7
Equilibrium absorption of water

7.1 Introduction

It has been known for a long time that fibres take up moisture from the air. Leonardo da Vinci (1452–1519) has, in his notebooks, two drawings of self-indicating balances with cotton on one pan and wax on the other; the increased weight of the cotton in a damp atmosphere alters the setting of the balance so that it can be used 'for knowing the quality and density of the air and when it will rain'. Earlier, Nicholas of Cusa (1401–1463) had measured the increase in weight of wool for the same purpose. The first detailed investigation of the subject was carried out by Schloesing [1] in 1893. Between 1924 and 1932, Urquhart and his collaborators conducted an investigation of the absorption of cotton, rayons and acetate that will remain a classic of painstaking experiment.

The property of absorbing moisture is a valuable feature of clothing materials. Apart from its direct utility in keeping the skin dry, the absorption of water causes the fabric to act as a heat reservoir, protecting the body from sudden changes of external conditions. However, it may be a disadvantage in drying the hygroscopic fibres that it is necessary to remove the absorbed moisture that is not present in the non-hygroscopic synthetic fibres.

The absorption changes the properties of fibres. It causes swelling to occur, which alters the dimensions of the fibre, and this, in turn, will cause changes in the size, shape, stiffness and permeability of yarns and fabrics, The mechanical properties and the frictional properties are altered, so affecting the behaviour of the fibres in processing and in use. Wetting and drying may lead to permanent set or creasing. The moisture condition of the material is one of the most important factors in determining its electrical properties; 'static' is much less likely to occur in damp conditions.

The above examples show the technological importance of moisture absorption in fibres. There is also a direct commercial interest. In 100 kg of raw cotton, for example, there may be up to 12 kg of water. Since it is expensive to pay for this at the price of raw cotton, it must be allowed for in calculating the weight to be charged.

7.2 Definitions

7.2.1 Humidity

The *absolute humidity h* of an atmosphere is defined as the mass of water in unit volume of air. The dampness of the air is also indicated by the *vapour pressure p* that

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is, the partial pressure of the water vapour in the atmosphere. The most convenient term is the relative humidity H, given by:

$$H = 100 \left(\frac{h}{h_s} \right) \qquad (7.1)$$

where h_s is the absolute humidity of saturated air at the same temperature. At ordinary air temperatures, this ratio differs inappreciably from the corresponding ratio of vapour pressures.

Since the properties of fibres vary with the moisture condition, testing should be done under controlled conditions. For this purpose, a *standard temperate atmosphere* is defined as one of 65% r.h. and 20 °C[1]. The permitted tolerances for testing are ± 2% r.h. and ± 2 °C. An uncontrolled indoor atmosphere is usually drier than this.
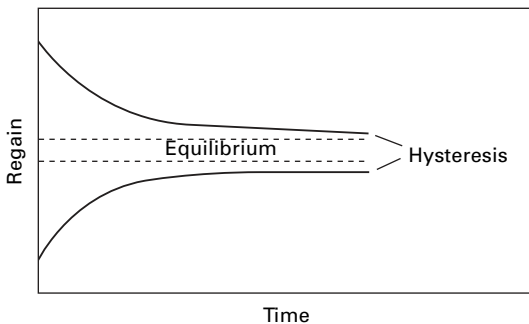
7.2.2   Equilibrium

When a textile material is placed in a given atmosphere, it takes up or loses water at a gradually decreasing rate (Fig. 7.1) until it reaches equilibrium, when no further change takes place. This is a dynamic equilibrium, which occurs when the number of water molecules evaporating from the specimen in a given time becomes equal to the number condensing and being absorbed.

7.2.3   Regain and moisture content

The amount of water in a specimen may be expressed in terms of either the regain or the moisture content:

$$\text{regain} = \frac{\text{mass of absorbed water in specimen}}{\text{mass of dry specimen}} \times 100\% = R \qquad (7.2)$$

7.1 The approach to moisture equilibrium, with hysteresis depending on whether sample is gaining or losing water.

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[1] In tropical and sub-tropical countries, 27 °C may be used as a secondary standard.

$$\text{moisture content} = \frac{\text{mass of absorbed water in specimen}}{\text{mass of undried specimen}} \times 100\% = M \quad (7.3)$$

The two are simply related, for, if the dry mass $= D$ and the mass of absorbed water $= W$, we have:

$$R = \frac{100\,W}{D} \quad (7.4)$$

$$M = \frac{100\,W}{D + W} = \frac{100\,W/D}{1 + W/D} = R\frac{1 + R}{100} \quad (7.5)$$

7.2.4   Recommended allowance

For commercial transactions, a set of values of recommended allowance[2] has been agreed on. The mass of a consignment of a textile material on which the charge is to be based is known as the *correct invoice mass* and is equal to the mass that the consignment would have if its regain were the recommended allowance.

It should be noted that the values of the recommended allowances are chosen purely for convenience, since they are near the values found in practice and are not the regains in a standard atmosphere. The values of the recommended allowances are included in Table 7.3.

7.3   **Measurement of regain**

7.3.1   The gravimetric method

The gravimetric method is the basic method of measuring regain or moisture content, and any indirect method must be calibrated by it. The sample to be tested is weighed, dried and then weighed again. The regain R is calculated as follows:

mass of undried specimen $= W + D = m_1$

mass of dried specimen $= D = m_2$

$$R = \frac{100\,W}{D} = 100\,\frac{(m_1 - m_2)}{m_2}\% \quad (7.6)$$

No difficulty is involved in the first weighing, except that care should be taken that the regain of the sample does not change before or during the weighing. The determination of the dry weight does involve certain difficulties.

7.3.2   Difficulties involved in drying the specimen

To obtain the most accurate results, the sample should be dried by exposing it in an enclosed space containing an efficient drying agent, such as phosphorus pentoxide,

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[2]*Commercial regain* in the United States

at room temperature. The high affinity of the drying agent for water results in complete drying of the specimen, and, since the temperature is not raised, other changes in the specimen are not likely to occur. This method, however, has the disadvantage that it is extremely slow. Davidson and Shorter [2] found that a period of from 4 to 6 weeks was necessary to dry 8 g specimens of cotton. This slowness renders the method impracticable except for very special investigations.

The usual method in practice is to dry the specimen in an oven at about 110 °C. The raising of the temperature of the air lowers its relative humidity, since, although the absolute humidity of the air changes very little, the saturation humidity increases enormously. Water must then evaporate from the specimen until it reaches equilibrium. Since all chemical processes are more rapid at higher temperatures, this does not take long.

