### 9.1 Introduction

Textile materials take a long time to come into equilibrium with their surroundings. The drying of washing is a simple example of this and shows that the rate depends on a variety of factors: temperature, air humidity, wind velocity, surrounding space, thickness of material, density of material, nature of the fibre, and so on. The slowness of conditioning may be a nuisance technically, since textiles often have to be conditioned before further processing or sale. On the other hand, a slow process may act as a valuable stabilising influence, for example absorbent fibrous materials in a room will prevent rapid changes of humidity or temperature.

In this chapter, we shall be considering the factors that play a part in the change of conditions in textile materials. To avoid the tedious repetition of alternatives, it will usually be written on the assumption that the material is *taking up* water. In general, drying follows the reverse procedure.

# 9.2 Diffusion of moisture

#### 9.2.1 The diffusion equation and its solution

The most obvious way of explaining the slowness of conditioning is to assume that it is due to the slowness with which water molecules diffuse through the fibre and through the air to the fibre.

If the concentration of water molecules (or of any other substance with which one is concerned) varies from place to place in a given medium (e.g. air or fibre substance), the molecules will diffuse from regions of high concentration to regions of low concentration until their distribution becomes uniform. The rate of transport, dm/dt, of the diffusing substance across an area A of a plane perpendicular to the concentration gradient  $\partial c/\partial x$  is given by Fick's equation:

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -DA \,\frac{\partial c}{\partial x} \tag{9.1}$$

where D is called the diffusion coefficient.

From this equation, we can derive a differential equation giving the relation between concentration, position and time. If we consider an element of unit area and of

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thickness dx, as shown in Fig. 9.1, then in a time dt the mass diffusing across the lefthand face into the element is  $[-D(\partial c/\partial x) dt]$ , and the mass diffusing out of the element across the right-hand face is

$$\left[ -\left\{ D \, \frac{\partial c}{\partial x} + \frac{\partial}{\partial x} \left( D \, \frac{\partial c}{\partial x} \right) \mathrm{d}x \right\} \mathrm{d}t \right]$$

The difference in these two amounts gives the increase of mass of the diffusing substance in the element, that is, the change of concentration multiplied by the volume of the element. Hence:

$$\frac{\partial c}{\partial t} dt \cdot dx = -D \frac{\partial c}{\partial x} dt + \left[ D \frac{\partial c}{\partial x} + \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) dx \right] dt$$
$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right)$$
(9.2)

This is the diffusion equation in one dimension. It may be generalised to apply to three dimensions. In the simplest, and fairly common, case, the diffusion coefficient D is constant, and the equation becomes:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{9.3}$$

This equation can be solved for appropriate initial and boundary conditions, but the solutions are of a complexity beyond the scope of this book. They have been discussed in detail for many systems by Crank [1].

In more complicated systems, such as fibres, the diffusion coefficient may vary with concentration. Equation (9.2) cannot then be solved analytically unless some relation between D and c can be substituted in it. Other complications arise when absorption takes place, because this removes molecules from the diffusion process. If there is swelling, the medium is moving as well as the diffusing substance. Crank [1] discusses ways of dealing mathematically with these problems.



9.1 Diffusion across unit area perpendicular to concentration gradient.

However, avoiding the mathematical complexity of exact solutions, we can often obtain useful approximate results by simpler methods. A special case of the equation gives the effect of diffusion from an infinite source of concentration  $c_0$  to a receiver whose mean concentration is c at a time t. This is illustrated in Fig. 9.2. Under these conditions, we have:

$$\frac{\mathrm{d}c}{\mathrm{d}t} \propto \frac{\mathrm{d}m}{\mathrm{d}t} \propto \left(-\frac{\mathrm{d}c}{\mathrm{d}x}\right) \propto \left[-\left(c-c_{0}\right)\right]$$

$$\frac{\mathrm{d}c}{c-c_{0}} = \frac{\mathrm{d}t}{\tau}$$
(9.4)

where  $\tau$  is a time constant.

On integrating, and assuming as initial conditions that c = 0 at t = 0, this gives:

$$-\log(c_0 - c) = \frac{t}{\tau} - \log c_0$$
(9.5)

which leads to

$$c = c_0 (1 - e^{-t/\tau}) \tag{9.6}$$

At  $t = \tau$ , we have

$$c = c_0 \left( 1 - \frac{1}{e} \right) \tag{9.7}$$

and thus  $\tau$  is the time taken for 63% of the total change to be completed, as shown in Fig. 9.3.

Differentiating Equation (9.6), we have:

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{c_0}{\tau} \,\mathrm{e}^{-t/\tau} \tag{9.8}$$

At t = 0 this becomes:

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{c_0}{\tau} \tag{9.9}$$

and thus it follows that  $\tau$  is also the time that the whole process would take if carried out at the initial rate.



9.2 Diffusion into a receiver from an infinite source of concentration  $c_0$ .



9.3 Change of relative concentration  $c/c_0$  in receiver, following diffusion from an infinite source of concentration  $c_0$ . The parameter  $\tau$  is a time constant depending on the particular diffusion conditions.



9.4 Diffusion across an air space to an absorbent.

If we consider the system shown in Fig. 9.4, where moisture is diffusing across a length l of air to the absorbing substance, we see that time for whole process at initial rate

$$\tau = \frac{M}{\mathrm{d}m/\mathrm{d}t}$$

mass needed to bring the absorbent into equilibrium. Applying equation (9.1), this becomes:

$$\tau = \frac{Ml}{D(c_0 - c_1)A}$$
(9.10)

where  $c_1$  = initial concentration at surface of absorbent and  $c_0$  = concentration at surface of conditioning solution.

For a homogeneous cylinder of length L and radius r in which there is a change of conditions at the surface, such as to cause a change in the equilibrium concentration in the cylinder from  $c_1$  to  $c_0$ , the mass absorbed will be given by the product of the volume of the cylinder and the change in concentration and the diffusion length is of

the order of the radius *r*. We can apply equation (9.10) to obtain the order of magnitude of  $\tau$ .

$$\tau \approx \frac{\pi r^2 L(c_0 - c_1) r}{D(c_0 - c_1) 2 \pi r L} \approx \frac{r^2}{2D}$$
(9.11)

This is one example of a general result, suggested by dimensional analysis, that in a single medium the order of magnitude of time involved in a diffusion process equals  $l^2/D$ , where *l* is the length along which diffusion has to take place.

### 9.2.2 Diffusion coefficients of fibre materials

Application of the theory of diffusion would enable one to work out diffusion coefficients in fibres from observations of the rate of uptake of water or of the movement of water into a fibre. However, a much simpler method may be applied when the same materials can be obtained in the form of thin films. Constant concentrations may then be maintained on either side of the film, and the rate of transport of water across the film may be measured when a steady state has been reached.

