres Taylor's experiments [26, 27] on the absorption of viscose rayon and cotton below 5% r.h. also show that the BET equation does not fit the results in this range. He finds a good fit in this region with the Freundlich relation ($r = Kp^{1/n}$, where K and n are constants, $n > 1$) though this relation lacks a sound theoretical basis.

Cassie [28] has attempted to take account of swelling by applying the BET equation to his reduced regain–relative humidity curve (see Section 12.3.5). There is improved agreement at high humidities when the reduced vapour pressure, p_F, is substituted for the actual vapour pressure.

Windle [29] has modified Cassie's theory, in an application to wool, by assuming that the absorbed water molecules may be divided into three types: localised water,

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[2] A more detailed discussion of the BET equation is given in earlier editions of this book, but, since its predictive value for fibres is limited, a shorter version is included here.

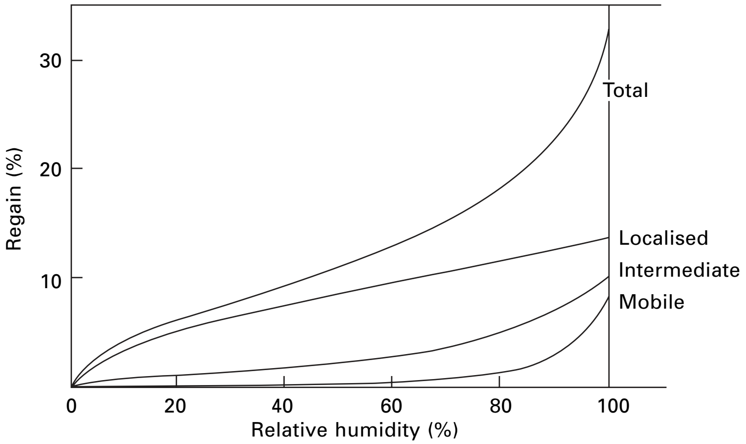
[3] Cassie's derivation has been criticised [12], and Hill's differs from it in certain details.

directly absorbed onto absorption sites and limited to one per site; intermediate water, absorbed onto localised water molecules and limited to one on each localised water molecule; and mobile water, absorbed on intermediate water molecules, with no restriction on numbers. There are three arbitrary constants to be fitted and, when this is done, the theory shows good agreement with experimental data on absorption and heat of wetting. The number of absorption sites is what would be expected from the molecular structure, and the energies of absorption are reasonable. The theory has been used to explain the dielectric data at very high frequencies (see Section 19.5). The division between the three phases is shown in Fig. 12.12.

This theory differs from Speakman's three-phase theory [19] in that the three types of water are absorbed on top of each other, whereas in Speakman's theory the first two phases were absorbed in parallel on different types of absorption site. It is likely that there ought to be a division of the localised water on Windle's theory in the same way, for the torsional rigidity is found to have a linear relation with the sum of the localised and intermediate water only when this is greater than 4%. This suggests that the first 4% is absorbed on different positions in the molecules.

Another version of this line of approach, due to Feughelman and Haly [30], is based on the assumption that each water molecule has four associations with its neighbours. The water is thus split up into five types, depending on whether the water molecules have zero, one, two, three or four associations with a keratin molecule. The first group, with four associations with other water molecules, is completely free; the fifth group is the most strongly bound.

A number of modifications [31–35] have been applied to Hill's derivation [31] of the BET equation; these take into account such factors as swelling, the presence of more than one type of absorption site, interaction between layers, varying heats of absorption, and so on, but none of them shows a marked improvement in the agreement with experiment.



12.12 Division of water into three phases on Windle's theory for wool [29].

12.2.3 Solution theories

Adsorption theories are based on the attachment of water molecules to particular sites (localised on the surface or at definite positions in the volume of the material), but there is an alternative view, which considers the mixing of molecules of different types with no limitation on the positions of the molecules. Such a mixture of molecules is a solid solution, and solution theory can be applied to it.

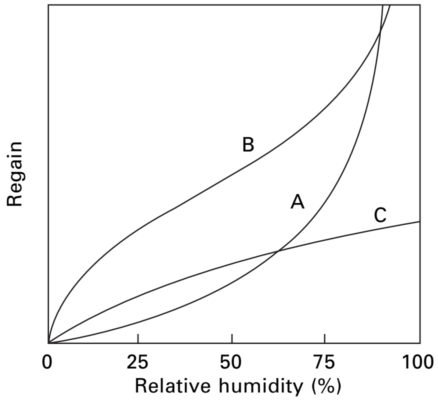
Barrer [36] has derived a solution theory for absorption by using statistical thermodynamics, which fit the practical results for the absorption of gases in rubber-like polymers. This solution theory gives a curve that is concave to the regain axis, in contrast to the convex Langmuir isotherm and the sigmoidal BET isotherm, as shown in Fig. 12.13. This type of theory is thus unlikely to fit the results at low humidities.

Extending the current thermodynamic theories of solution to take account of the energy involved in elastic deformation of the polymer, Rowen and Simha [37] obtained the following isotherm:

$$\log_e \frac{H}{100} = \log_e v_1 + v_2 + \mu v_2^2 + \frac{KV}{RT}\left(\frac{1}{-v_2^{1/2}} - 1\right)\left(\frac{5}{3v_2^{1/2}} - 1\right) \qquad (12.22)$$

where H = relative humidity %, v_1 = volume fraction of the material, v_2 = volume fraction of the absorbed water, V = partial molal volume of liquid, μ = a constant, determined by the heat and entropy of mixing, and K = a constant, depending on the mechanical reaction of the polymer to sorption.

This equation gives a better fit above 50% r.h than the BET isotherm, but shows the failure of a simple solution theory at low humidities[4].



12.13 Comparison of plots of regain against relative humidity on: A solution theory, B BET isotherm and C Langmuir isotherm.

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[4] A comparative plot for cotton was included in earlier editions of this book.

