D_e = effective diffusivity
D_i = diffusivity of species i
f = functional symbol
k = local mass transfer coefficient
k_f = forward reaction-velocity constant
K, K_α, K_β = equilibrium constants
K_i = modified equilibrium constants defined by Equation (17)
K' = effective equilibrium constant defined by Equation (33)
L = film thickness, jet length in Figure (1)
n = number of species
N_i = flux of species i
N_t = flux of total solute
N_t' = flux defined by Equation (38)
r_i = volumetric rate of production of species i by reaction
$\vec{r}$ = position vector
x, y = generalized position coordinates
Δ = displacement from chemical equilibrium
θ = time
∇ = gradient
∇^2 = Laplacian operator
$D/D\theta$ = substantial derivative

Subscripts

B = boundary
i, j = indices taking on values 1, 2, ... n.
m = main stream
0 = time zero
I = boundary I
II = boundary II

Superscript

^{0} = absence of reaction

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Mechanism of Drying Thick Porous Bodies During the Falling-Rate Period

II. A Hygroscopic Material

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A further analysis of the second falling-rate period in the drying of thick highly porous textile structures is made, this time in the case of drying wool, special attention being paid to the adsorbed water held by the wool in the air-dry region. As the solid-to-void ratio is low, the quantities of adsorbed water are small and have little effect on the general equilibrium. Values of thermal conductivity are calculated for wet wool.

In part 1 (*1*) experimental results were given for the heating and air drying of two thick highly porous textile structures. Extremes were chosen in a Terylene (British form of a polyester fiber) net fabric of open structure and a woolen flannel of close structure and the results compared for the two materials. It was found that despite the difference in structure a similar equilibrium between heat transfer inward and vapor diffusion outward was established at a constant pseudo-wet-bulb temperature during the second falling rate period.

A further important difference between the fabrics, which was neglected in the first treatment, is the hygroscopic nature of the wool, whereby some 30% of bound water is in equilibrium with the fibers when the surrounding atmosphere is saturated with water vapor. In this paper the data given previously for the wool are further analyzed with the adsorbed water taken into account. Values of the apparent thermal conductivity of the wet porous solid are also calculated.

WATER DISTRIBUTION IN WOOL BOBBIN

The woolen cloth, being wound on a spindle, formed an annular package just over 1 in. thick of about 3-in. O.D. and 6-in. long. The hot air flowed parallel to the outer surface, and thermocouples situated at each succeeding $\frac{1}{8}$ in. in depth and also just below the surface thickness of cloth provided a record of the temperature distribution during the drying cycle. Weighing gave the total weight of water held by the package as drying proceeded.

The General Distribution Deduced from the Temperature Record

In Figure 1 the curves showing the temperatures at the different depths are reproduced. In the case of Terylene it was shown that when the temperature registered by a thermocouple embedded in the cloth rises from the pseudo-wet-bulb temperature level, the material outside the position of the thermocouple is dry and the material within is wet. In other words, as the thermocouple is left

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in the dry region by the retreating water surface, the temperature rises sharply. In the case of the wool it is assumed that this temperature rise of the thermocouples marks the passing of a boundary within which there is pore water and the maximum quantity of adsorbed water associated with the wool. Outside the boundary the layers will be termed *air-dry*.* The liquid-water boundary is considered to be of uniform cylindrical shape, whereas in practice it will be irregular owing to slight inconsistencies in the material.

The time at which the water surface passed each thermocouple was noted from Figure 1, and hence the position of the water surface was noted with respect to time plotted in Figure 2. It is interesting to note from this figure that the water surface appears to leave the fabric surface just after the end of the first falling rate period. Thus the drying out of the surface could coincide with the linearity in agreement with the classical concept.

An average weight of free-water content per unit volume appertaining within the water surface can be calculated from the total weight of water and the radius of the water surface at any time. Such values are plotted in Figure 3.

The rapid fall of over-all free-water content (assumed uniform throughout the wet portion of the bobbin) during the constant-rate period represents the diminution of the water content through the flow of water to the surface. This is followed by a period of transition to the new equilibrium conditions when the temperature of the free water is rising from the wet bulb to the pseudo-wet-bulb temperature, after which the average free-water content appears to remain constant with time.

The Distribution of Adsorbed Water in the Falling-Rate Period

Although one cannot be certain that the limiting equilibrium between the amount of bound water and the vapor atmosphere in the pores is always reached, it is reasonable to assume that this is so and to obtain the amounts of adsorbed water from the appropriate desorption curve. King and Cassie (*2*) have deduced that the time to establish equilibrium conditions at the fiber is very short; it is the movement of vapor and changing temperature conditions which prolong the process. In the second falling rate period conditions are changing very slowly, and one might expect equilibrium conditions to be reached. McCready and McCabe (*3*) assumed this to be so in their analysis of the drying of slabs of paper pulp.