In a typical experimental arrangement, shown in Fig. 9.5, water vapour is continually pumped away from one side so that c = 0, and the other side is maintained at a constant value  $c_1$ . By repeating this for various values of c, one can obtain a series of values of the average diffusion coefficient over ranges from 0 to  $c_1$ . Since the system is in a steady state, the rate of flow dm/dt across unit area is independent of x, the position in the film, and we must therefore have:

$$\int_0^l \frac{\mathrm{d}m}{\mathrm{d}t} \,\mathrm{d}x = \frac{\mathrm{d}m}{\mathrm{d}t} \int_0^l \mathrm{d}x = l \,\frac{\mathrm{d}m}{\mathrm{d}t} \tag{9.12}$$

Substituting from Equation (9.1), we then obtain:

$$\frac{dm}{dt} = \frac{1}{l} \int_0^l -D \frac{dc}{dx} \, dx = -\frac{1}{l} \int_0^l -D \, dc \tag{9.13}$$

By a numerical process of successive approximations, the experimental results giving values of dm/dt for various values of  $c_1$  may be fitted to this equation, and the diffusion coefficients at the various concentrations may be determined.

Some results of measurements of this sort are given in Fig. 9.6. The wide range of values, from  $10^{-7}$  to less than  $10^{-9}$  cm<sup>2</sup>/s, should be noted. Diffusion is very slow in the dry state, but it becomes much more rapid at moderate or high regains. This



9.5 Flow through a thin film under steady conditions.



9.6 Variation of diffusion coefficients with regain: (a) keratin, after King [2]; (b) nylon, after Rouse [3]; (c) polyethylene, after Rouse [3]. Note differences in scales, especially different powers of 10 in values of D.

explains the extreme difficulty of removing the last traces of water from a fibre. An exception to this behaviour is polyethylene, which absorbs little water and in which diffusion becomes slower at higher regains.

From studies on the initial rate of absorption by fibres, Watt [4] and Mackay and Downes [5] report values of about  $2 \times 10^{-10} \text{ cm}^2/\text{s}$  for dry wool, and values in agreement with those shown in Fig. 9.6(a) for wool at higher regains.

Fukuda and Kawai [6] measured the rate of diffusion of water into para-aramid fibres by following the rate of uptake of water in by 200 mg of yarn. Values of diffusion coefficients are shown in Table 9.1.

### 9.2.3 Penetration into a dry fibre

Because the diffusion coefficient increases so rapidly with increasing concentration of water in fibres, it follows that the variation in moisture content through a fibre that is absorbing water will show a sharp boundary. The initial diffusion through the dry fibre is slow and determines the position of the advancing front, but, once some absorption has occurred, the diffusion becomes faster, and so one has a rapid buildup to the final value of the moisture content.

Crank [1] has calculated the variation of concentration with distance for diffusion coefficients related in various ways to the concentration. Examples with differing degrees of sharpness of the advancing front are shown in Fig. 9.7.

Hermans and Vermaas [7] have shown that this advancing front may be observed in thick filaments under the microscope because of the change in refractive index associated with it. Photographs of this effect are shown in Fig. 9.8. Observation of this rate of advance of the boundary is another method of determining the diffusion coefficient in fibres.

There is another effect that may slow down the approach to the final equilibrium moisture absorption. When water is absorbed by the fibre, swelling stresses are set up. Newns [8] has suggested that after the initial diffusion process, there is a second stage in which these stresses relax (see Section 16.3). This relaxation of stress in the fibres will, in effect, alter the equilibrium moisture condition towards which the diffusion is proceeding. It will thus delay the attainment of a final steady state.

Fibre	p/p <sub>s</sub>	$D_{ m skin} \ ( m cm^2/s  imes 10^{-12})$	$D_{ m core} \ ( m cm^2/s  imes 10^{-12})$
Regular <i>Kevlar</i>	0.140	2.38	3.56
C C	0.213	3.97	5.96
	0.303	4.10	6.15
	0.482	5.01	10.0
	0.668	5.40	21.6
	0.896	6.51	26.0
Kevlar 49	0.144	1.39	2.77
	0.264	1.45	2.90
	0.396	1.36	5.42
	0.652	1.54	6.18
	0.800	1.76	12.4
Kevlar 149	0.343	2.52	1.61
	0.464	3.15	2.02
	0.583	4.03	2.62
	0.825	6.18	2.61
	0.934	_	_

Table 9.1 Diffusion coefficients of para-aramid fibres. From Fukuda and Kawai [6]



9.7 (a) Relations between diffusion coefficients, D and  $D_0$ , and concentrations, c and  $c_0$ . (b) Concentration-distance curves for penetration into materials with different relations between diffusion coefficient and concentration. D =diffusion coefficient at concentration c,  $D_0$  = diffusion coefficient at concentration  $c_0$ , x = distance into material, t = time. After Crank [1]. Relation between D and c Ratio of *D* at  $c = c_0$  to *D* at c = 0 $D/D_0 = 1 + ac/c_0$ A: 26 A': 101  $D/D_0 = \exp(kc/c_0)$ B: 2 B': 95  $D/D_0 = 1 + 50 \log_e(1 + kc/c_0)$  C: 28 D: 5 D': 50  $D/D_0 = 1/(1 - \alpha c/c_0)$ 



*9.8* Micrographs showing boundary gradually penetrating into filament. After Hermans and Vermaas [7].

Newns has derived a mathematical analysis for a process in which diffusion and stress relaxation are coupled together.

# 9.2.4 Conditioning of a mass of fibres

During the conditioning of a mass of fibres, diffusion must take place in three stages. First, there will be diffusion (or convection) in the air from the source of water vapour to the surface of the mass of fibres. Secondly, there will be diffusion in the air in the interstices between fibres, from the surface of the mass to the surface of a fibre. Thirdly, there will be diffusion from the surface of a fibre to its interior.

A value of  $10^{-7}$  cm<sup>2</sup>/s may be taken for the diffusion coefficient within a hygroscopic fibre at medium humidities and, with a fibre radius of  $10^{-3}$  cm, equation (9.11) would give  $\tau = (10^{-3})^2/(2 \times 10^{-7}) = 5$  seconds.

The time taken for diffusion in the air, whether inside or outside the specimen, will depend on the size, shape and density of the specimen; that for the diffusion outside will also depend on the ease of access to a source of moisture. The result for diffusion outside the specimen is calculated here for a typical case illustrated in Fig. 9.9. Suppose we have 100 g of dry cotton in a package 10 cm long and 2 cm in radius, placed in a close container, 10 cm from a solution giving a relative humidity of 65% at its surface, that is, a concentration of water vapour of  $10^{-5}$  g/cm<sup>3</sup> at 20 °C. The mass of water to be absorbed for equilibrium is about 7 g. In still air at 20 °C, *D* is about 0.25 cm<sup>2</sup>/s. The area across which diffusion is occurring varies with the distance from the package, but we may take as the approximate area the surface of a sphere of radius 10 cm, that is,  $400\pi$  cm<sup>2</sup>. Applying equation (9.10), we then have:

$$\tau = \frac{7 \times 10}{0.25 \times 10^{-5} \times 400\pi} = 20 \times 10^3 \text{ s (5 hours)}$$

It is difficult to calculate the time taken for diffusion in the air within the specimen,



*9.9* Diffusion into a mass of fibres in three stages: A, in outside air; B, in air spaces between fibres; *C*, within the fibre.

but, since the area and length are both less than they are outside, we should expect the times to be of the same order of magnitude.