However, the relative humidity in the oven is not zero. If the air outside the oven has a relative humidity of 50% at 20 °C, when it is heated to 110 °C its relative humidity will be 0.8%. The moisture that is left in equilibrium with this humidity is known as the *residual regain* and is the first inherent source of error in the oven method. It results in a measured value of the regain that is too low, since the loss of weight on drying is not as great as it should be.

The heating of the specimen may cause substances other than water, for example, oils and waxes present as impurities, to be driven off from the sample. This is known as *permanent loss* and is the second inherent source of error in the oven method. It causes the measured loss of weight to be greater than it should be and thus gives a high value of the regain. Figure 7.2 illustrates the two sources of error. Figure 7.2(a) shows the permanent loss of soda-boiled and unbleached cotton after 3 h heating, dry, in a vacuum. Figure 7.2(b) shows the residual regain in cotton due to a water vapour pressure of 8 mm of mercury (1.07 kPa) at various temperatures. The change of weight of bleached cotton follows this curve closely, but the raw cotton shows a greater change in weight owing to the permanent loss. The amount of permanent loss can be shown by allowing the specimen to reabsorb water and then drying again at 90 °C; for bleached cotton, this shows little difference from the previous value, but the value for raw cotton is almost 0.2% lower than the previous value owing to the permanent loss in the first drying to 130 °C.

The amounts of error due to these causes will vary with the conditions but they may both be of the order of 0.2% in the value of the regain. The true dry weight is given by:

true dry weight = oven-dry weight – residual regain + permanent loss

7.3.3   Experimental practice

For commercial and routine testing, a special oven is usually used. It contains a basket in which about 1 kg of material can be placed and weighed *in situ*. The material is then dried until its weight becomes constant in a current of heated air. The dry sample is weighed with the air current switched off. Stephenson [3] has described the experimental errors that may occur:
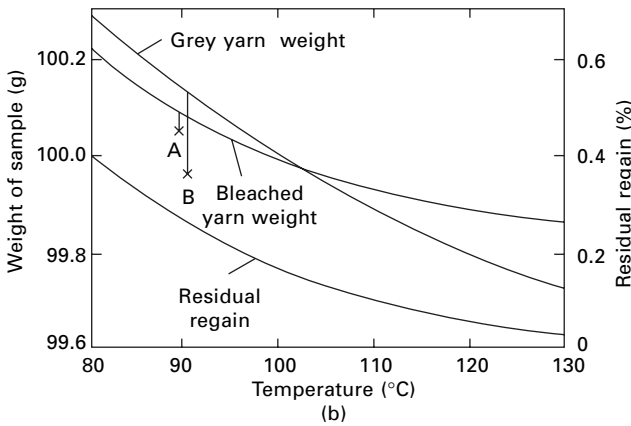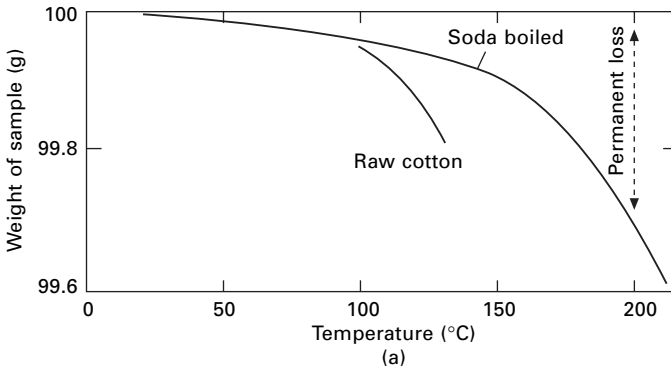
7.2 (a) Permanent loss on heating 100 g of dry cotton for 3 h *in vacuo*. (b) Change in weight of samples of cotton dried at water vapour pressure of 8 mm of mercury (1.07 kPa). Points A and B are for material dried at 130 °C, allowed to reabsorb water at room temperature, and then dried at 90 °C. From Davidson and Shorter [2].

- The differing density of hot and cold air will affect the buoyancy of the specimen.
- Convection currents may affect the balance, but this can be minimised by a well-designed oven.
- Absorption may occur during weighing, after the air current has been switched off.

The errors should not total more than 0.1% in the value of the regain. Balls [4] found that random errors in routine oven-testing amounted to ±0·2% in the regain value for cotton at 10% regain.

More rapid tests may be made by using an apparatus in which a stream of hot air is blown through a container holding the specimen. The container can be removed and closed for weighing. In another instrument, a standard weight of material is used, and, after drying, the regain is directly indicated on a scale.

Laboratory tests are usually made on smaller samples, which are placed in weighing bottles. For the most accurate work, they are dried in a desiccator with a drying agent.

A more rapid method is to dry them in a small chemical oven at 110 °C. The bottles are removed from the oven, stoppered up and cooled before being weighed. The errors liable to occur in this method are:

- absorption of moisture before the stopper is replaced;
- enclosure of hot air in the container, giving it added buoyancy (the amount of the error due to this cause will depend on the relative size of container and sample);
- convection errors, which should be negligible if the bottle is cooled;
- diffusion of moisture into the bottle, which can be prevented by a good seal.

Stephenson [3] estimates that the errors due to these causes may be between 0.2 and 0.8% in the value of the regain.

Table 7.1 gives a comparison of results obtained by LeCompte and Lipp [5] when using various methods for determining moisture in wool. They conclude that toluene distillation (Section 7.3.4) is the most accurate method in this case. Impurities accounted for less than 0.01% in the water distilled over.

The techniques involved in obtaining accurate relations between equilibrium regain and relative humidity have been reviewed by McLaren and Rowen [6].

7.3.4   Other direct methods

Another method of determining the water in the material is by heating the sample with toluene (boiling point 111 °C) and measuring the amount of water that distils over and is collected in a receiver. The toluene used should be saturated with water. The method is not open to the error of residual regain, since a fresh atmosphere of toluene is continually being supplied. Errors due to permanent loss can be checked by analysis of the water collected.

Van Lamoen and Borsten [7] have described a method for the titration of water, which they consider to be superior to the use of drying ovens, though the reagents are relatively expensive.

7.3.5   Indirect methods

Methods based on the variation of the electrical properties of fibres have been used to indicate their moisture condition.

Table 7.1 Regain determination for wool [5]

Method	Average	Range of values of regain % in three tests
Vacuum oven over P_2O_5	7.13*	0.22
Conditioning oven 110 °C	7.16	0.19
USDA suction drier 150 °C	7.27	0.15
Forced-draught drier	7.33	0.16
Toluene distillation	7.77	0.17

*Still falling at 0.05% per day at end of test.