The amount of adsorbed water in a layer thus depends on the vapor pressure appertaining, which in turn depends on how the vapor concentration gradient varies between the water surface and the air stream. Use is made here of the analogy between temperature gradient and concentration gradient. In Figure 4 the temperature gradients are shown to be linear, and the assumption is therefore made that the concentration gradients are linear as well.

For particular times the values of p/T representing concentrations were calculated for each $\frac{1}{8}$-in.-thick layer by proportion from the gradient $(p_w/T_w - p_a/T_a)$; thus the mean partial vapor pressures and relative humidities for each layer were evaluated. Speakman's desorption data (*4*, *5*) were used to give the moisture regain for each value of relative humidity. In this manner the moisture content of each of the $\frac{1}{8}$-in. layers outside the water boundary was calculated at a number of different times in the second falling-rate period.

Table 1 gives the calculated values at times $t = 500$ and 800 min. along with the results of some experimental determinations. The latter were obtained at a later date, when the bobbin was cut up so that it might consist of a central portion and eight $\frac{1}{8}$-in.-thick layers which could be unwrapped and weighed after the bobbin had been dried for the appropriate time under similar experimental conditions.

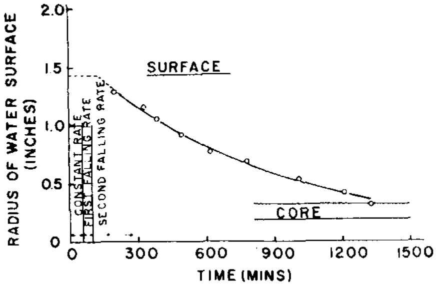

Fig. 2. Water radius vs. time.

There is good agreement between calculated and experimental values, which supports the many assumptions made in the calculations. The fact that the saturated vapor pressure increases rapidly with temperature means that the relative humidity falls off quickly with increased distance from the water surface. This and the sigmoid nature of the desorption curve produce the rapid fall off in the quantities of adsorbed water in the succeeding layers from the water surface; that is, most of it lies in the $\frac{1}{4}$ in. adjacent to the water boundary.

When one subtracts the adsorbed water in the air-dry region from the total water, the sloping dotted line in Figure 3 is produced, showing that the average free-water content within the boundary gradually decreases, a fact which is borne out by the experimental values. This presumably means that there is some form of water movement to the water surface. The experimental values also show that the free-water content is not constant throughout but increases slightly with increasing depth.

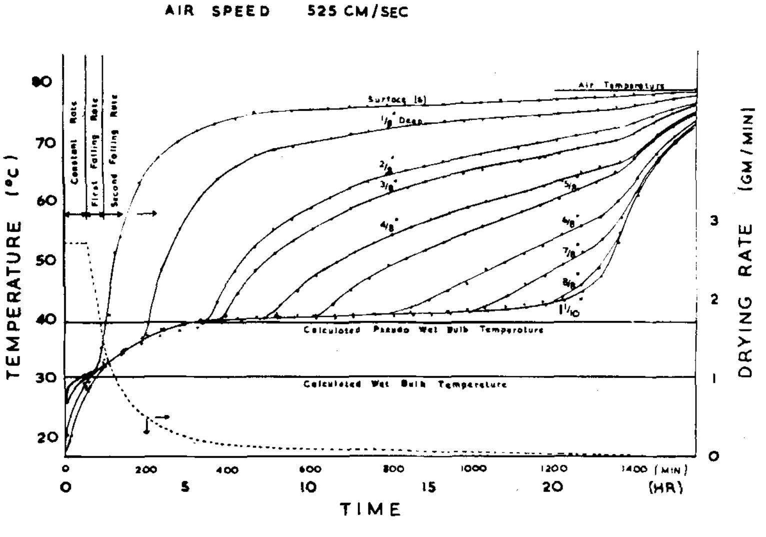

Fig. 1. Temperature vs, time at various depths in wool bobbin.

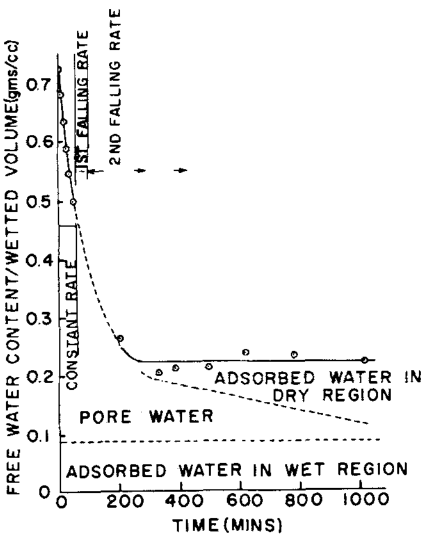

Fig. 3. Wetted-volume free-water content vs. time.