12.2.4 Hailwood and Horrobin's theory

In one of the most interesting theoretical treatments, Hailwood and Horrobin [38] have combined an attachment of the first water molecules onto particular sites in the polymer molecule with a solution theory for the further absorption of water by the material.

They consider that some of the water is present as hydrates formed with definite units of the polymer molecule and that the remainder forms an ideal solid solution in the polymer. By consideration of the chemical equilibrium, they derive an equation relating the amount of water absorbed to the relative humidity. Their derivation is a general one, allowing for a variety of different hydrates to be formed but, in fitting the results, they find that it is sufficient to assume that only one type of hydrate is involved. To simplify the working, this assumption is made at the beginning of the derivation of the equation given here, and consequently there are only two chemical equilibria involved.

It is assumed that the dissolved water, the unhydrated polymer and the polymer hydrate form a single solid phase. In this phase, there will be an equilibrium between water combined with a unit, P of the polymer molecule to form the hydrate, and water present as dissolved water

$$\mathrm{P{\cdot}H_2O = P + H_2O_{sol}}$$

By the Law of Mass Action, we have

$$[\mathrm{P{\cdot}H_2O}] = K_1[\mathrm{H_2O_{sol}}][\mathrm{P}] \tag{12.23}$$

where K_1 is the equilibrium constant.

There is also an equilibrium between the dissolved water and the water vapour in the atmosphere:

$$\mathrm{H_2O_{sol}} \rightleftharpoons \mathrm{H_2O_{vap}}$$

giving:

$$[\mathrm{H_2O_{sol}}] = K_2[\mathrm{H_2O_{vap}}] \tag{12.24}$$

The activity of the water vapour, at the low water vapour concentration involved, is given by the fractional humidity. If the relative humidity is $H\%$, we thus have

$$[\mathrm{H_2O_{vap}}] = H/100 \tag{12.25}$$

and hence from equation (12.24)

$$[\mathrm{H_2O_{sol}}] = KH \tag{12.26}$$

where $K = K_2/100$.

The activities of the three types of molecule present in what is assumed to be an ideal solid solution are given by the mole fractions of each type of molecule present, that is:

$$[\mathrm{H_2O_{sol}}] = \frac{n_\mathrm{w}}{n_\mathrm{w} + n_0 + n_1} \tag{12.27}$$

$$[\mathrm{P}] = \frac{n_0}{n_\mathrm{w} + n_0 + n_1} \tag{12.28}$$

$$[\mathrm{P{\cdot}H_2O}] = \frac{n_1}{n_\mathrm{w} + n_0 + n_1} \tag{12.29}$$

where n_w = number of moles of water in solution in polymer, n_0 = number of moles of the unhydrated polymer units and n_1 = number of moles of polymer hydrate.

It follows from equations (12.26) and (12.27) that:

$$n_\mathrm{w} = \frac{n_0 + n_1}{1 - [\mathrm{H_2O_{sol}}]}[\mathrm{H_2O_{sol}}] = \frac{(n_0 + n_1)\,KH}{1 - KH} \tag{12.30}$$

and from equations (12.23), (12.26), (12.28) and (12.29) that:

$$n_1 = \frac{n_0[\mathrm{P{\cdot}H_2O}]}{[\mathrm{P}]} = n_0 K K_1 H \tag{12.31}$$

The number of moles of water taken up by the material (whether dissolved or as hydrate) is equal to $(n_\mathrm{w} + n_1)$, and the number of moles of the polymer unit present (whether hydrated or not) is equal to $(n_0 + n_1)$. The percentage regain r is therefore given by:

$$r = \frac{1800\,(n_\mathrm{w} + n_1)}{(n_0 + n_1)\,M} \tag{12.32}$$

where M = molecular weight of the polymer unit, and 18 = molecular weight of water. Thus:

$$\frac{Mr}{1800} = \frac{n_\mathrm{w}}{n_0 + n_1} + \frac{n_1}{n_0 + n_1} \tag{12.33}$$

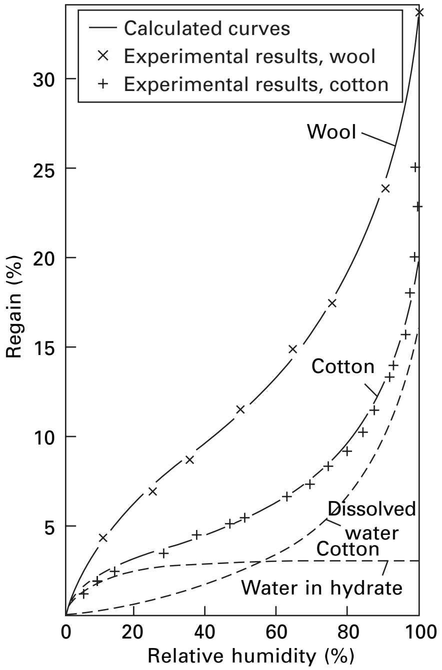
and from equations (12.30) and (12.31):

$$\frac{Mr}{1800} = \frac{KH}{1 - KH} + \frac{KK_1H}{1 + KK_1H} \tag{12.34}$$

which is the equation relating regain and relative humidity derived by Hailwood and Horrobin [38].

This equation contains three constants M, K and K_1 which can be chosen to give the best fit with the experimental data. Figure 12.14 gives a comparison of the observed and calculated results for cotton and wool at 25 °C and shows the division of the water taken up by cotton between the hydrate and the solution. Hailwood and Horrobin also found a good fit between the calculated and observed results for hair, silk and nylon. It has, however, been pointed out that any equation of this form must give a sigmoidal curve with a suitable choice of the three constants, and thus the significance of the fit is reduced.

From the equilibrium constants chosen, the heats of the reaction can be calculated, and a reasonable agreement with results from calorimetric measurements is found for wool. The theory also leads to a prediction of the variation of specific volume with



12.14 Comparison of Hailwood and Horrobin's equation [38] with experimental results for wool and cotton.

regain, which is in fair agreement with the experimental results for wool, except at the higher humidities.