The Shirley Moisture Meter [8] was, at one time, widely used for the measurement of electrical resistance of cotton, and, although it is no longer manufactured, its essential features could be reproduced in other equipment. As illustrated in Fig. 7.3, an electronic circuit measures the resistance between the inner and outer electrodes of the cone, which is pressed onto the sample of fibre. Other types of electrode may be used for material in other forms. Because of the rapid variation of electrical resistance with moisture content, the method is sensitive. The resistance values depend on fibre type and are sensitive to temperature, additives, contact pressure and material form, but, if a resistance meter is properly calibrated for the test, it gives an accurate measure of resistance. Instruments based on the variation of dielectric constant are also available, but they suffer from the disadvantages that the weight and distribution of material between the plates of the condenser must be controlled and that the variation of dielectric constant with moisture content is much less than the variation of resistance. The capacity method has been extensively used in process-control applications, but, where it can be applied, a resistance method is better.

Another indirect method of measuring regain is to shake up a known weight of the sample with calcium carbide in a closed container. This reacts with the water and generates acetylene; measurement of the pressure indicates the regain.

The Shirley Moisture Regain Indicator may also be mentioned. A prepared sample of material is hung on a balance, and, as the relative humidity changes, its weight changes, and the regain is directly indicated on a scale. This may be placed in a spinning room and used for calculating the dry or standard weights of the material being processed.

7.4   Relation between regain and relative humidity

7.4.1   General

There is hysteresis in the relation between the regain of a textile material and the relative humidity of the atmosphere with which it is in equilibrium. This is illustrated
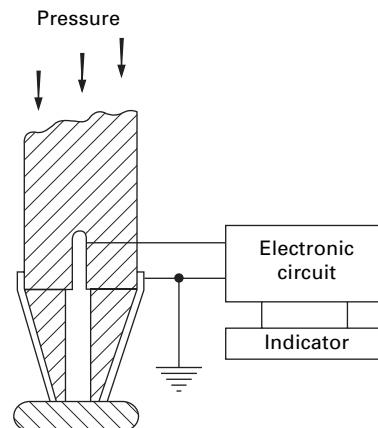

7.3 Basic features of Shirley Moisture Meter.

in Fig. 7.1, which shows the approach to equilibrium in the same atmosphere of two specimens initially at different regains. The specimen that originally had the higher regain also has the higher regain at equilibrium. Depending on its previous history, the specimen may come to equilibrium anywhere in a range of metastable states and does not come to a true thermodynamic equilibrium. In relating regain to relative humidity, it is usual to plot two curves (Fig. 7.4). The first curve A, commonly called the absorption isotherm, is a plot of equilibrium regains at successively higher humidities of a specimen initially bone-dry; the second curve B, the desorption isotherm, is a plot for a specimen initially wet, at successively lower humidities. The nomenclature is unfortunately in confusion. *Desorption* always refers to the loss of water, but the terms *sorption*, *absorption* and *adsorption* are used variously by different authors for the uptake of water or for the whole general phenomenon. Adsorption is, however, best reserved for a specialised meaning implying a particular mechanism of attachment of the water molecules.

The curves usually have the sigmoidal shape shown in Fig. 7.4: a rapidly increasing regain at low humidities, followed by an almost linear portion, and then a more rapid rise at high humidities. The two curves must join at the origin, but Urquhart and Eckersall's experiments [9] indicated that they were separate at 100% r.h. Wetting the specimen caused the values to lie on a higher curve than could be reached by exposure in a saturated atmosphere. Ashpole [10] has disputed this view and produced experimental results indicating that there is a rapid rise in the absorption curve near the saturation point (Fig. 7.5). Experiments are difficult near saturation, since the rapid rise in the absorption means that a large amount of water has to be taken up under a small vapour pressure gradient when conditioning is very slow, while, if there are any temperature fluctuations, it is easy for supersaturation and condensation to occur. Ashpole devised the technique of enclosing the specimen in waxed gauze surrounded by a cellophane membrane and placing this in a solution of sugar of the concentration needed to give the required humidity. This reduces the distance over which diffusion has to occur and so hastens the attainment of equilibrium. By special precautions, temperature fluctuations were kept below 10^{-4} °C. At the highest humidities,
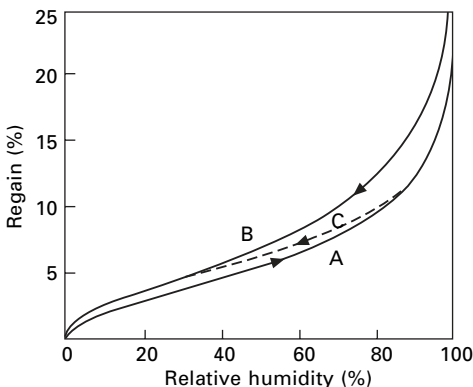
7.4 Typical curves of regain of soda-boiled cotton against relative humidity: A, absorption; B, desorption; C, intermediate [9].
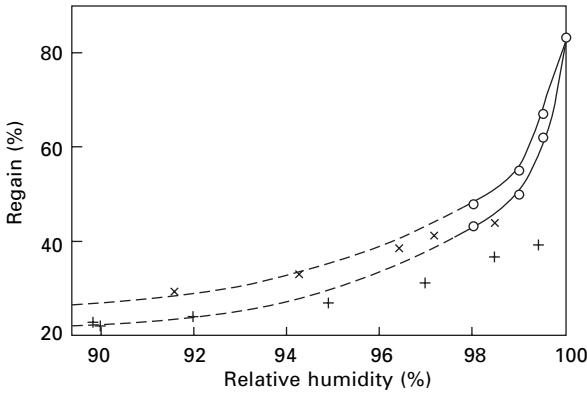
7.5 Hysteresis loop for viscose rayon near saturation. o Ashpole's experimental values [10]; + absorption; × desorption values found by Urquhart and Eckersall [9].

Ashpole found that the regain varied continuously with time, and, to allow for this, he extrapolated back to zero time. This effect casts some doubt on the validity of his results, and the exact form of the curves near saturation remains uncertain.

The two curves are the limiting equilibrium values. Equilibrium can be attained at any point between them by taking the specimen through a suitable chain of humidities. The curve C in Fig. 7.4 shows a typical result for the desorption of a specimen that had previously been absorbing. The intermediate curves are also sigmoidal in shape.