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*The air-dry layer is one which is free from liquid water but which has a regain (% moisture content - dry basis) dictated by the local humidity of the air in the pores of the layer.

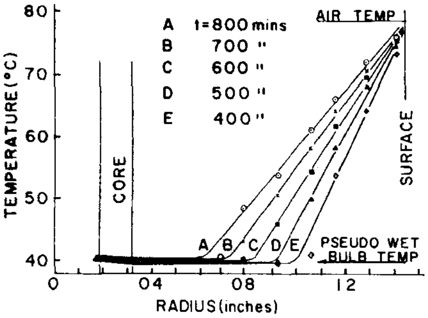

Fig. 4. Temperature vs. radius.

HEAT CONDUCTION

Heat transfer in the drying-wool bobbin is studied, the bound water being taken into account as required. The method used in Part I of dividing the bobbin into $\frac{1}{8}$-in.-thick annuli and considering steady state conditions to apply for 5-min. intervals is again employed.

The Total Heat Transfer

Use is made of the drying-rate curve and temperature record (Figure 1) to calculate the total heat received by the bobbin from the air stream.

$$q = hA_s(\Theta_a - \Theta_s) = \frac{dX}{dt}\lambda$$

$$+ \text{ sensible heat to wool, water, vapor, and heat of adsorption.*}$$

From this formula the heat transfer coefficient may be calculated, and Figure 5 represents the variation of h with time. The first term on the right-hand side of Equation (1) is the dominant one, representing some 95% of the total heat.

There appears to be a significant fall in h during the first falling-rate period. The final tailing off of the plotted points is probably due to the high error in measuring the small temperature difference $(\Theta_a - \Theta_s)$; a very slight overestimate of Θ would produce such a fall off.

If it is possible to rely on a thermocouple just below the surface as a measure of surface temperature, then Figure 5 means that the heat transfer to the bobbin is greater when the surface is wet than when it is dry. Coplan (7) has attributed the fact that a hairy surface dries slower than a smooth one, which is borne out by the present work, to some modification (thickening) of the boundary layer as a result of the protruding hairs. Thus when a wool surface is dry the degree of hairiness would be increased and cause reduction of heat transfer.

Table 1. Values of Percentage Regain to Nearest 1% in Successive ⅛-in. Thick Layers From the Surface

Layer	1	2	3	4	5	6	7	8
Experimental values								
At critical moisture content	124	175	186	199	208	212	210	209
At end of first falling-rate period	85	118	125	131	135	140	131	165
			Air-dry			Wet		
At t = 500 min.								
Calculated	4	7	10	22		61 (average)		
Experimental	3	5	8	20	58	70	77	82
				Air-dry				Wet
At t = 800 min.								
Calculated	3	5	7	9	12	23	49 (average)	
Experimental	2	2	4	6	9	18	54	62

Table 2. Values of $k \times 10^4$ c.g.s. Centigrade Units

Time, min.	Average free-water content, gm./cc. of wetted fabric	Average k, annuli 2-7 inclusive
10-15	0.670	10.1
15-20	0.645	9.6
20-25	0.620	8.6
25-30	0.595	8.4
30-35	0.570	7.3
35-40	0.545	7.3
40-45	0.525	7.6
45-50	0.500	6.5

k for Wet Wool

The first 50 min. of the temperature record, representing the heating of the wet wool, has been used, in the manner already described in Part I for the dry material, to give values of k for the $\frac{1}{8}$-in.-wide annuli; that is

$$\frac{\begin{Bmatrix}\text{rate of heat}\\ \text{entering}\end{Bmatrix} + \begin{Bmatrix}\text{rate of heat}\\ \text{leaving}\end{Bmatrix}}{2}$$

$$= (k \text{ annulus}) \times \begin{Bmatrix}\text{mean area}\\ \text{of annulus}\end{Bmatrix}$$

$$\times \begin{Bmatrix}\text{temperature gradient}\\ \text{across annulus}\end{Bmatrix} \quad (2)$$

The rate of heat leaving an annulus is compounded from the rate of supply of sensible heat to water and wool contained in the enclosed portion of the bobbin. When one uses the average free-water content value from Figure 3, it is assumed that the water distribution is uniform throughout the wet material. Adsorbed and pore water are considered identical so far as uptake of sensible heat is concerned, the wool and water being dealt with separately. Wahba and Nashed (8) from their experiments with cellulose suggest that the specific heat of adsorbed water may be higher than for ordinary water.