The two effects would take place to some extent concurrently. We note that the times for diffusion in the air are much greater than the time for diffusion in a fibre. The latter is very rapid because of the small diameter of a fibre. Consequently, in calculations concerning a mass of fibres, the individual fibres may usually be taken to be in equilibrium with the air at their surfaces; this also applies in the more complicated mechanism discussed later.

### 9.2.5 Comparison with experimental results

From the considerations discussed above, diffusion times can be estimated. These are found to be much shorter than the times needed in practice for conditioning specimens. For example, Clayton and Peirce [9] report that 90% of the total change in a single cotton hair takes about 32 minutes, and not 5 seconds as the diffusion calculation indicates; Roberts and Haly [10] obtained values of about 1 minute for single wool fibres. A cop takes about 5 days, compared with the value of 5 hours calculated above; a bale, in which diffusion calculations indicate a few weeks, takes years.

It is thus clear that other factors, besides the diffusion of moisture, are involved. The heat that is evolved when the fibres absorb water, and which must be dissipated during conditioning, plays a dominant role in fibre assemblies.

However, in single fibres, there may be delays due to other causes. Mackay and Downes [5], using a vibroscope system, found very slow rates of change of regain in single wool fibres under conditions of forced convection, where the temperature changes due to heat of sorption were believed to be small. They investigated a variety of steps in both absorption and desorption. Some typical results are shown in Fig. 9.10. In many circumstances, there was an initial rapid change, followed by a slower change: the first stage is slowed down by an increase in fibre thickness, but the

second-stage rate is unaffected, which suggests that it is not controlled by diffusion but is a structural relaxation. The length changes of fibres as the absorption proceeds are complicated, and this also indicates structural changes.

## 9.3 The interaction of moisture and heat

### 9.3.1 The conditioning process

When textile fibres absorb moisture, they generate heat, as was described in Chapter 8. The evolution of heat raises the temperature of the fibres and increases their water



9.10 Examples of the rate of absorption and desorption of a 16.9  $\mu$ m diameter merino wool fibre at 20 °C from the studies of Mackay and Downes [5]. (a) Small changes (about 2% regain) in steps between the following values of r.h. %: (1) 0 and 12; (2) 23 and 35; (3) 46 and 58; (4) 68 and 74; (5) 95.0 and 96.4. (b) Changes between 0 and 100% r.h. (on facing page)



9.10 (Continued)

vapour pressure, consequently reducing the vapour pressure gradient and slowing down the rate of absorption.

The nature of the changes occurring during conditioning may be seen in the diagrams (Fig. 9.11). Owing to the higher vapour pressure in the atmosphere at the start of the process, moisture will pass into the specimen, which gives an increase in regain, generation of heat and a rise in temperature. The vapour pressure of the fibres will therefore increase, partly because of the increased regain but to a greater extent because of the rise in temperature. This process will continue until the vapour pressure of the fibres has become almost equal to that outside. This is a state of transient equilibrium in which further absorption is impossible until heat has been lost by the specimen. As heat is lost to the surrounding atmosphere, the temperature decreases, which allows a further increase in regain to occur and maintains the vapour pressure close to that of the atmosphere. This continues until final equilibrium is reached with both temperature and vapour pressure equal in fibre and atmosphere. It must be remembered that, throughout this cooling process, the absorption that occurs is generating heat which must also be lost to the surroundings.

For a change of regain  $\Delta R$  in a specimen of 100 g dry weight, the heat evolved will be  $Q_v \Delta R$ , where  $Q_v$  is the differential heat of sorption, and hence, if no heat is lost to the surroundings, we must have:

$$Q_{\rm v}\Delta R = (100 + R) (\Delta T) C$$

$$\frac{\Delta T}{\Delta R} = \frac{Q_{\rm v}}{(100 + R) C}$$
(9.14)

where  $\Delta T$  = rise in temperature and *C* = specific heat.

This equation governs the change of temperature during the approach to transient



*9.11* Changes in regain, temperature and vapour pressure during conditioning.

equilibrium. We may use it to calculate the position of transient equilibrium in a particular case on the assumption that no heat is lost during the initial stage.

Suppose 100 g of cotton are taken from an atmosphere of 28% r.h., 20 °C, in which the cotton would have an equilibrium regain of 3.7%, to an atmosphere of 70% r.h., 20 °C, giving an equilibrium regain of 7.7%. Trials with different final regains show that transient equilibrium occurs at a regain of 4.3%, as confirmed by the following calculation. The saturation vapour pressure at 20 °C is 17.5 mm of mercury. At 70% r.h., the vapour pressure is  $0.7 \times 17.5 = 12.25$  mm. The rise in temperature for an increase of 0.6% in regain is given by the above equation:

$$\Delta T = \frac{2600}{104 \times 1.45} \times 0.6 = 10.3 \ ^{\circ}\text{C}$$

The temperature is therefore  $30.3 \,^{\circ}$ C, for which the saturation vapour pressure is  $31.8 \,\text{mm}$ . Experimental data show that the relative humidity corresponding to 4.3% regain at  $30.3 \,^{\circ}$ C is 38.6%, and thus the vapour pressure over the specimen is  $0.318 \times 38.6 = 12.27 \,\text{mm}$ . Thus the vapour pressure over the specimen equals that in the conditioning atmosphere and there is transient equilibrium at 4.3% regain at  $30.3 \,^{\circ}$ C. Final equilibrium involves a rise in the regain to 7.7%.

The calculation shows that transient equilibrium results from only a small change of regain. Its attainment is thus a comparatively rapid process, and the main factor in determining the time for the whole process is the rate at which the heat being generated by the absorption can be dissipated. The lower rise in temperature given later in Fig. 9.16 indicates that the above rise in temperature is a maximum value on the assumption that the heat is generated throughout the fibre mass with no external heat loss.

Heat transfer by conduction follows the same law as diffusion, with heat replacing mass, temperature replacing concentration, and thermal capacity replacing volume in the equations. The heat diffusion constant is the thermal conductivity divided by the specific heat per unit volume. The changes thus follow the diffusion equations, already discussed, but with the complications arising from the interaction of two diffusion processes, which are discussed in the next section. One result of this is that final equilibrium is delayed.

Experiments on clumps of wool by King and Cassie [11] and Watt and McMahon [12] confirmed the above behaviour.