Taylor [11, 12] has shown that hysteresis occurs even in cycles at low relative humidities. The results given in Table 7.2 show that at about 1% r.h. the hysteresis due to desorption from 4% r.h. may be only a little less than half the hysteresis due to desorption from saturation.
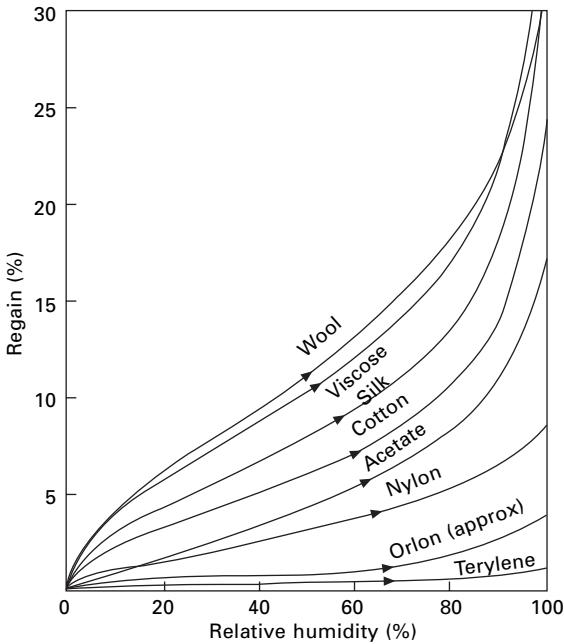
7.4.2   Comparison of various materials

Figure 7.6 shows the relations between regain and relative humidity for various textile fibres, and Table 7.3 gives values of regains at 65% r.h. and the widths of the hysteresis loops.

Cotton shows the typical behaviour. There are small differences between cottons of different origins, for example, at 57.6% r.h. Urquhart and Williams [25] found

Table 7.2 Hysteresis in cycles at low regains [11, 12]

Material	r.h. (%)	Absorption regain (%)	(Desorption regain – absorption regain) (%)	
			cycle 0–4% r.h.	Cycle 0% r.h. to saturation
Viscose rayon	0.85	0.95	0.23	0.49
(Fibro)	1.7	1.38	0.14	0.69
	4	2.19	–	0.69
Cotton	1.7	0.66	0.036	0.095
	4	1.07	–	0.159

7.6 Regain versus relative humidity for cotton [13], viscose rayon [14], acetate [14], silk [15], wool [16], nylon [17], *Terylene* polyester (PET) [18] and *Orlon* acrylic [18].

absorption regains ranging from 6.76% for a Texas cotton to 7.19% for a Peruvian cotton. After soda-boiling to remove impurities, the difference between these two cottons decreased to 0.12%. Processing, especially wet processing, may cause large changes in the amount of moisture absorbed. There are two principal effects: a removal of highly absorbing non-cellulosic impurities; and a change in the internal arrangement of the cellulose molecules. Heating the sample dry lowers the curve of regain against relative humidity, but wet heating raises it. Mercerisation without tension can increase the regain at a given relative humidity to 1.5 times its previous value; mercerisation under tension does not cause such a large increase [19].

A sample of cotton straight from the boll of the cotton plant or immediately after hot-wet processing shows a desorption curve higher than the usual one (Fig. 7.7). This is known as the *primary desorption curve*. Once the material has been dried below 50% r.h., it follows the usual curves. The intermediate curves for cotton are very long, as shown in Fig. 7.8. For example, if absorption is started from 10% r.h. on the desorption curve, the absorption curve will not be joined below 80% r.h. To be sure of getting on either the absorption or the desorption curve, it is necessary to start from almost complete dryness or wetness, respectively.

The effects of processing were shown to a marked extent by experiments by Gu [26] on naturally coloured green cotton, which contained 14.19% of fat, lignin and pectin, compared with 1.8% in white cotton. The moisture regain of the green cotton was 3.87% and of white was 8.6%. After treatments in NaOH solutions of varying

Table 7.3 Moisture absorption of fibres. Based on data by Ford [19] and other workers

| Material	Recommended allowance *or* commercial regain *or* conventional allowance* (%)	Absorption regain at 65% r.h. 20 °C** (%)	Desorption regain *minus* absorption regain at 65% r.h. 20 °C** (%)
Cotton [13]	8.5	7–8	0.9
Mercerised cotton [20]	–	up to 12	1.5
Hemp [21]	12	8	–
Flax [21]	12	7	–
Jute [22]	13.75	12	1.5
Viscose rayon [14]	13	12–14	1.8
Secondary acetate [14]	9	6, 6.9	2.6
Triacetate	–	4.5	–
Silk [15]	11	10	1.2
Wool [16]	14–19	14, 16–18	2.0
Casein [23]	–	14	1.0
Nylon 6.6, Nylon 6 [17]	$5^3/_4$ or $6^1/_4$	4.1	0.25
Polyester [18]	1.5 or 3	0.4	–
Acrylic	–	1–2	–
Modacrylic	–	0.5–1	–
Polyvinyl alcohol [18]	–	4.5–5.0	–
Polylactic acid [24]	–	0.4–0.6	–
Para-aramid (*Kevlar*, *Twaron*)		low modulus 7 to high modulus 1.2	–
Meta-aramid (*Nomex*)	–	5	–

Polyethylene. polypropylene, polyvinyl chloride, carbon, glass and ceramic fibres have zero moisture absorption.
*As given in BS 4784:1973; other standardising organisations may quote different values.
**The earlier measurements were at 70 °F (21.1 °C).
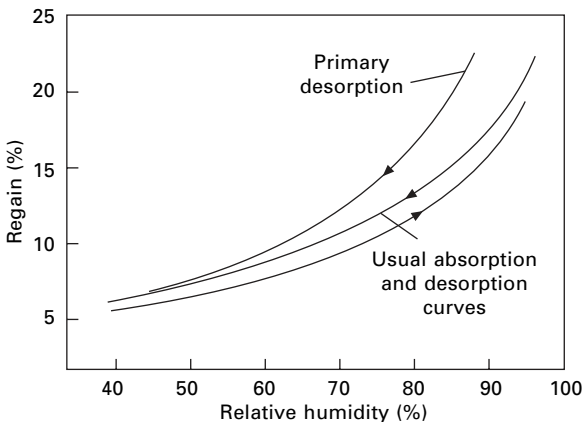
7.7 Primary desorption curve of raw cotton from boll. From Urquhart and Eckersall [9].
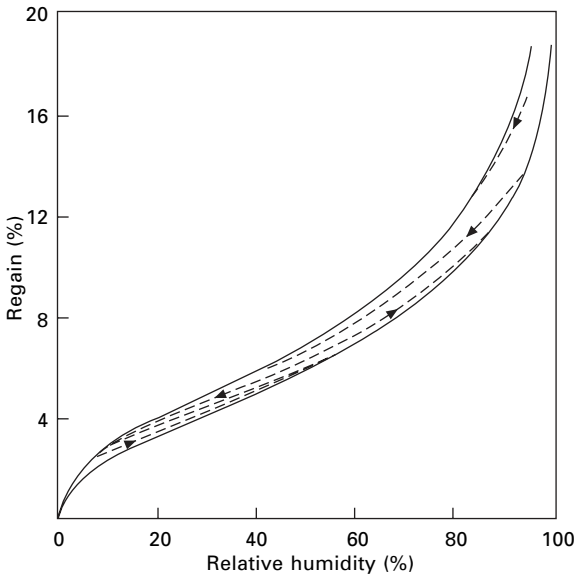
7.8 Intermediate curves for raw cotton. The outer full lines are for absorption and sorption between 0 and 100% rh; The inner dashed lines are for absorption and addesorption between intermediate humidities. From Urquhart and Eckersall [9].