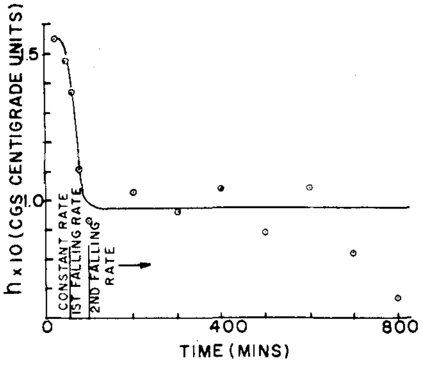

Fig. 5. h vs. time.

The complete results are given in Table 2. Values for the outermost and innermost annuli are omitted from the final-average values. In the case of the former these tend to be low, possibly because there may be less water in the layer; in the case of the latter a high error can be present in measuring the small amount of heat passing through the annulus. Another value which might be added to Table 1 is the value when the wool is in equilibrium with tunnel humidity, that is, when the free-water content is zero. The value previously reported from a dry wool experiment was $k = 1.07 \times 10^{-4}$ c.g.s. centigrade units.

Calculating k for fibers packing into a space between two concentric cylinders, Schuhmeister (9) assumed that they were distributed uniformly in all directions or, for the purposes of calculation, that $\frac{1}{3}$ were plane slabs parallel to the direction of heat flow and $\frac{2}{3}$ were slabs at right

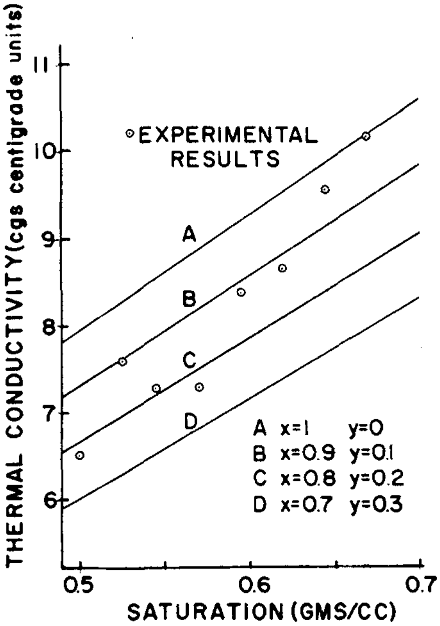

Fig. 6. k vs. average free-water content for wet wool.

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*Data reported by Hedges (6) were used to obtain this small quantity of heat.

angles to the direction of heat flow. On these assumptions

$$k_m = \tfrac{1}{3}(k_1v_1 + k_2v_2) + \tfrac{2}{3}\left(\frac{k_1k_2}{k_1v_2 + k_2v_1}\right) \qquad (3)$$

Using k for wool fiber as 4.6×10^{-4} and k for air at the average experimental temperature as 0.661×10^{-4}, one gets

$$k_m \times 10^4 = 0.53 + 0.55$$
$$= 1.08$$

Thus the experimental value in the dry case fits this formula. If the formula is extended to three components, it becomes

$$k_m \times 10^4 = x(k_1v_1 + k_2v_2 + k_3v_3) + y\left(\frac{k_1k_2k_3}{k_2k_3v_1 + k_1k_3v_2 + k_1k_2v_3}\right) \qquad (4)$$

where the mixture is represented by comparison with an arrangement of x parts where conductors are in parallel and y parts where they are in series. In Figure 6 the experimental values are compared. A value of $k = 7.0 \times 10^{-4}$ is used for saturated wool fiber and values appropriate to the average temperature for the rest of the water and air. It can be seen that when the wool is very wet the system giving the closest agreement is the one where all the conductors are in parallel. One might expect the dominant conduction of the water to tend to produce the parallel case as all the pores are filled. At the lower end of the experimental range of saturation the line representing $x = 0.8$ $y = 0.2$ gives better agreement.

k for Air-Dry Layers

Values were calculated for the quantities of adsorbed water in the various annuli at times 300, 400 ⋯ 900 min. after the method given previously. The amount in an annulus at 500 min. minus that at 700 min. would give the loss of adsorbed water in 200 min., the rate of loss of water being taken as that applying at $t = 600$ min. In this manner rates of evaporation of adsorbed water were calculated for $t = 400, 500 \cdots 800$ min.; for example at $t = 800$ min. the rates in grams per minute were 0.0003 (outer annulus), 0.0008, 0.001, 0.002, 0.005, 0.008, and at the water surface 0.043, making a total rate of drying of 0.06 g./min. Thus some 90% of the evaporation takes place within ¼ in. from the pore-water surface. Allowance was made for the latent heat and heat of adsorption required by the rate of evaporation, as well as for the sensible heat to the water present, in the case of each layer when the k value was calculated for a particular layer. The temperature gradient, the same for all layers, came directly from Figure 4.