### 9.3.2 Penetration of a change into a mass of fibres

Heat effects and moisture absorption in hygroscopic materials, such as fibres, are inseparably interrelated: it is impossible to change one without affecting the other, and final equilibrium is impossible in one without the other. A complete description of changing conditions requires both the diffusion of moisture and the conduction of heat to be taken into account. Both are transfer phenomena following differential equations of the same form but with different constants, and they are linked by the heat of absorption and the change of moisture content with temperature at constant absolute humidity. Henry [13] carried out a mathematical analysis of the system for a simplified linearised model. Other studies, taking advantage of advances in computation, have treated more realistic models [14]. The general conclusion of the analysis is that, when a mass of fibres is exposed to new conditions, the change passes through the mass in two waves of diffusion, with different diffusion constants,  $D_1$  and  $D_2$ . To the parts of the change associated with each wave, we may apply the methods discussed in Section 9.2.1, the appropriate diffusion constant being used.

By steady-state methods, in which constant conditions are maintained on either side of the material, as in Fig. 9.12, the diffusion coefficient,  $D_{\rm M}$ , for moisture in a system involving no temperature changes and the diffusion coefficient,  $D_{\rm H}$ , for heat in a system involving no moisture changes can be found. If the moisture and heat effects were independent of one another or only weakly coupled, then, in a system in which both were changing, each would diffuse independently, and we should have  $D_1 = D_{\rm M}$  and  $D_2 = D_{\rm H}$ .



*9.12* Steady-state conditions: (a) vapour pressure gradient at constant temperature; (b) temperature gradient at constant vapour pressure.

In most textile systems, however, the coupling between the two is strong, since the heats of absorption are high, and the moisture content changes rapidly with temperature at constant vapour pressure. In Henry's analysis, the strength of the coupling is given by a quantity which he refers to as  $(1 - \lambda v)$  and which would be one if the two were independent but tends to zero as the coupling becomes stronger. He has shown that, for hygroscopic fibres under most circumstances, it is reasonable to take:

$$(1 - \lambda v) = \frac{1}{1 + \frac{Q_v}{C} \left( -\frac{\partial M}{\partial T} \right)_c}$$
(9.15)

where  $Q_v$  = differential heat of sorption of the vapour in J/g (of water), C = specific heat of the material in J/(gK) of dry material, and  $(-\delta M/\delta T)_c$  = rate of decrease of moisture content as temperature increases, the concentration of water vapour remaining constant.

For cotton at room temperature, the values of  $(1 - \lambda v)$  are as follows:

r.h. (%)	10	30	50	70	90
$(1 - \lambda v)$	0.35	0.22	0.15	0.08	0.025

The value of  $(1 - \lambda v)$  increases slightly as the temperature increases and reaches 0.6 at 110 °C at 10% r.h.

Henry has shown that, when  $(1 - \lambda v)$  is small compared with 1, as would be the case in many textile applications, the following approximations hold<sup>1</sup>:

$$D_{1} = \frac{D_{\rm M} D_{\rm H}}{D_{\rm M} + D_{\rm H}}$$
(9.16)

$$D_2 = \frac{D_{\rm M} + D_{\rm H}}{1 - \lambda \nu}$$
(9.17)

If the two diffusion coefficients  $D_{\rm M}$  and  $D_{\rm H}$  have the same values, it follows that  $D_1$  is equal to half that value; if they are different,  $D_1$  is less than either but tends to equal the lower value as the difference becomes greater. Thus one wave travels through the material at a rate that is slower than would be expected from independent moisture or heat diffusion and may be as slow as half the rate of the slower of the two processes. Since  $(1 - \lambda v)$  is small, it follows from equation (9.17) that  $D_2$  is large. Consequently, the other wave passes through the material at a rate that is much faster than either of the two independent processes.

Table 9.2 gives values of the diffusion coefficients worked out by Henry for cotton under various conditions. These figures show how the diffusion rates decrease as the humidity increases; increase as the temperature increases; and decrease as the density of packing increases. They show that under some conditions  $D_{\rm M}$  is greater than  $D_{\rm H}$ , but under other conditions this is reversed. The values of  $D_1$  and  $D_2$  are related to them as described above.

<sup>&</sup>lt;sup>1</sup>Henry [15] also gives more exact expressions for the diffusion coefficients and provides nomograms to assist in their calculation.

Density (g/cm <sup>3</sup> )	Temperature	r.h.	Diffusio	on coeffic	р	n		
	(°C)	(%)	D <sub>M</sub>	D <sub>H</sub>	<i>D</i> <sub>1</sub>	D <sub>2</sub>		
0.2	70	20	4.5	34	4.1	130	0.094	0.0037
		65	3.1	12	2.5	140	0.192	0.0040
		90	0.93	3.2	0.72	160	0.22	0.0013
	50	65	21	16	9.3	230	0.39	0.041
	80	65	90	20	17	690	0.17	0.11
0.5	20	20	1.4	16	1.3	63	0.050	0.0016
		65	0.92	5.7	0.80	66	0.13	0.0019
		90	0.28	1.5	0.24	62	0.15	0.0006
	50	65	5.7	7.7	3.4	99	0.38	0.023
	80	65	27	9.8	7.4	210	0.24	0.087

Table 9.2 Coupled diffusion for cotton assemblies [15]

In addition to the speed of the two waves, the magnitudes of the changes they carry are also important. Henry has shown that, if  $f_1$  and  $f_2$  are functions of position and time, being the appropriate solutions of the diffusion equation for the particular problem and differing only in their timescale (owing to the different diffusion constants,  $D_1$  and  $D_2$ ), then, for a change of temperature at the outside of a mass of material without change of vapour pressure:

$$\frac{\Delta T}{(\Delta T)_{\rm f}} = (1 - p)f_1 + pf_2 \tag{9.18}$$

where  $\Delta T$  is the change in temperature at a given time at a given position in the material,  $(\Delta T)_{\rm f}$  is the final change of temperature and *p* is the fraction determining the relative magnitudes of the two waves.

This means that a change of temperature  $p(\Delta T)_f$  passes through the material with the velocity of the fast wave, defined by  $f_2$  and  $D_2$ , while the remainder of the change  $(1 - p) (\Delta T)_f$  is transmitted with the velocity of the slow wave. The shape of the waves varies with circumstances but is indicated in Fig. 9.13 most of the change takes place over a narrow interval and tails off at a distance from the main wave front. Values of p are given in Table 9.2, and they show that an appreciable proportion of a temperature change may be carried on the fast wave. For a change of humidity at the outside of the material without change of temperature, the vapour concentration, or absolute humidity, in the air over the fibres passes through the specimen according to the same relation with the same value of p.

It is more convenient in following the conditioning process to consider changes  $\Delta M$  in the moisture content of the material, owing to a change in external circumstances, such as a change in vapour pressure at constant temperature or a change in temperature at constant vapour pressure. The change in moisture content does not follow the same equation as the changes in temperature or vapour concentration but follows approximately the equation:

$$\frac{\Delta M}{(\Delta M)_{\rm f}} = (1+n)f_1 - nf_2 \tag{9.19}$$



9.13 Fast and slow waves in diffusion into a material.



*9.14* Transmission of temperature change through a cotton cylinder by diffusion. A, outer air temperature; B, observed temperature at centre of cylinder; C, theoretical temperature at centre of cylinder. After Cassie and Baxter [16].

where n is the fraction defining the relative magnitude of the two waves. The negative sign of the fast wave means that it is carrying a change in the opposite direction to the main change. However, values of n are small, as shown in Table 9.2, and the magnitude of the fast wave is less than that of the forward part of the slow wave. Consequently, the resultant disturbance is never negative. Almost the whole change is carried on the slow wave. The effect of the fast wave is to cause a slowing down of the first part of the change in moisture content, but it has little effect on the major part of the change.