strengths at different temperatures and for different times, the regain of the green cotton increased to 7.53–8.69%.

Viscose rayon has regain values that can be obtained by multiplying the regain values for cotton at the same humidity by an almost constant factor. For a particular specimen of viscose rayon, the figures were [14]:

r.h. (%)	5	20	40	60	80
Regain of viscose rayon/regain of cotton	1.99	2.13	2.08	2.03	1.98

For other specimens of viscose rayon, this ratio, which is often called the *sorption ratio* of the material, may not be as close to 2 as the values quoted, but it is a general feature of cellulosic fibres that their sorption ratios remain almost constant over the whole range of humidity.

Taylor's results [11] (Table 7.2) show that, although the absorption regain of viscose rayon is twice that of cotton, the difference between the desorption and absorption regains at low humidities is four times that of cotton. Above 30% r.h., this behaviour is reversed and cotton shows the greater hysteresis, in proportion to its regain.

Acetate has a curve of a different shape and does not show a rapid rise of regain at low humidities. The regains are lower than those of cotton, but the rate of change of regain with r.h. in the practical range above 20% r.h. is about the same.

Wool has a regain curve close to that of viscose rayon but of slightly different

shape. In particular, at high humidities the regain of wool is lower. The type of wool and its processing also affect the regain values. For example, Speakman [16] found regains at 63.3% r.h. ranging from 13.97% for a merino wool to 14.54% for a Wensleydale. Nicholls and Speakman [27] have shown that acid-treated wool has a lower equilibrium regain; thus, at 53.8% r.h., untreated wool had a regain of 12.68%, but wool containing 40 milliequivalents of acid per gram of wool had regains ranging from 11.89% for sulphuric acid to 9.79% for picric acid.

Figure 7.9, from Speakman and Cooper [28], shows that the intermediate hysteresis curves for wool are shorter than those for cotton, a change of 18% r.h. being sufficient to pass between the main absorption and the main desorption curves. This range is independent of the value of the regain.

Casein fibres have regains very close to those of wool at the same humidity but show a rather large difference between absorption and desorption values [23].

Silk has a regain intermediate between cotton and wool. Silk gum has a high regain, and the degumming causes a reduction in regain at 65 r.h. from 10.65 to 9.9% [15].

The synthetic fibres have low regains. Nylon has about half the regain of cotton. Some workers have suggested that hysteresis is absent, but Hutton and Gartside [17] showed that a small hysteresis definitely existed. At 80% r.h., they obtained regain values of 5.48% in absorption and 5.64% in desorption. Forward and Smith [29] have shown that the moisture absorption of undrawn nylon yarn can be appreciably altered by chemical treatment. Polyester (PET) fibres have a small regain. Many other polymer fibres have zero moisture absorption, as do inorganic fibres.

7.4.3   Influence of temperature

The curves of regain against relative humidity depend to a slight extent on temperature, the result being a family of isothermals. Figure 7.10 shows data for cotton. Except at
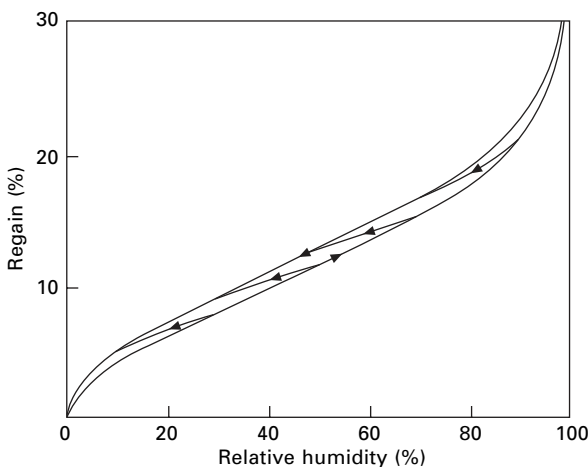
7.9 Intermediate curves for wool. The outer full lines are for absorption and sorption between 0 and 100% rh; the crossing lines are for absorption and sorption between intermediate humidifier From Speakman and Cooper [28].
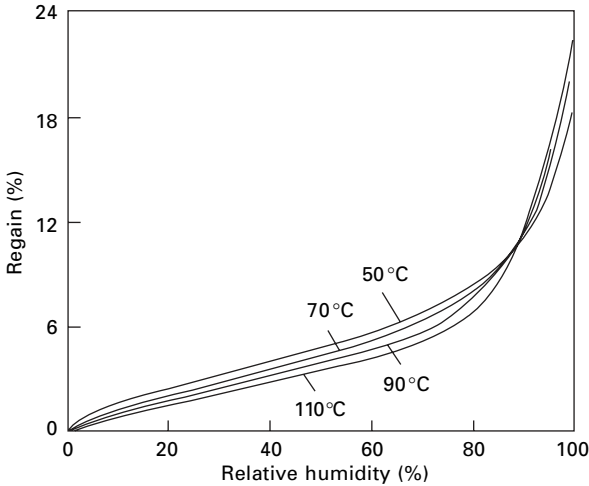
7.10 Effect of temperature on absorption of cotton. From Urquhart and Williams [30].
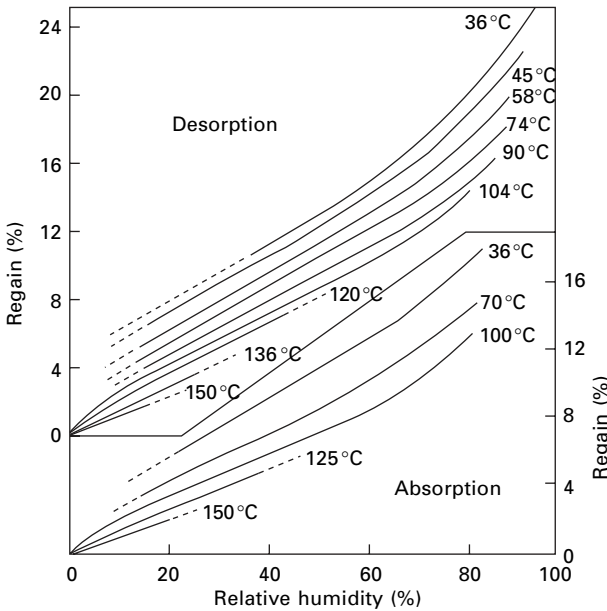
7.11 Effect of temperature on absorption of wool. From Wiegerink [31].