The values of M that are found are all greater than the molecular weight corresponding to a single polar group in the fibre molecule. It is assumed that this is due to the fact that the crystalline material is not accessible to moisture and adds to the mass of polymer present. Consequently, the value of M can be used to estimate the amount of inaccessible material present, and the values obtained are in reasonable agreement with values obtained by other methods.

Hailwood and Horrobin's theory has been criticised mainly because of the assumption that an ideal solid solution is formed, whereas mixtures of large and small molecules usually depart from the ideal.

12.3 The relations between absorption, swelling and elastic properties

12.3.1 Swelling and osmosis

Quite a different approach to moisture sorption has been developed by Barkas [39], starting from the analogy between swelling and osmotic phenomena. In osmosis, water passes through a semipermeable membrane from a region of low solute concentration to a region of high solute concentration until a pressure sufficient to prevent the flow of water is built up. The same sort of thing happens in swelling.

Water passes into the region of high polymer concentration, and the polymer swells. This continues until the stresses generated by the deformation of the polymer are sufficient to prevent more water from flowing in.

Consequently, the moisture absorption will be very dependent on the stresses developed in the fibre owing to internal or external effects, and thermodynamic relations similar to those applicable in osmosis can be applied to swelling.

12.3.2 Qualitative view of influence of mechanical forces on absorption

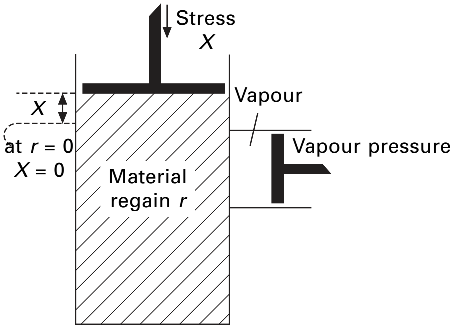
We can consider a substance absorbing from an atmosphere of given vapour pressure and subject to a stress. The exact form of the specimen is unimportant for the qualitative argument: one simple form is illustrated in Fig. 12.15. Let vapour pressure = p, regain of material = r, stress applied to material = X, with a compression, i.e. a force reducing swelling, taken as positive, and strain, or swelling = x, with an increase in size taken as positive. The origin $x = 0$ is taken at $r = 0$, $X = 0$.

Figure 12.16 (a) shows the curves of regain against vapour pressure that would be obtained at various values of the applied stress X. As the stress increases, the regain decreases. Figure 12.16(b) shows stress–strain curves for various values of the regain of the material. Owing to swelling, the position of the origin of the stress–strain curves (i.e., the value of x at $X = 0$) varies with the regain.

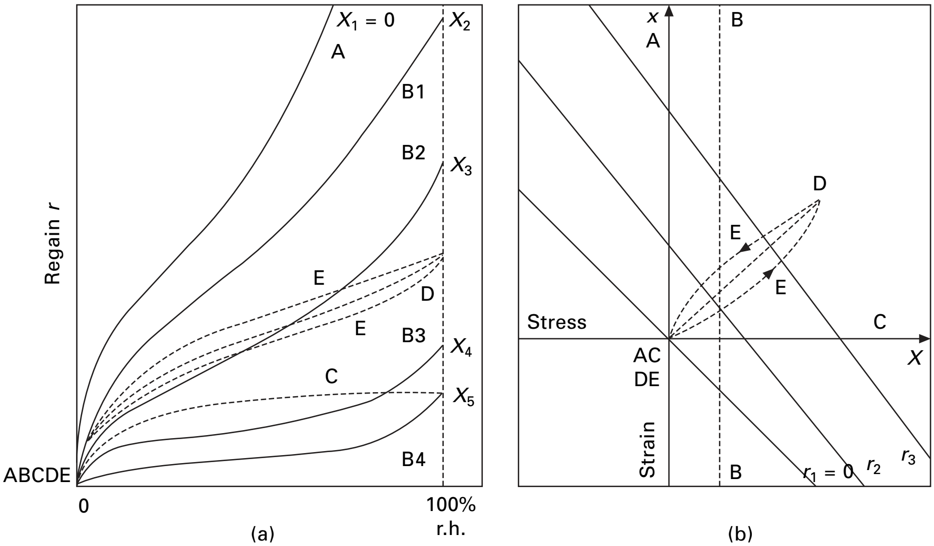
The system being considered has two degrees of freedom (at constant temperature) for, when any two of the quantities considered are specified (for example, the stress and vapour pressure), the other quantities involved are necessarily determined. This means that any given point on the stress–strain curve corresponds to a particular point on the regain vs vapour pressure curve, and vice versa.

It is interesting to see what happens under various conditions that might occur in practice.

(A) Free swelling. There will be zero applied stress, so the line AA will be followed.
(B) Swelling under constant stress, X_2. The line BB will be followed. The lower full lines are at increasing values of stress X_3, X_4, X_5.
(C) Moisture absorption at constant volume. In this case, x does not vary, so the



12.15 Model for absorption under stress.



12.16 (a) Absorption curves (full lines at constant stress). (b) Stress–strain curves (full lines at constant regain). Practical cases: A, free swelling; B1–B4, swelling under stress; C, swelling at constant volume; D, swelling restrained by ideal spring; E, swelling restrained by internal restraint, with mechanical hysteresis.

stress increases as the swelling proceeds. This gives the curve CC, showing a reduced moisture absorption.