Figure 9.14 shows experimental results obtained by Cassie and Baxter [16] for the transmission by diffusion alone of a temperature change through the wall of a cylinder made of cotton of density  $0.12 \text{ g/cm}^3$  in a linen cover. The external air was suddenly changed in temperature from 17 to 29 °C, without change of vapour pressure. The change in temperature at the inside of the cylinder was measured, and the graph clearly shows the division of the change into two parts corresponding to two waves. The agreement with theory is fairly good, part of the divergence being due to the effect of the linen cover.

To summarise the work of Henry, and Cassie and Baxter, changes of temperature and absolute humidity, transmitted by diffusion through a mass of hygroscopic fibres, are divided roughly equally between fast and slow waves. Even where there are no final changes in temperature or vapour concentration, there may be transient changes transmitted on the fast wave, with the slow wave restoring the original condition. Several examples of the changes, which are of obvious importance in clothing materials, are given in Fig. 9.15. Changes of moisture content are transmitted almost entirely by the slow wave. In fibres that absorb no water, moisture and heat will diffuse independently at their own rates. The water vapour will pass solely through the spaces between the fibres.

### 9.3.3 Experimental confirmation of a computational model

Approximations in Henry's analysis were reduced in a computational model by Li and Luo [14]. The predictions were verified by experiments on double jersey fabrics



*9.15* Changes in temperature, absolute humidity (or vapour pressure) in air in contact with fibres, and moisture content during diffusion, for (a) rise in humidity at constant temperature; (b) rise in temperature at constant absolute humidity; and (c) rise in temperature at constant relative humidity. Dotted lines: F, fast wave; S, slow wave. Full lines: total change. Left-hand end of lines (surface of material) shows final condition. Right-hand end of lines (interior of fibre) shows initial conditions. For falls in humidity and temperature, the curves will be the negative of those shown here.

of wool, cotton, an acrylic with micropores and polypropylene [17]. Fabric samples,  $3 \text{ cm} \times 15 \text{ cm}$ , were suspended in a cell at 20 °C and the relatively humidity was changed in a single step from 0 to 99% with an air-flow of  $1.7 \text{ m s}^{-1}$  over the fabric surface. Table 9.3 gives details of the fabrics. For the moisture-absorbing fibres the first and second-stage diffusion coefficients  $D_1$  and  $D_2$  have a complicated non-linear dependence on moisture content M.

Figure 9.16 shows the changes in moisture uptake and temperature. The predictions, based on the arbitrary constants in the expressions for diffusion coefficients, are in good agreement with experimental results. The very small change in the polypropylene fabric takes place rapidly. The changes are increasingly slower and the temperature increases greater with increasing moisture absorption of the materials. Figure 9.17 shows 3D plots of changes through the thickness of the fabric with time. The water vapour pressure quickly reaches a constant equilibrium value through the whole thickness. The trough in the plots of moisture content and the inverted trough for temperature reflect the faster changes at the two fabric surfaces and the slower changes within the fabric.

### 9.3.4 Changes under forced draught

So far we have been considering changes due to diffusion processes, but changes due to blowing air through the material are also of interest. This subject has been studied by Cassie and his coworkers [16, 18, 20] and Daniels [19].

If air is forced through a mass of hygroscopic fibres, theory indicates that the change in conditions will be transmitted in two waves, similar to the two waves found in the diffusion process. The first wave passes through with the same velocity as the air-stream, and the second wave lags behind. If diffusion effects are neglected and it is assumed that the air velocity is constant at all places (which it will not be, owing to variations in the resistance to air-flow), theory shows that the waves should both be sharp changes, as in Fig. 9.18, if there is a sudden change in conditions. In fact, the slow wave is so slow that diffusion is not negligible, and a more exact theory enables its shape to be calculated. As in diffusion, temperature and vapour concentration

Wool	Cotton	Acrylic	Polypropylene
20.6	13.3	18.4	20.0
20	20	21	18
272	275	287	279
2.96	2.19	2.14	2.42
1.04 + 68.2 <i>M</i> -1342.59 <i>M</i> <sup>2</sup>	0.8481 + 50.6 <i>M</i> -1100 <i>M</i> <sup>2</sup>	11.2 + 4100 <i>M</i> -82 000 <i>M</i> <sup>2</sup>	13
1.614{1-exp[-18.163 × exp(-28.0 <i>M</i> )]}	2.5{1-exp[-3.5385 × exp(-45 <i>M</i> )]}	62.3	13
	Wool 20.6 20 272 2.96 1.04 + 68.2 <i>M</i> -1342.59 <i>M</i> <sup>2</sup> 1.614{1-exp[-18.163 × exp(-28.0 <i>M</i> )]}	Wool         Cotton           20.6         13.3           20         20           272         275           2.96         2.19           1.04 + 68.2 M         0.8481 + 50.6 M $-1342.59 M^2$ $-1100 M^2$ 1.614{1-exp[-18.163         2.5{1-exp[-3.5385 $\times exp(-28.0 M)$ ] $\times exp(-45M)$ ]	Wool         Cotton         Acrylic           20.6         13.3         18.4           20         20         21           272         275         287           2.96         2.19         2.14           1.04 + 68.2 M         0.8481 + 50.6 M         11.2 + 4100 M $-1342.59 M^2$ $-1100 M^2$ $-82 000 M^2$ 1.614{1-exp[-18.163         2.5{1-exp[-3.5385         62.3 $\times exp(-28.0 M)$ ] $\times exp(-45M)$ ] $\times exp(-45M)$ ]

Table 9.3 Double jersey fabrics tested by Li and Luo [17]



*9.16* Diffusion into fabrics in change from 0 to 99% r.h. Theoretical lines and experimental points: (a) moisture uptake; (b) temperature change at surface of fabric. From Li and Luo [17].

changes are roughly equally divided between the two waves, and there may be transient changes on the fast wave, whereas moisture content changes occur mainly on the slow wave.

The theory has been tested experimentally by blowing air through the walls of a hollow cylinder as shown in Fig. 9.19. The walls of the cylinder were 1 cm thick, and the fibres were packed to a density of 0.147 g/cm<sup>3</sup>; the air velocity was 1.75 cm/s. When steady conditions had been attained at one temperature, the temperature of the incoming air was suddenly changed, without change of vapour pressure, and the change in temperature of the outgoing air was measured. Figure 9.20 shows the good agreement between experiment and theory. Results for various fibres are given in Fig. 9.21 and Table 9.4. It is found that the time taken for the slow wave to pass

![](_page_20_Figure_0.jpeg)

9.17 Change in fabrics from 0 to 99% r.h. with time and depth into fabric: (a)–(c) cotton; (d), (e) acrylic; (a), (d) vapour concentration; (b), (e) moisture content; (c) (f) temperature. From Li and Luo [17].