high temperatures and humidities, the regain decreases as the temperature increases. This is the expected thermodynamic behaviour for an exothermic reaction such as absorption. The increase above 50 °C at high humidities is due to a change in the internal structure and is associated with the irreversible hysteresis effects.

Wiegerink [31] tested a variety of fibres between 35 and 150 °C, and the curves for wool, shown in Fig. 7.11, are typical of his results. He found that when the logarithms

of the regains were plotted against the reciprocal of temperature, straight lines were obtained, with a change of slope at about 100 °C. Figure 7.12 illustrates this for viscose rayon. Darling and Belding [32] tested the same materials at low temperatures, but, owing to the slowness of conditioning, they were able to test only at a limited set of conditions. Their results indicate that the linear relations cease to apply below 20 °C. Below about 0 °C, the regain decreases. Values for the regain at 70% r.h. are given in Table 7.4.

7.4.4   Effect of stresses

The swelling of fibres during absorption means that the application of stresses will change the regain. Table 7.5 shows the increases in regain due to the application of a tension to filaments that were reported by Treloar [33, 34].

By contrast, the lateral compression of fibres, such as would come from applying tension to a twisted yarn, would lower the regain. For example, Nickerson [35] states
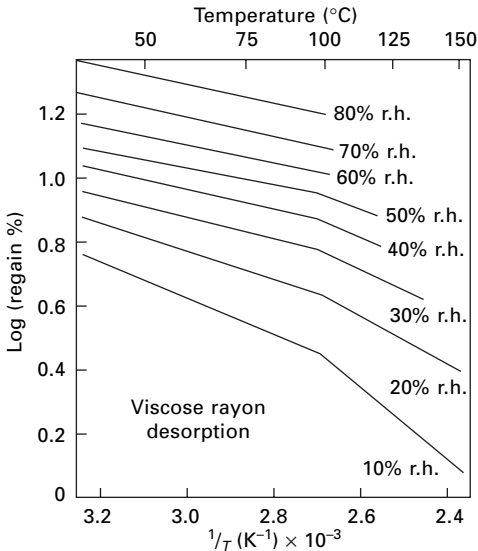
7.12 Effect of temperature on absorption of viscose rayon. T is absolute temperature in Kelvin (K). From Wiegerink [31].

Table 7.4 Change of regain with temperature [32]

Temperature	Regain at 70% r.h.			
(°C)	Cotton	Wool	Viscose rayon	Secondary acetate
−29	8.5	17	16	7.9
−18	9.8	18	17	9.6
4	9.7	17.5	17	9.0
35	7.8	15	14	7.1
71	6.7	13	12	6.2

Table 7.5 Effect of axial applied stress on moisture absorption at 75.5% r.h., 25 °C. From Treloar [33, 34]

Isotropic cellulose		Oriented cellulose		Horsehair	
Stress (MPa)	Increase in regain (%)	Stress (MPa)	Increase in regain (%)	Stress (MPa)	Increase in regain (%)
5.7	0.2	10.2	0.1	25.8	0.14
10.2	0.4	17.7	0.4	47.3	0.28
13.6	0.6	35.6	1.1		
27.4	1.5				
40.5	1.1				
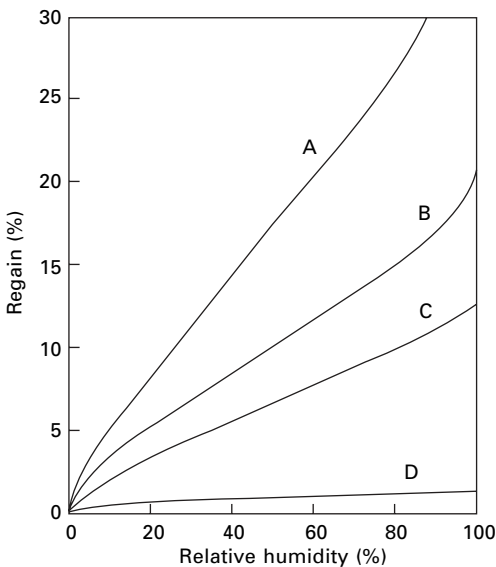
7.13 Absorption of spruce wood under stress: (A) material completely free of stress; (B) natural sorption, including internal restraints on swelling of block of wood; (C) volume of block of wood held constant, but allowing swelling into void spaces in wood cells; (D) wood cell walls (internal and external) held at constant volume.
Curve B is experimental; remainder are calculated. From Barkas [36].

that the application of 60% of its breaking load to a cotton yarn lowered the regain from 8.78 to 8.19%. Barkas [36] has studied this effect in wood, and the curves in Figure 7.13 show the large changes that can occur when severe restraints are applied.

7.5   References

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8.1   Definitions

When a fibre absorbs water, heat is evolved. If liquid water is taken up, this is similar to the heat of solution that occurs, for instance, when sulphuric acid and water are mixed. It results from the attractive forces between the fibre molecules and water molecules. If water vapour is absorbed, there is also heat similar to latent heat of condensation. The heat evolved may be expressed in various ways.

The *differential heat of sorption Q* (sometimes called the heat of absorption) is the heat evolved when 1 g of water is absorbed by an infinite mass of the material at a given moisture regain. It is expressed in joules per gram (of water absorbed).

The water may be absorbed from water vapour, to give a value Q_v, or from liquid water, to give a value Q_l. The relation between the two quantities is illustrated in Fig. 8.1. It follows from the First Law of Thermodynamics that the total heat evolved must be the same along each path, and therefore:

$$Q_v = Q_l + L \tag{8.1}$$

where L is the latent heat of condensation of water in J/g at the temperature concerned. The quantity Q_l is sometimes called the heat of swelling.