TABLE 3. VALUE OF $k \times 10^4$ C.G.S. CENTIGRADE UNITS

	t = 400 min.		500 min.		600 min.		700 min.		800 min.	
Annulus	Regain %	k,	Regain %	k,	Regain %	k,	Regain %	k,	Regain %	k,
1 (Outer)	4.0	1.66	3.5	1.34	3.4	1.39	3.3	1.19	3.2	1.00
2	9.5	1.67	6.6	1.44	5.8	1.53	5.3	1.29	5.0	1.08
3	22.7	1.58	10.4	1.46	8.3	1.63	7.3	1.41	6.7	1.18
4			22.1	1.35	12.1	1.68	9.9	1.52	8.8	1.29
5					23.4	1.58	14.8	1.54	12.2	1.38
6							25.0	1.48	23.1	1.42

Table 3 sets out the results for the five times considered. The k values are compared with the appropriate average regains for the layers. There is a fair amount of scatter in these results; the correlation coefficient is only 0.436, but the regression line to give the best value of k, in terms of R^*, is

$$k \times 10^4 = 1.30 + 0.011\,R^* \qquad (5)$$

Thus when the regain increases from 2 to 20%, k increases from 1.32 to 1.52, an increase of 0.20. Baxter (*10*) reports an increase from 1.10 to 1.25, an increase of 0.15, when the bulk density is 0.335 g./cc. compared with 0.283 g./cc. in the present case. Thus the variation with regain is reasonable, though the absolute values are high.

Nevertheless the agreement is sufficient to indicate that the general approach, involving the calculated distribution of adsorbed water, fits the experimental data.

CONCLUSION

The basic theory of the second falling-rate period indicates that a balance between heat transfer to and water vapor diffusing from the retreating water surface establishes equilibrium at the pseudo-wet-bulb temperature. If the textile adsorbs water, most of the evaporation of the adsorbed water takes place close to the boundary of the pore water, so that the over-all balance remains.

The theory in its present stage is still descriptive. It could be used to predict the second falling-rate curve only if some further knowledge is available as to the variation of the free-water content with time and depth. It is also necessary to find whether the pseudo-wet-bulb temperature appears with systems other than textile fibers or whether it is specific to these systems alone.

Current work along these lines is aimed at establishing further the generality of the pseudo-wet-bulb temperature and at deriving exact quantitative evaluation of the rate of drying during the falling rate period.

NOTATION

A_s = area of bobbin surface, sq. cm.
h = surface heat transfer coefficient, cal. cm.$^{-2}$ sec.$^{-1}$ (°C.)$^{-1}$
k = thermal conductivity coefficient, cal. cm.$^{-1}$ sec.$^{-1}$ (°C.)$^{-1}$
k_m = thermal conductivity coefficient of mixture, cal. cm.$^{-1}$ sec.$^{-1}$ (°C.)$^{-1}$
k_1 = thermal conductivity coefficient of first component, cal. cm.$^{-1}$ sec.$^{-1}$ (°C.)$^{-1}$
k_2 = thermal conductivity coefficient of second component, cal. cm.$^{-1}$ sec.$^{-1}$ (°C.)$^{-1}$
k_3 = thermal conductivity coefficient of third component, cal. cm.$^{-1}$ sec.$^{-1}$ (°C.)$^{-1}$
p = vapor pressure, mm. Hg.
p_a = vapor pressure in air stream, mm. Hg.
p_w = vapor pressure at water surface, mm. Hg.
q = rate of flow of heat, cal. sec.$^{-1}$
r = radius of water surface, cm.
R = radius of bobbin surface, cm.
R^* = regain, dimensionless (gm. gm.$^{-1}$)
t = time, sec.
T = absolute temperature, ° abs.
T_a = absolute temperature of air stream, ° abs.
T_w = absolute temperature of water surface, ° abs.
v_1 = volume of first component, cc.
v_2 = volume of second component, cc.
v_3 = volume of third component, cc.
X = free-water content of bobbin, g.
E = void fraction, dimensionless (cc. cm.$^{-3}$)
Θ_a = temperature of air stream, °C.
Θ_s = temperature of bobbin surface, °C.
Θ_w = temperature of water surface, °C.
λ = latent heat of evaporation, cal. g.$^{-1}$

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