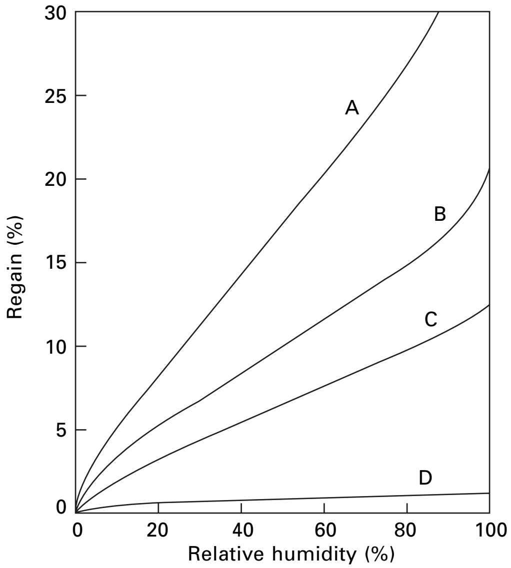
(D) Swelling restrained by an ideal spring. In this case, the stress will increase in proportion to the strain x and the absorption will be reduced, but not as much as in the previous case. The curves DD will be followed.

(E) Swelling restrained by a spring showing hysteresis. There will be hysteresis in the X/x relation, and this will be transferred to the relation between regain and vapour pressure. The curves EE result.

Figure 12.17 illustrates a practical example of these effects. It shows the reduction of moisture absorption that would occur in wood under two restraining conditions, namely, when the volume of a block of wood is held constant, and when the volume of the wood cell walls is constant.

12.3.3 Internal restraints; plasticity and hysteresis

The above discussion has been concerned with external forces, and it is also these to which thermodynamics is immediately applicable. However, the swelling of a fibre is limited by restraints arising from the arrangement of the molecules in a three-dimensional network. There will be stresses acting on a small element of an amorphous region that is absorbing water, because the molecules are held firmly fixed elsewhere in crystalline regions. On a larger scale, there may be forces arising from the interference from one part of the fibre with the swelling of another part. This will occur when the



12.17 Absorption of spruce wood under stress: A, material completely free of stress; B, natural sorption, including internal restraints on swelling of block of wood; C, volume of block of wood held constant, but allowing swelling into void spaces in wood cells; D, wood cell walls (internal and external) held at constant volume. Curve B is experimental; remainder are calculated. From Barkas [39].

swelling is non-uniform, for example, when there is a skin on the fibre. All these internal forces in a fibre will thus be important in determining its moisture absorption. For example, Fig. 12.17 shows the increased absorption that would occur in stress-free wood with the internal restraints removed, except for those in the molecular structure itself.

Fibres are not perfectly elastic, however. There is plasticity. When a stress is removed, recovery is incomplete. The internal stress–strain curve would be a loop similar to the curve EE in Fig. 12.16(b) and would thus cause hysteresis in the moisture absorption as well. In other words, wherever there is mechanical hysteresis in a fibre, there must also be moisture hysteresis. Experimentally it is found that in natural and regenerated fibres both forms of hysteresis occur to a marked extent. In nylon, where the elastic recovery is good, there is also very little moisture hysteresis.

12.3.4 Thermodynamic relations

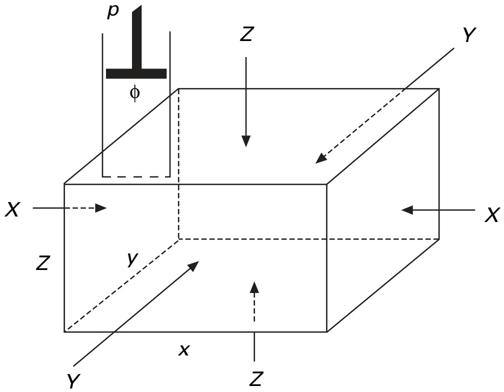
By the use of thermodynamics, quantitative relations between swelling, moisture absorption and mechanical properties can be derived. It should be remembered that thermodynamic equations (as distinct from inequalities) apply only to reversible changes, and they break down when there is hysteresis.

The general equation may conveniently be derived, in the method proposed by Hearle [40], by considering a rectangular parallelepiped under stresses normal to its faces and swelling in directions parallel to its sides. This can be modified for other shapes and for other types of stress and deformation.

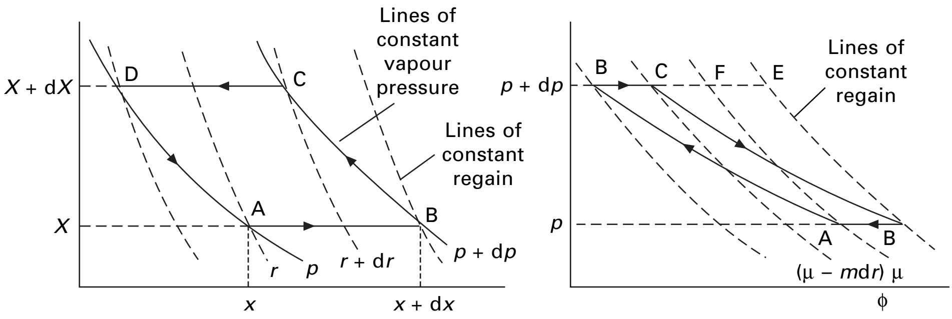
Figure 12.18 illustrates a specimen of mass m (when dry); of volume mV (i.e. V is the volume of a specimen having unit mass when dry); with sides x, y, z; at a fractional regain ρ (i.e. containing a mass $m\rho$ of water) ; and having compressive stresses, X, Y, Z, normal to its faces. It is assumed that water can only be lost to or gained from a container of volume ϕ containing a mass μ of vapour at a vapour pressure p. Let the specific volume of the vapour be v.

We consider a general isothermal change in condition of this specimen, in which the stresses change from X to $X + \mathrm{d}X$, Y to $Y + \mathrm{d}Y$, and Z to $Z + \mathrm{d}Z$; the lengths of the sides change from x to $x + \mathrm{d}x$, y to $y + \mathrm{d}y$, and z to $z + \mathrm{d}z$; the regain changes from ρ to $\rho + \mathrm{d}\rho$;. and the vapour pressure changes from p to $p + \mathrm{d}p$. The mass of vapour in the container will change from μ to $(\mu - m\mathrm{d})\rho$.