The *integral heat of sorption W* (sometimes called the *heat of wetting*) is the heat evolved when a specimen of the material at a given regain, whose dry mass is 1 g, is completely wetted. It is expressed in joules per gram (of dry material) and is almost always given in terms of absorption from the liquid state.

The relation between the differential and integral heats can be seen by considering the graph of integral heat of sorption against regain (Fig. 8.2). The increase of the regain by dr causes an amount of heat equal to $Q_l \cdot dr/100$ to be evolved. If this is
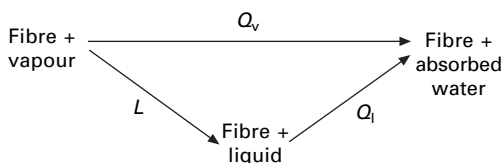
8.1 Relation between heats of sorption from vapour and liquid.

195
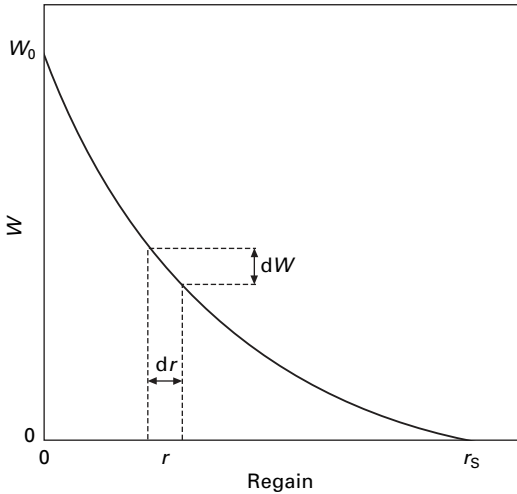
8.2 Variation of integral heat of sorption with regain.

integrated from a regain r to the saturation regain, r_s, it will give the total amount of heat evolved when the specimen is wetted, that is, the heat of wetting for the regain r. Thus:

$$W = \int_r^{r_s} \frac{Q_1 \cdot dr}{100} \qquad (8.2)$$

Conversely, the heat $Q_1 \cdot dr/100$ equals the decrease in the heat of wetting for the regain change dr, giving:

$$Q_1 = -100 \frac{dW}{dr} \qquad (8.3)$$

An integral heat of sorption defined as the heat evolved when 1 g of dry material is raised to the given regain is sometimes used. If we call this quantity W' and let W_0 be the heat of wetting from dryness to saturation, we have:

$$W' = W_0 - W \qquad (8.4)$$

8.2   Measurement

Heats of wetting may be measured calorimetrically. A known mass of the material at the required regain is placed in a calorimeter, and an excess of water is added. From the rise in temperature and the thermal capacity of the system, the heat evolved can be calculated and the heat of wetting determined. Because a large amount of water is needed to secure satisfactory wetting of the fibres, the temperature rise will be small, and careful experimental technique and sensitive temperature measurement are necessary. Several workers have described methods in detail [1–3].

The differential heats of sorption, which are of more practical and theoretical importance, may be obtained from the experimental values of the heats of wetting by

using equation (8.3). They may also be determined by calculation from the absorption isotherms. The Clausius–Clapeyron equation for water vapour, if the specific volume of liquid water is neglected in comparison with that of water vapour, is:

$$\frac{\mathrm{d}p_s}{\mathrm{d}T} = \frac{L}{TV_s} \tag{8.5}$$

where p_s = saturation vapour pressure of water, T = absolute temperature and V_s = specific volume of vapour at saturation vapour pressure.

Application of the equation to a textile system at constant regain r gives:

$$\left(\frac{\partial p}{\mathrm{d}T}\right)_r = \frac{Q_v}{TV} \tag{8.6}$$

where p = vapour pressure in equilibrium with the textile and V = specific volume of vapour at this vapour pressure.

But relative humidity = $H = (p/p_s \times 100)\%$. Thus

$$\log_e H = \log_e p - \log_e p_s + \log_e 100 \tag{8.7}$$

Differentiating with respect to temperature at constant regain, we have:

$$\left(\frac{\partial \log_e H}{\partial T}\right)_r = \frac{1}{p}\left(\frac{\partial p}{\mathrm{d}T}\right)_r - \frac{1}{p_s}\left(\frac{\mathrm{d}p_s}{\mathrm{d}T}\right)$$

$$= \frac{Q_v}{pTV} - \frac{L}{p_s TV_s} \tag{8.8}$$

If we assume the ideal gas laws, $pV = p_s V_s = RT$, this gives:

$$\left(\frac{\partial \log_e H}{\partial T}\right)_r = \frac{1}{RT^2}(Q_v - L) = \left(\frac{1}{RT^2}\right)Q_l \tag{8.9}$$

$$Q_l = RT^2\left(\frac{\partial \log_e H}{\partial T}\right)_r = -R\left[\frac{\partial \log_e H}{\partial(1/T)}\right]_r \tag{8.10}$$

Thus the differential heat of sorption can be obtained from the slope of the curve of $\log_e H$ against $1/T$ at constant regain. This relation, based on thermodynamics, only holds when one is dealing with a system in effective thermodynamic equilibrium. The results in Fig. 7.11 (see p. 191), which show that at high humidities, moisture regain increases with rise in temperature, so that $(\delta\log_e H/\delta T)_r$ becomes negative though Q_l remains positive, indicate that this is not always so for textile fibres. Where hysteresis exists, there can only be metastable equilibrium. Different results will be obtained depending on whether absorption or desorption values are used. It has also been pointed out by Rees [1] that the results obtained by this method depend to a great extent on the care with which the curves are drawn, and different workers calculate widely different results from the same data.

8.3   Results

Table 8.1 shows values of the heat of wetting of dry fibres, and Fig. 8.3 indicates how the heats of wetting decrease to zero at saturation regain. As would be expected, the heat of wetting is greatest for the most highly absorbing fibres and is very small in the non-hygroscopic fibres. Figure 8.4 shows that the heat evolved in going from 0% to 65% r.h. is proportional to the regain of the fibre at 65% r.h. Plotting these particular values eliminates the effect of loosely held water near saturation, which contributes little to the heat evolved.

Bright *et al.* [3] found that, for three specimens of polyester fibre of the same draw-ratio but different linear density, the heat of wetting was proportional to the external surface area, a value of 16×10^{-4} J/cm^2 being obtained.