![](_page_21_Figure_1.jpeg)

9.18 Ideal transmission of change by a forced draught.

![](_page_21_Figure_3.jpeg)

*9.19* Textile cylinder for testing change of condition on blowing air through a mass of fibres. After Cassie and Baxter [16].

through increases as the steepness of the curve of regain against relative humidity increases. Consequently, the more absorbent the fibres, the slower is the change. In addition to the results given by Baxter and Cassie, some values have been calculated for synthetic fibres and are included in Table 9.4. These are only very approximate, since such factors as the specific heat of the material, which can be neglected for hygroscopic fibres, will be important for hydrophobic fibres.

# 9.4 Practical effects

# 9.4.1 Conditioning

The above discussion has shown that the rate of conditioning (meaning the change of regain) of fibres will depend on the slow wave resulting from the combination of heat

![](_page_22_Figure_1.jpeg)

*9.20* Transmission of temperature change through a textile cylinder by forced draught: A, ingoing air temperature; B, temperature after passing through cylinder, experimental; C, temperature after passing through cylinder, theoretical. After Daniels [19].

![](_page_22_Figure_3.jpeg)

*9.21* Transmission of temperature change from 20 to 35 °C through various fibres in textile cylinder. The curves show temperature of air after passing through cylinder: A, acetate; B, cotton; C, wool. After Baxter and Cassie [20].

Material	Time for slow v	wave	Amplitude (°C)				
	Calculated	Observed	Fast wave	Slow wave			
Cotton	15.7	13.8	5.7	9.3			
Flax	20.5	19.5	5.9	9.1			
Kapok	19.9	23.6	6.0	9.0			
Viscose rayon	26.6	30.0	5.9	9.1			
Acetate	16.1	19.6	6.5	8.5			
Wool	22.1	28.4	5.9	9.1			
Silk	19.0	19.8	6.4	8.6			
Nylon	8						
Polyester (PET)	4						
Acrylic (PAN)	2						

*Table 9.4* Transmission of temperature changes under forced draught through apparatus shown in Fig. 9.19 with dimensions in text [16]

and moisture diffusion. The change will take place roughly exponentially, as is shown in Fig. 9.22. For a given set of conditions, a given proportion of the total change will always take the same time irrespective of the magnitude of the total change. For example, three-quarters of the change from 8 to 10% regain will take the same time as three-quarters of the change from 9 to 9.1%. The actual time taken for a change to occur will depend on the ease with which heat and moisture can be dissipated from the specimen. This is influenced by many factors: the size, shape and density of packing of the mass of fibres; the type of fibre; the temperature; and the general level of regain at which the change occurs.

The numerical values for the effect of these factors can be based on a standard half-change period of 12 hours for a slab of cotton fibres 2.5 cm thick, with a density of  $0.5 \text{ g/cm}^3$  when dry, at a regain of 7%, and at a temperature of 18 °C. The time for other percentages of the total change may be obtained by multiplying the basic half-change period of 12 hours by the factors given in Table 9.5<sup>2</sup>.

The effects of the principal factors that influence the rate of conditioning are as follows.

• *Size and shape of package.* The greater the distance for which heat has to be transferred through the mass of fibres (which is an effective heat insulator), the slower will be the rate of conditioning. Heat generated in the centre of a bale will take a long time to escape. It will escape more rapidly from a smaller package or from the same mass of material spread out in a thin layer.

The total amount of heat that has to be lost is proportional to the volume of the package. The rate of loss of heat will depend partly on the time taken for the heat to reach the surface, decreasing as the distance to the surface increases, and partly on the rate of loss of heat from the surface, increasing as the surface area increases. In fact, mathematical analysis shows that:

![](_page_23_Figure_6.jpeg)

9.22 Rate of conditioning in practice.

<sup>&</sup>lt;sup>2</sup>Based on information from the Cotton Silk and Man-made Fibres Research Association.

*Table 9.5* Time for conditioning. Basic half-change period of 12 hours has to be multiplied by appropriate factors for other conditions

Percentage of total change	5	10	20	30	40	50	60	70	80	90	95	99
Factor	<u>1</u> 80	<u>1</u> 20	<u>1</u> 6	<u>1</u> 3	<u>2</u> 3	1	$1\frac{1}{2}$	2	3	6	8	14
						Den: (g/cr	sity m³)		F	actor		
Size and shape	of pack	age:					0.09			-	<u>1</u>	
с. (0.8 ×	volume	e of pa	ckage	) <sup>2</sup>			0.17			-	1 3	
Factor = ( surface area )						$0.35 \frac{2}{3}$		23				
(measured in cm)						0.5			1			
						0.7			1	<u>1</u> 2		

Material	Factor	Average regain	Factor	Temperature (°C)	Factor
Cotton	1	0	6	5	2 <sup>3</sup> / <sub>8</sub>
Mercerised cotton	$1\frac{1}{4}$	1	2	10	1 <u>3</u>
Viscose rayon	2	2	1	15	$1\frac{1}{4}$
Cuprammonium rayon	1 <u>3</u>	4	2 3	20	<u>7</u> 8
Fortisan	$1\frac{2}{3}$	6	$\frac{3}{4}$	25	<u>5</u> 8
Acetate	$1\frac{1}{4}$	7	1	30	<u>3</u> 8
Silk	$1\frac{1}{2}$	8	1 <u>-1</u>		
Nylon	$\frac{2}{3}$	10	2		
		12 14	3 5		
		( volume	$)^2$		

conditioning time  $\propto \left(\frac{\text{volume}}{\text{surface area}}\right)$ 

(-----)

For packages of the same shape, this reduces to:

conditioning time  $\propto$  (linear dimension)<sup>2</sup>

Different specimens will have values of these quantities differing by at least a million times, and this is the most important factor in determining whether the time taken in conditioning is seconds or years. The other factors to be considered have smaller effects, though they may be more easily changed.

• *Bulk density*. The mass of moisture absorbed, and so the amount of heat evolved, for a given change of regain is proportional to the density of packing of the material. It is therefore found that:

conditioning time  $\propto$  density

- *Material*. There are some variations depending on the nature of the material. The numerical values are given in Table 9.5.
- *Regain.* The rate of conditioning is slower at the extreme values, as shown in Table 9.5. This results from differences in the diffusion constants.
- *Temperature*. Conditioning is more rapid at higher temperatures, since the heat transfer, in common with most other processes, occurs more rapidly at higher temperatures. At low temperatures, conditioning is slow. Darling and Belding [21] found the following times for 80% of the change in wool yarn: 5 °C, 10 hours; -18 °C, 95 hours; -30 °C, 260 hours.
- *Air circulation*. The ventilation around a mass of fibres is important in affecting the rate of loss of heat from the surface of the specimen and thus the rate of conditioning.