In order to find the relations between these changes, we can take the specimen through a suitable cycle. Since this will be a reversible isothermal cycle, it follows from the Second Law of Thermodynamics that the total work done is zero. The cycle chosen, and illustrated for the x-direction in Figure 12.19, is as follows:



12.18 Parallelepiped model.



12.19 X, *x* and *p*, *ϕ* cycles.

- a →b: an increase in vapour pressure from p to $p + \mathrm{d}p$ at constant applied stress. Specimen absorbing moisture from container.
- b → c: an increase in applied stress by dX, dY and dZ, at constant vapour pressure. Moisture evaporating into container.
- c → d: a decrease in vapour pressure to p at constant applied stress. Moisture evaporating.
- d → a: a decrease in stress to X, Y, Z. Moisture being absorbed.

The work done may be evaluated as follows:

- by force on the X-face:

$$\text{work} = \oint (\text{force} \times \text{displacement})$$

$$= \text{area of } X\text{-face} \times \text{area enclosed by } X,\, x \text{ cycle}$$

$$= \frac{mV}{x}\left(\frac{\partial x}{\partial p}\right)_{X,Y,Z} \mathrm{d}p \cdot \mathrm{d}X \tag{12.35}$$

- similarly for the Y- and Z-faces;
- by force on the vapour container:

$$\text{work} = \oint (\text{pressure} \times \text{volume})$$

$$= -\text{area of } p,\, \phi \text{ cycle}$$

The negative sign is introduced because the cycle is enclosed in the reverse direction to that of the stress cycles.

$$\text{Area of } p,\, \phi \text{ cycle} = \mathrm{d}p\ (\text{increase in } \phi_{a\to d}) \tag{12.36}$$

This change in ϕ may be expressed in one of two ways. Either:

$$\text{increase in } \phi_{\mathrm{a}\to\mathrm{d}} = \text{increase in mass of vapour in container} \times \text{specific volume}$$

$$= -\,m\left[\left(\frac{\partial \rho}{\partial X}\right)_{p,Y,Z} + \left(\frac{\partial \rho}{\partial Y}\right)_{p,Z,X} + \left(\frac{\partial \rho}{\partial Z}\right)_{p,X,Y}\right] v \tag{12.37a}$$

The negative sign is introduced because an increase of mass of vapour in the container corresponds to a decrease of regain in the material.

Or:

$$\text{increase in } \phi_{\mathrm{a}\to\mathrm{d}} = \text{increase in } \phi_{\mathrm{c}\to\mathrm{e}} - \text{increase in } \phi_{\mathrm{c}\to\mathrm{f}}$$

$$= -mv\ (\text{increase in regain}_{c\to d} - \text{increase in regain}_{c\to a})$$

$$= -\,mv\left[\left(\frac{\partial \rho}{\partial p}\right)_{X,Y,Z} (-\,\mathrm{d}\rho) - (-\,\mathrm{d}\rho)\right] \tag{12.37b}$$

Hence, from equations (12.36) and (12.37):

$$\text{work} = mv\,\mathrm{d}p\left[\left(\frac{\partial \rho}{\partial X}\right)_{p,Y,Z} + \left(\frac{\partial \rho}{\partial Y}\right)_{p,Z,X} + \left(\frac{\partial \rho}{\partial Z}\right)_{p,X,Y}\right] \tag{12.38a}$$

or

$$= -\,mv\,\mathrm{d}p\left[\left(\frac{\partial \rho}{\partial p}\right)_{X,Y,Z}\mathrm{d}p - \mathrm{d}\rho\right] \tag{12.38b}$$

Summing the work done, and equating it to zero, we then have, from equations (12.35) and (12.38a), by cancelling *m* and d*p* throughout:

$$\frac{V}{x}\,\mathrm{d}X + \frac{V}{y}\left(\frac{\partial y}{\partial p}\right)_{X,Y,Z}\mathrm{d}Y + \frac{V}{z}\left(\frac{\partial z}{\partial p}\right)_{X,Y,Z}\mathrm{d}Z$$

$$+\,v\left[\left(\frac{\partial \rho}{\partial X}\right)_{p,Y,Z}\mathrm{d}X + \left(\frac{\partial \rho}{\partial Y}\right)_{p,Z,X}\mathrm{d}Y + \left(\frac{\partial \rho}{\partial Z}\right)_{p,X,Y\mathrm{d}Z}\right] = 0 \tag{12.39}$$

Collecting the coefficients of d*X*, d*Y* and d*Z*, we obtain the series of useful relations:

$$\frac{V}{x}\left(\frac{\partial x}{\partial p}\right)_{X,Y,Z} = -\left(\frac{\partial \rho}{\partial X}\right)_{p,Z,X} \tag{12.40}$$

and similarly for the other two directions.

Alternatively, from equations (12.35) and (12.38b), we obtain:

$$\frac{V}{x}\left(\frac{\partial x}{\partial p}\right)_{X,Y,Z}\mathrm{d}X + \frac{V}{y}\left(\frac{\partial y}{\partial p}\right)_{X,Y,Z}\mathrm{d}Y + \frac{V}{z}\left(\frac{\partial z}{\partial \rho}\right)_{X,Y,Z}\mathrm{d}Z$$

$$= v\left(\frac{\partial \rho}{\partial p}\right)_{X,Y,Z}\mathrm{d}p - v\,\mathrm{d}\rho \tag{12.41}$$