Figure 8.5 shows the decrease in the differential heat of sorption as the regain increases. At zero regain, the differential heat of sorption of the cellulosic fibres is of

Table 8.1 Heats of wetting from zero regain W_0 (J/g)

Cotton [1]	46
Mercerised cotton [1]	73
Flax [2]	55
Viscose rayon [2]	106
Secondary acetate [2]	34
Wool [3]	113
Silk [4]	69
Nylon [3]	31
Polyester (PET) 2.4 dtex [3]	5
Acrylic (PAN) [3]	7
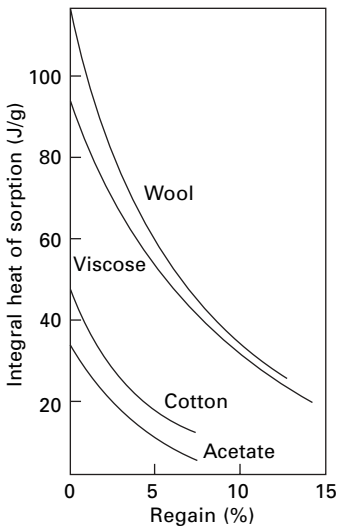
8.3 Variation of integral heats of sorption of cotton, viscose rayon, secondary acetate [2] and wool [3] with regain.
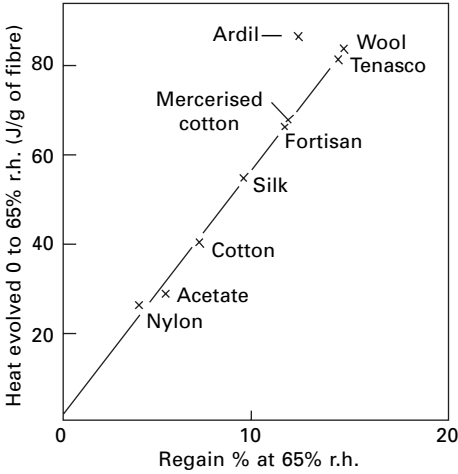
8.4 Relation between evolution of heat and regain [5].
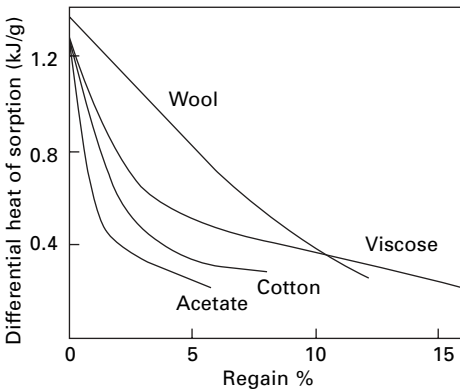
8.5 Variation of differential heats of sorption of cotton, viscose rayon, secondary acetate [2] and wool [3] with regain.

the order of 1250 J/g, which is about the same as the heat of hydration of hydroxyl ions. As absorption continues, the water is more loosely attached, and consequently less heat is evolved. Owing to the similarity in the nature of the absorption, all cellulosic fibres have differential heats of sorption that are close together at a given relative humidity. This is shown by the results in Table 8.2, which also includes values for other fibres. Wool and nylon have values that are close together, which indicates absorption on similar sites. The results given in Table 8.2 are typical values; there will be slight variations from these according to the particular specimen tested, as shown in Table 8.3.

Values of the differential heat of sorption found by calculation from sorption isotherms are usually somewhat lower than those obtained by direct measurement. Some examples of this are given in Table 8.4.

The values of the differential heat of sorption given here have been for absorption

Table 8.2 Differential heats of sorption Q_l (kJ/g)

Fibre	Relative humidity (%)					
	0	15	30	45	60	75
Cotton [2]	1.24	0.50	0.39	0.32	0.29	–
Mercerised cotton [1]	1.17	0.61	0.44	0.33	0.23	–
Viscose rayon [2]	1.17	0.55	0.46	0.39	0.32	0.24
Secondary acetate [2]	1.24	0.56	0.38	0.31	0.24	–
Wool [3]	1.34	0.75	0.55	0.42	–	–
Nylon [6]	1.05	0.75	0.55	0.42	–	–

Table 8.3 Integral and differential heats of sorption

Fibre	At zero regain		At 65% r.h.
	W (kJ/g)	Q_l (kJ/g)	Q_l (kJ/g)
Cotton			
Bengals [2]	47.3	1.33	0.25
Texas [1]	46.1	1.19	0.20
Sea Island [2]	46.9	1.24	0.28
various sorts and methods [1, 7]	41–54	–	–
Viscose rayon			
continuous filament [2]	106	1.17	0.30
staple fibre [2]	97	1.22	0.27
various sorts and methods [1, 7]	84–105	–	–

Table 8.4 Direct and calculated differential heats of sorption

Material	Regain (%)	Differential heat of sorption (kJ/g)	
		Calorimetric method	From sorption isotherms
Viscose rayon [2]	0	1.17	1.09 [8]
	5	0.53	0.44
	10	0.39	0.25
Acetate [2]	5	0.27	0.21
Cotton [1]	5	0.32	0.27
Wool [9]	6	0.59	0.54
	12	0.40	0.40
	18	0.17	0.26

Table 8.5 Heat evolved (in kJ) by 1 kg of material in going from 40 to 70% r.h.

Wool	159
Cotton	84
Viscose rayon	168
Acetate	50
Nylon	42
Terylene	4

from the liquid. Values for absorption from the vapour can be obtained by adding the latent heat of vaporisation of water (2.45 kJ/g at 20 °C). This is several times as great as most values of differential heat of sorption from liquid, and its addition reduces the proportional difference between the various fibres. At low humidities, the differential heat of sorption from the vapour will be about 4000 J/g, but, over the middle range of humidities, it will lie between 2500 and 3000 J/g, depending on the particular fibre and humidity.

8.4   Effects of evolution of heat

The evolution of heat has a considerable effect on the rate of conditioning of textile materials, as will be described in the next chapter. It is also an important feature of clothing materials. For example, on going from an atmosphere of 18 °C, 45% r.h., indoors to one of 5 °C, 95% r.h., outdoors, the regain of wool would change from 10 to 27%. A man's suit, weighing 1.5 kg, would give out 6000 kJ owing to this change, that is, as much heat as the body metabolism produces in 12 h. This evolution of heat is of physiological advantage, since it gives the body time to adjust itself to the new conditions. The greater the moisture absorption of the fibre, the greater will be the amount of heat evolved. Comparative values are given in Table 8.5.

8.5   References

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