Quantitative values for the influences of the above factors are summarised in Table 9.5.

Conditioning may be speeded up by carrying it out in two stages. The theory has been worked out by Crank and Henry [22] for sheet and cylindrical specimens. Figure 9.23 shows the theoretical behaviour during conditioning of an initially dry plane sheet. The conditioning is more rapid when the specimen is first placed in an atmosphere much damper than is required, for the final state and then, after a period, transferred to an atmosphere, giving the required equilibrium condition. Since the outer layers will have come into equilibrium with the damper atmosphere, there is a fall in the amount of moisture in the specimen after the transfer, and thus the optimum procedure involves allowing the specimen to absorb somewhat more moisture than is finally required. Another procedure that may be adopted is to place the material in a

![](_page_25_Figure_7.jpeg)

*9.23* Methods of conditioning in practice: A, infinite atmosphere of required condition; B, two-stage processes; C, closed systems containing correct total amount of water. After Crank and Henry [22].

closed system containing the required total amount of water: this gives more rapid conditioning than the use of an infinite atmosphere of the required condition but is less rapid than the shortest two-stage process.

#### 9.4.2 Influence in clothing

The value of the heat of absorption in clothing was mentioned in the last chapter. The discussion in this chapter shows that, in a hygroscopic material, a considerable part (the fraction carried on the slow wave) of an external temperature change is delayed in its passage through the material.

This happens even if air is being blown through the material. Thus only a part of the total change reaches the body immediately, and the body is given time to adapt itself to the remainder of the change. Under almost all conditions, this will be beneficial in clothing materials. The best fibres from this point of view will be the most hygroscopic fibres. In non-absorbing fibres, the delay in the transmission of temperature change will be only that due to the insulating power of the material.

Farnworth [23] extended the treatment to multilayer clothing and also took account of condensation and wet insulation. An extensive account of thermal and moisture transport in fibrous materials, with particular reference to clothing is given in the book edited by Pan and Gibson [24].

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# 10.1 Introduction

The account of moisture absorption given in the last three chapters has been concerned with the behaviour of fibres exposed to atmospheric humidity, but the interactions of fibres with liquid water are also important. The removal of water from masses of fibres has practical application in the drying of textiles, where the initial surplus water may be removed by squeezing, by centrifuging, or merely by gravity, as in 'drip-dry' materials.

Fundamental experimental investigations have made use of two methods: centrifuging and suction. The latter is particularly useful, since it can easily be related to the behaviour at high relative humidities.

# 10.2 Centrifuging of wet fibres

# 10.2.1 Experimental method

The centrifugal method has been used by Preston and his colleagues [1, 2]. It is basically simple. The mass of fibres is swung round in a centrifuge, so that it is subject to a high field of force, which in Preston's experiments ranged from 1000 to 5000 times the gravitational field. Under the action of this force, the water rapidly drains out of the fibre mass.

The method of supporting the fibres in the centrifuge influences the results. If they are placed in a hollow container, so that the centrifugal field presses them against a porous plate, then this will tend to compact the fibre mass and reduce the space that can be filled with water, but if the material is in the form of yarn wound in small hanks and placed on hooks, this compacting will not occur.

# 10.2.2 Theoretical estimate of water retention

In a waterlogged state, all the spaces between the fibres will be filled with water. Under the action of gravity, and to a much greater extent under high centrifugal fields, this water will drain out. Finally a stage will be reached in which the water that remains is held by surface tension in capillary spaces between the fibres, just as a column of water will remain suspended in a fine capillary tube. The exact form of these spaces will depend on the way in which the fibres are packed together. The retention of water will also be affected by the alignment of the spaces with respect to the centrifugal field.

For the simple case, illustrated in Fig. 10.1, in which circular fibres are closepacked parallel to the direction of the centrifugal field, it is possible to work out the equation for the equilibrium condition. We shall also make the simplifying assumption that the curvature of the meniscus is negligible at the end of the tube from which the water empties.

The spaces between the fibres will be roughly triangular tubes, and these hold the capillary water. If *p* is the length of the perimeter formed by the three sides of one of these tubes, then the force due to surface tension will be  $\sigma p \cos \theta$ , where  $\sigma$  is the surface tension and  $\theta$  is the contact angle. The centrifugal pull on the water in a tube is *mg*, where *m* is the mass of water in the tube and *g* is the acceleration due to the centrifugal field. At equilibrium, these two forces must balance, and we have

$$mg = \sigma p \cos \theta \tag{10.1}$$

It is clear from this equation that as the centrifugal field increases, the mass of water that can be retained in a tube of a given perimeter decreases.

As can be seen from the plan view of the close packing, Fig. 10.1(b), the length of each side of the tube is equal to one-sixth of the circumference of a fibre. This can be related to the linear density (mass/unit length), c, of the fibre and its density,  $\rho$ , for, if R is the fibre radius, we have:

$$\pi R^2 \rho = c \tag{10.2}$$

$$p = 3\left(\frac{2\pi R}{6}\right) = \pi R = \sqrt{\left(\frac{\pi c}{\rho}\right)}$$
(10.3)

It is also clear from the plan that there are twice as many spaces between fibres as there are fibres (since each fibre can be regarded as having one-third share in six spaces), and the mass M of fibre associated with one tube is therefore given by:

$$M = \frac{1}{2}ch$$
 (10.4)

![](_page_28_Figure_11.jpeg)

10.1 (a) Capillary spaces between fibres filled with water, in centrifugal field.(b) Plan of close-packed fibres, showing spaces between them.

where h is the total height of the fibre mass parallel to the centrifugal field.

The fractional water retention r of the specimen is given by:

$$r = \frac{\text{mass of water}}{\text{mass of fibre}} = \frac{m}{M}$$
(10.5)

Substituting from equations (10.1), (10.3) and (10.4), we obtain:

$$r = \frac{2\sigma\cos\theta\,\sqrt{\pi}}{gh\sqrt{(cp)}}\tag{10.6}$$

This equation will only apply exactly to the simple example that we have described, but it is reasonable to suppose that an equation of the same form, though with different numerical constants, would apply in the more complex cases that occur in reality. For a given system, it may be expected that:

$$r \propto \frac{\sigma \cos\theta}{gh\sqrt{(cp)}} \tag{10.7}$$

A more detailed analysis has been given by Kuppers [3].

### 10.2.3 Experimental results

In experiments in which they varied the surface tension, the centrifugal field, and the contact angle, Preston *et al.* [2] obtained good agreement with the theoretical relation (10.7). As would be expected, they found that the nature of the packing influenced the amount of water retained. For example, less water was held by randomly oriented viscose rayon fibres than by parallel ones. In addition, any compacting of the specimen, reducing the size of the spaces, increases the amount of water retained.