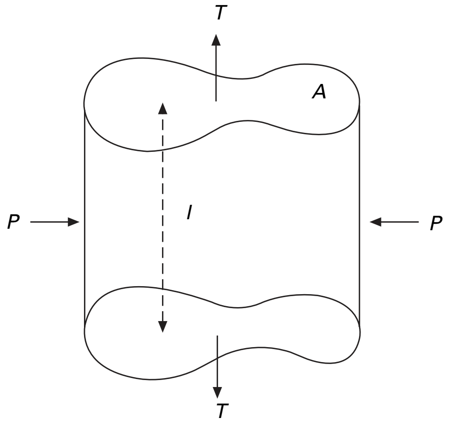
which, on multiplying through by $(\delta p/\delta \rho)_{XYZ}$, gives:

$$\frac{V}{x}\left(\frac{\partial x}{\partial \rho}\right)_{X,Y,Z}\mathrm{d}X + \frac{V}{y}\left(\frac{\partial y}{\partial \rho}\right)_{X,Y,Z}\mathrm{d}Y + \frac{V}{z}\left(\frac{\partial z}{\partial \rho}\right)_{X,Y,Z}\mathrm{d}Z$$

$$= v\,\mathrm{d}p - v\left(\frac{\partial p}{\partial \rho}\right)\mathrm{d}\rho \tag{12.42}$$

Equations (12.41) and (12.42) are alternative forms of the general equation relating the changes d*X*, d*Y*, d*Z*, d*p* and dρ. If other forces, such as shear forces, are involved, the appropriate work terms must be added to the equations.

It is convenient to modify the equations to apply them to single fibres. If we consider a fibre to be a cylinder of irregular cross-section, as shown in Fig. 12.20, with area *A* and length *l*, the forces on the fibre to be a tensile stress *T* (being a



12.20 Stresses on a fibre.

tension, this will have the opposite sign to the forces so far considered) and a uniform transverse pressure P the equations become

$$\frac{1}{l}\left(\frac{\partial l}{\partial p}\right)_{T,P} = \frac{v}{V}\left(\frac{\partial \rho}{\partial T}\right)_{p,P} \tag{12.43}$$

$$\frac{1}{A}\left(\frac{\partial A}{\partial p}\right)_{T,P} = -\frac{v}{V}\left(\frac{\partial \rho}{\partial P}\right)_{p,T} \tag{12.44}$$

$$-\frac{1}{l}\left(\frac{\partial l}{\partial p}\right)_{T,P} \mathrm{d}T + \frac{1}{A}\left(\frac{\partial A}{\partial p}\right)_{T,P} \mathrm{d}P = \frac{v}{V}\left[\left(\frac{\partial \rho}{\partial p}\right)_{T,P} \mathrm{d}p - \mathrm{d}\rho\right] \tag{12.45}$$

and, for the change in regain

$$-\frac{1}{l}\left(\frac{\partial l}{\partial \rho}\right)_{T,P} \mathrm{d}T + \frac{1}{A}\left(\frac{\partial A}{\partial \rho}\right)_{T,P} \mathrm{d}P = \frac{v}{V}\left[\mathrm{d}p - \left(\frac{\partial p}{\partial \rho}\right)_{T,P} \mathrm{d}\rho\right] \tag{12.46}$$

It may be noted that, for a fibre under constant transverse pressure, for example, a single fibre in air, $\mathrm{d}P = 0$, and thus the second term drops out of equations (12.45) and (12.46).

In applying these equations, two points must be remembered. First, they apply exactly only to reversible changes. Secondly, they are all differential equations, and direct integration is not possible, since the quantities involved vary with one another in ways that have not been analytically expressed, for example, v will be a function of p, and V will be a function of ρ, T, and P.

However, the equations may be used to obtain valuable approximate results that could not be obtained by direct experiment. For example, equation (12.44) would enable transverse pressures on fibres to be calculated approximately from the change in regain if the area-swelling behaviour of the fibre is known.

Figure 12.21 shows an experimental test of equation (12.43) made by Treloar [41]. The agreement between experiment and theory is quite good. Measurements of the converse effect, the stress ('hygrostress') that develops when wool fibres are taken from 100 to 0% r.h. at various extension levels, are reported by Haly [42].

12.3.5 Cassie's reduced regain–relative humidity curve

Cassie [28] has proposed another method of dealing with the influence of mechanical effects. He assumes that the water absorbed in wool is under a hydrostatic pressure P, which can be calculated from the swelling and the elastic properties. If the volume-swelling is $\mathrm{d}V/V$, the pressure P is given by:

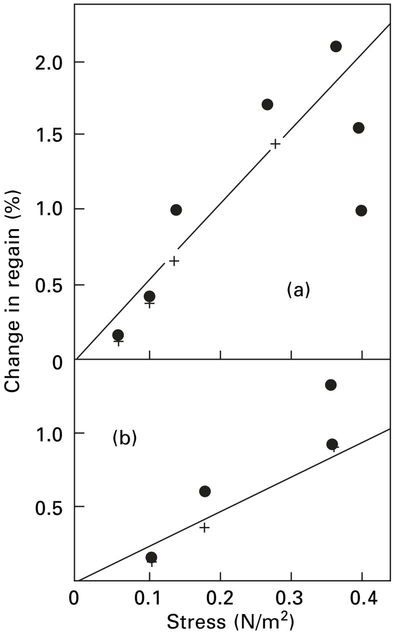
$$P = k\,\frac{\Delta V}{V} \qquad (12.47)$$

where k is the bulk modulus of elasticity.

If the fibres are assumed to be isotropic in elastic properties, this becomes

$$P = \frac{E}{3(1-2\sigma)}\,\frac{\Delta V}{V} = \frac{E}{1-2\sigma}\,\frac{\Delta D}{D} \qquad (12.48)$$

where E is the Young modulus, σ is the Poisson ratio, and is taken as 0.25, and $\Delta D/D$ is the diameter-swelling, which equals $\frac{1}{3}\Delta V/V$ if the swelling is isotropic.



12.21 Variation of regain of cellulose fibres with tension: (a) isotropic; (b) oriented. Experimental points compared with lines from equation (12.43). After Treloar [41].

The term $\Delta D/D$ is equivalent to a strain, and the values of $E.\Delta D/D$ were assumed to be equal to the stress at the corresponding strain on Speakman's tensile stress–strain curves [43] at the appropriate humidity. Hence values of P at each relative humidity were obtained.

The variation of the vapour pressure of water with hydrostatic pressure is given by the thermodynamic relation

$$P = \frac{RT}{V_M} \log_e \frac{p}{p_F} \qquad (12.49)$$

where R = gas constant, T = absolute temperature, V_M = molar volume, p = observed vapour pressure and, p_F = vapour pressure at zero hydrostatic pressure.

Putting in the appropriate numerical values, namely, $R = 8.31\,\text{J K}^{-1}\,\text{mol}^{-1}$, $T = 298\,\text{K}$ (20 °C) and $V_M = 18 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1}$ ($18\,\text{cm}^3/\text{mol}$), gives the pressure in pascals (N/m^2) as:

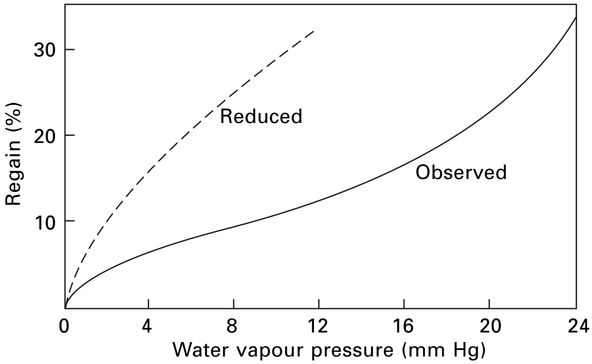
$$P = 3.16 \times 10^8 \log_{10}(p/p_F) \qquad (12.50)$$

Thus, by using the values of P calculated as above, the values of p_F, the vapour pressure reduced to zero hydrostatic pressure, can be obtained. The reduced relative humidity is the ratio of this reduced vapour pressure to the saturation vapour pressure of water.

Figure 12.22 shows a plot of regain against actual and reduced vapour pressure. The use of reduced values gives a simpler curve and, as has been mentioned earlier (Section 12.2.2), gives a good fit with the BET isotherm. However, the initial assumption that the water acts in a manner similar to liquid water, and that it may be regarded as being under a hydrostatic pressure, may be doubted. The assumptions with regard to the elastic properties of the fibre are drastic and may not be very near the truth.

12.4 Surface adsorption

The idea of adsorption on internal surfaces has already been discussed and has been shown to be of doubtful validity for fibres. There may, however, be adsorption on the



12.22 Cassie's reduced curve of regain against vapour pressure for wool [23].

external surface of fibres. In hygroscopic fibres, this would be a negligible proportion of the total regain, but in a non-hygroscopic fibre it may contribute most or all of the small moisture absorption.

Table 12.2 shows results obtained by Bright *et al.* [44] for the heat of wetting of similar specimens of polyester fibre. The heat of wetting is proportional to (linear density)$^{-1/2}$. In other words, the amount of heat evolved is proportional to the surface area (per unit mass), which suggests that the moisture taken up by polyester fibres is present on the surface of the fibre.

12.5 The effect of temperature

In order to correlate the relations between regain and relative humidity at various temperatures, Whitwell and his associates [45] analysed Wiegerink's data [46] on the basis of Othmer's method [47]. This depends on the application of the Clausius–Clapeyron equation, which for a pure substance is:

$$\frac{\mathrm{d}p_0}{\mathrm{d}T} = \frac{p_0 L}{RT^2} \tag{12.51}$$

where p_0 = vapour pressure, T = absolute temperature, L = latent heat of condensation and R = gas constant. For a fibre at a given regain, this becomes:

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{pQ_\mathrm{v}}{RT^2} \tag{12.52}$$

where p = vapour pressure over the fibre, Q_v = heat of absorption of the fibre.

Combining the two equations, we obtain:

$$\frac{\mathrm{d}p}{\mathrm{d}p_0} = \frac{pQ_\mathrm{v}}{p_0 L}$$

or

$$\frac{\mathrm{d}p/p}{\mathrm{d}p_0/p_0} = \frac{Q_\mathrm{v}}{L} \tag{12.53}$$

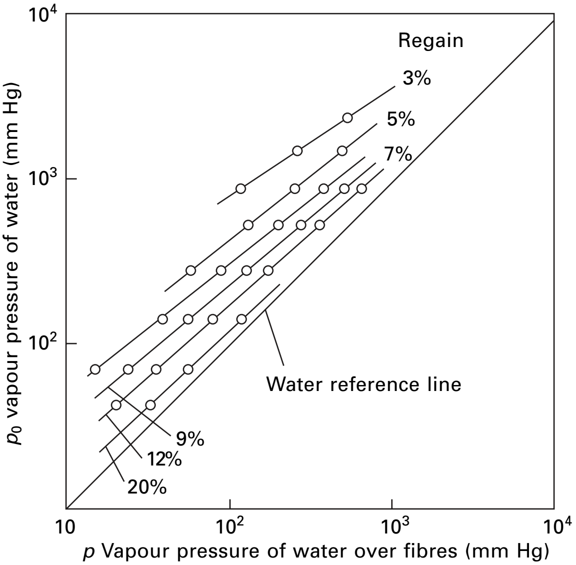
which on integration gives:

$$\log p = \frac{Q_\mathrm{v}}{L} \log p_0 + \text{constant} \tag{12.54}$$

Thus if values of log p for various temperatures at constant regain are plotted against the corresponding values of log p_0, straight lines should be obtained. This is illustrated

Table 12.2 Heat of wetting of polyester fibre at constant draw-ratio [44]

Linear density (dtex)	Heat of wetting	Heat of wetting × tex$^{1/2}$
2.2	0.85	0.401
4.4	0.56	0.373
8.9	0.39	0.368



12.23 Whitwell's plot of log p against log p_0 for cuprammonium rayon on desorption [45].

in Fig. 12.23. It has been further found that for most fibres the lines for various regains intercept in a common point.