Table 10.1 shows the amount of water retained by various fibre masses after centrifuging. It should be noted that centrifuging will never remove all the water held

	Regain (%)					
Material	Suction – 30 cm Hg, 40 kpa	Centrifuging 1000 <i>g</i> , 5 min				
Cotton yarn	52	48				
Viscose rayon yarn	106	103				
<i>Fortisan</i> yarn*						
0.11 dtex per filament	70	63				
1.1 dtex per filament	48	48				
Acetate yarn	31	31				
Loose wool	133	45				
Silk yarn	55	52				
Nylon yarn	14	16				

*Table 10.1* Water retained in centrifuging and suction. After Preston and Nimkar [4]

\**Fortisan*, which was an industrial rayon, is no longer made, but is included here to show the effect of fibre fineness.

in capillary spaces but will only reduce it to the amount given by equation (10.1). The method will not therefore give a reliable estimate of the water held in the fibre material itself at saturation.

# 10.3 Suction

## 10.3.1 Experimental method

An alternative method of investigation is to apply a hydrostatic tension to the waterlogged mass of fibres. A simple apparatus for doing this is shown in Fig. 10.2 and has been used by Preston and Nimkar [4]. The fibres are placed on a porous plate, below which there is a column of water leading to a mercury manometer. It is essential that there should be a continuous water-path between the mercury and the water surrounding the fibres. Lowering the right arm of the manometer puts the water into a state of hydrostatic tension, which will tend to pull the water away from the fibre mass. This will be resisted by the forces of surface tension.

### 10.3.2 Relation between suction, capillary size and humidity

The force exerted by surface tension depends on the curvature of the water meniscus. If the curvature is great, there will be a high capillary force, which will resist the hydrostatic tension, but, if it is low, the force will be small and the hydrostatic tension will empty the capillary space. The critical condition, when the two forces just balance, is given by the usual equation:

$$P = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{10.8}$$

where P = hydrostatic pressure, and  $r_1$  and  $r_2$  are the principal radii of curvature.

![](_page_30_Figure_9.jpeg)

10.2 Apparatus for removal of water from a mass of fibres by suction.

If the spaces are circular and the contact angle is zero, this relation reduces to  $P = 2\sigma/r$ , where *r* is the radius of the capillary. If the spaces have plane parallel walls, separated by a width 2w, it reduces to  $P = \sigma/w$ . The spaces between fibres will vary in shape and will lie somewhere between these two conditions. The re-entrant spaces in some rayon fibres will approximate to the second case.

The use of Kelvin's equation [5] enables the relative humidity corresponding to any hydrostatic tension to be calculated. The relation is:

$$\log_e H = \frac{PM}{\rho RT} \tag{10.9}$$

where H = relative humidity (fractional), M = molecular weight of water,  $\rho$  = density of water, R = gas constant and T = absolute temperature. Consequently, the results of suction experiments may be related to experiments in which the specimen attains equilibrium with a given relative humidity.

#### 10.3.3 Experimental results

Figure 10.3 shows some values of the moisture retained in the mass of fibres plotted against the hydrostatic tension (negative values of hydrostatic pressure). The corresponding values of humidity are also shown. Figure 10.4 shows the way in which data obtained by the suction method join on to normal absorption data.

It will be noticed that there is a very rapid rise near saturation. This is when water held in capillary spaces becomes important. The filling of capillary spaces does not cause any increase in volume. Hence, if the water causing volume swelling (plus that filling the void space between the fibre molecules, discussed in Section 12.1.6) is subtracted from the total water retained, we can get a figure for the amount of

![](_page_31_Figure_8.jpeg)

10.3 Removal of water from fibres by suction. After Preston and Nimkar [4].

![](_page_32_Figure_1.jpeg)

*10.4* Combination of suction data with normal sorption isotherms of viscose rayon. After Preston and Nimkar [4].

![](_page_32_Figure_3.jpeg)

*10.5* Hysteresis in removal of water by suction: viscose rayon. After Preston and Nimkar [4].

capillary water present. Preston and Nimkar [4] state that this is a significant amount only at relative humidities greater than 99%.

Hysteresis is found to persist even at the very high humidities corresponding to suction experiments. This is shown by Fig. 10.5, in which the water retained is plotted against the reciprocal of the hydrostatic tension, which is a more convenient way of presenting the results.

Comparative values for the water retained by various fibres after a suction experiment are given in Table 10.1. In the suction method, the force tending to remove the water is independent of the amount of water in the capillary space (if this is assumed to be constant in size). The space will consequently either be emptied completely if it is larger than the critical value given by equation (10.8), or left completely full if it is smaller. By contrast, in the centrifugal method, the force decreases as the space empties, and thus any spaces may be emptied to some extent, but none will be completely emptied unless the field is infinite. We should not therefore necessarily expect a close correlation between the results of suction and centrifugal experiments. However, the values given in Table 10.1 show that, for many fibre materials, a hydrostatic tension of 30 cm of mercury (corresponding to 99.97% r.h.) gives very similar results to the application of a centrifugal field of 1000g for 5 min. Capillary–sorption cycles in a variety of fibre assemblies have been studied by Burgeni and Kanpur [6].

Another method of estimating the amount of water retained as capillary water is to freeze the sample. Any free liquid water freezes at 0 °C, and thus its amount can be calculated from the latent heat at 0 °C. Absorbed water has an influence over a range of temperatures. Haly [7] used this method and found that the saturation regain of wool was 33.9% at 0 °C. Any excess over this amount is free water.

A practical example of the removal of water by means of hydrostatic tension occurs when a wet textile material is hung up vertically. The water at any point will be under a hydrostatic tension determined by the length of the continuous column of water below it. If evaporation is prevented, one would expect an equilibrium to be obtained in which there would be a gradient of wetness from top to bottom. Preston and Nimkar [1] have confirmed that this is so.

#### 10.4 Interactions

If capillary water is present in the spaces between fibres, the fibres will be attracted to one another by the hydrostatic tension in the water. Consequently, when a waterlogged mass of fibres is dried, the individual fibres will be drawn together and there will be forces of adhesion wherever they cross. This adhesion will persist down to any humidities at which capillary water is present, even if it is only in amounts that are insignificant by comparison with the total water absorption.

Preston and Nimkar [4] have both calculated and measured the force of adhesion between fibres due to this cause, and Table 10.2 gives examples of their results. The agreement between experiment and theory is good for the glass fibres. The low experimental values obtained with the cellulosic fibres are probably due to surface irregularities.

Wettability is another response related to surface tension and contact angles, Lee and Michielsen [8] review aspects of surface tension, contact angles and contact angle hysteresis in the context of super-hydrophobicity and the Lotus effect, which leads to water drops rolling off a tilted surface.

			Force (µN)	
Fibre	Radius (µm)	r.h. (%)	Calculated	Measured
Viscose rayon	16	93	15	1
Cuprammonium rayon	158	93	145	6
Glass	41	0	0	0
		31	37	34
		64	37	26
		93	37	32
		Wet	0	0
Glass	54	31	49	48
		64	49	34
		93	49	37

*Table 10.2* Force of adhesion between fibres due to surface tension of water. After Preston and Nimkar [4]

### 10.5 References

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