Plotting results in this way enables them to be extrapolated beyond the experimental range of temperatures and, by making use of the common point, allows a line to be drawn for other values of the regain if a single point is known. At low temperatures, other effects must be involved, since the values obtained by Darling and Belding [48] at low temperatures do not agree with this theory.

12.6 References

1. I. C. Watt and J. D. Leeder. *J. Text., Inst.* 1968, **59**, 353.
2. N. H. Kolkmeyer and A. N. J. Heyn. *Proc. Konink. Nederland Akad. Wetenschap.*, 1934, **37**, 92.
3. L. J. Lynch and K. H. Marsden. *J. Chem. Phys.*, 1969, **51**, 5681.
4. C. E. Boesen. *Cell. Chem. Technol.*, 1970, **4**, 149.
5. R. J. B. Marsden. In *Fibre Science* J. M. Preston (Editor), The Textile Institute, Manchester, 2nd edition, 1953, p. 229.
6. Jeffries, D. .M. Jones, J. G. Roberts, K. Selby, S.C. Simmens and J. O. Warwicker Cellulose Chem. Tech., 1969, **3**, 255.
7. A. R. Urquhart. *J. Text. Inst.*, 1929, **20**, T125.
8. P. H. Hermans. *Physics and Chemistry of Cellulose Fibres*, Elsevier, Amsterdam, Netherlands, 1949.
9. R. Meredith. In *Fibre Science* J. M. Preston (Editor), The Textile Institute, Manchester, 2nd edition, 1953, p. 246.
10. A. D. McLaren and J. W. Rowen. *J. Polymer Sci.*, 1951, **7**, 289.
11. A. B. D. Cassie. In *Fibrous Proteins Symposium*, Society of Dyers and Colourists, Bradford, 1946, p. 86.

12. G. A. Gilbert. In *Fibrous Proteins Symposium*, Society of Dyers and Colourists, Bradford, 1946, p. 96.
13. T. P. Labuza *Moisture Absorption: Practical Aspects of Isotherm Measurement and Use, Amer*. Association of Cereal Chemists, St Paul, Minnesota, 1984.
14. C. Van den Berg and S. Bruin. In *Water Activity: Influences on Food Quality*, L. B. Rockland and G. F. Stewart (Editors), Academic Press, New York, 1981, p. 147.
15. M. J. Sabchez-Montero, C. Herdes, F. Salvador and L. F. Vega. *Appl. Surface Sci.*, 2005, **25**, 519.
16. F. T. Peirce. *J. Text. Inst.*, 1929, **20**, T133.
17. J. W. S. Hearle. *J. Text. Inst.*, 1952, **43**, T354.
18. D. N. E. Cooper. *J. Text. Inst.*, 1961, **52**, T433.
19. J. B. Speakman. *Trans. Faraday Soc.*, 1944, **40**, 6.
20. J. W. S. Hearle. *Text. Res. J.*, 1954, **24**, 307.
21. I. Langmuir. *J. Amer. Chem. Soc.*, 1918, **40**, 1361.
22. S. Brunauer, P. H. Emmett, and E. Teller. *J. Amer. Chem. Soc.*, 1938, **60**, 309.
23. A. B. D. Cassie. *Trans. Faraday Soc.*, 1945, **41**, 450.
24. T. L. Hill. *J. Chem. Phys.*, 1946, **14**, 263.
25. H. B. Bull. *J. Amer. Chem. Soc.*, 1944, **66**, 1499.
26. J. B. Taylor. *J. Text. Inst.*, 1952, **43**, T489.
27. J. B. Taylor. *J. Text. Inst.*, 1954, **45**, T642.
28. A. B. D. Cassie. *Trans. Faraday Soc.*, 1945, **41**, 458.
29. J. J. Windle. *J. Polymer Sci.*, 1956, **21**, 103.
30. M. Feughelman and A. R. Haly. *Text. Res. J.*, 1962, **32**, 1966.
31. T. L. Hill. *J. Chem. Phys.*, 1946–50, 'Statistical Mechanics of Adsorption', I–X.
32. H. J. White and H. Eyring. *Text. Res. J.*, 1947, **17**, 523.
33. H. J. White and P. B. Stam. *Text. Res. J.*, 1949, **19**, 136.
34. A. D. McLaren and M. Ottesen. *Compt. Rend. Trav. Lab. Carlsberg, Ser. Chim.*, 1950, **27**, 325.
35. M. Dole. *J. Chem. Phys.*, 1948, **16**, 25.
36. R. M. Barrer. *Trans. Faraday Soc.*, 1947, **43**, 3.
37. J. W. Rowen and R. Simha. *J. Phys. Colloid Chem.*, 1949, **53**, 921.
38. A. J. Hailwood and S. Horrobin. *Trans. Faraday Soc.*, 1946, **42B**, 84.
39. W. W. Barkas. *The Swelling of Wood under Stress*, HMSO, London, 1949.
40. J. W. S. Hearle. *Text. Res. J.*, 1957, **27**, 940.
41. L. R. G. Treloar. *Trans. Faraday Soc.*, 1953, **49**, 816.
42. A. R. Haly. *Text. Res. J.*, 1965, **35**, 889.
43. J. B. Speakman. *J. Text. Inst.*, 1927, **18**, T431.
44. N. F. H. Bright, T. Carson and G. M. Duff. *J. Text. Inst.*, 1953, **44**, T587.
45. J. C. Whitwell *et al. Text. Res. J.*, 1946, **16**, 255, 307; 1947, **17**, 7, 99, 664.
46. J. G. Wiegerink. *Text. Res.*, 1940, **10**, 357.
47. D. F. Othmer. *Industr. Engng Chem.*, 1940, **32**, 841.
48. R. C. Darling and H. S. Belding. *Industr. Engng Chem.*, 1946, **38**, 527.