alcoholic groups in summer. Hence, relative to strength and degree of polymerisation, the copper number of the summer-exposed yarn is greater than that of the winter-exposed yarn.

Confirmation that oxidation as distinct from hydrolysis is greater in summer than in winter is supplied by the fact that production of carboxyl groups, which is small in summer, is even smaller in winter.

That the chemical changes which occurred in cotton yarn exposed in winter during the hours of darkness only had nothing to do with ageing is shown by the fact that the sample stored in the dark indoors for the same period had suffered, as would be expected, no change whatever. The results obtained nevertheless indicate that degradation does occur in the winter in the absence of light, although, because of the lack of completely comparable conditions, it is not possible to calculate the extent of modification due to light and air and that due to acid hydrolysis. But the extent of degradation during darkness in winter strongly suggests that the deterioration of cotton exposed in winter in an industrial region is not an additive function of summer oxycellulose formation together with a slight amount of hydrocellulose formation due to atmospheric acid, but rather a very considerably reduced oxycellulose formation and a substantial hydrocellulose formation due to atmospheric acidity.

The much greater atmospheric acidity in industrial regions in winter as compared with that in summer is due in the main to two causes—

(*a*) Domestic fuel consumption is at least three times greater in winter than in summer. In Leeds, in which the above experiments were carried out and which may be cited as a typical industrial area, there are 136,000 houses, each consuming an allocation of 50 cwt. of coal per annum. An average sample of coal contains approx. 1% of sulphur over and above that required, after oxidation, to neutralise the ammonia in the coal. Accordingly, assuming that the whole of the free sulphur is converted into sulphuric acid, there is an average daily discharge into the atmosphere of 28·6 tons of sulphuric acid from domestic fires alone. Since most of the domestic fuel is consumed during the winter months, it is probable that the average daily discharge of sulphuric acid from domestic fires during winter is considerably in excess of 40 tons, whereas that during summer is less than 15 tons.

(*b*) At most periods of the year, there is at least a slight breeze which disperses the acid discharged from coal fires and industrial plant. Periods of intense industrial fog, however, which are invariably confined to the winter months, are accompanied by a complete stillness of the atmosphere and a settling of acid along with solid particles in the vicinity of their place of origin. Consequently, in industrial regions the acidity of the atmosphere, which is normally greater in winter than in summer, is greater still during periods of winter fog.

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COMMUNICATION

The Combination of Wool with Acids—a Quantitative Interpretation in terms of the Donnan Theory of Membrane Equilibrium*

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A quantitative interpretation of the combination of wool with hydrochloric acid, sulphuric acid, and hydrochloric acid in presence of different concentrations of potassium chloride has been obtained in terms of the Donnan theory of membrane equilibrium. The course of combination is determined by the *p*H inside the fibre, which can be calculated although it is incapable of direct measurement. When the amount of combined acid is plotted as a function of the "internal" *p*H, the mid-point of the titration curve is found to lie between *p*H 4·15 and 4·35 in the case of hydrochloric acid, as would be expected if combination were due to back-titration of the carboxyl groups of salt linkages. Similarly, in the case of sulphuric acid the mid-point is at *p*H 4·45, and the unification of the hydrochloric acid and sulphuric acid titration curves, as well as the agreement between the observed and expected *pK* values, affords strong evidence in support of the Donnan theory. In addition, it has been shown that the curves obtained by titrating wool with hydrochloric acid in presence and absence of potassium chloride, the amounts of potassium chloride being sufficient to give a constant chloride ion concentration, are unified when the amounts of combined acid are plotted against the calculated "internal" *p*H values. The Donnan theory also provides a precise interpretation of the manner in which the *p*H corresponding to half-maximum combination with acid varies with changing salt concentration.

When wool is treated with simple acids, the salt linkages between the main peptide chains are broken in accordance with the following equation—

$$R{\cdot}COO^- \{H_3\overset{+}{N}{\cdot}R + H^+ \rightarrow R{\cdot}COOH + H_3\overset{+}{N}{\cdot}R$$

The course of combination is determined by the hydrogen ion concentration inside the fibre, which differs from the external concentration on account of the insolubility of wool and the resulting membrane effects. Up to the present, however, it has

* Part of a lecture given before the Manchester Section on 17th October 1947

been found impossible to determine the hydrogen ion concentration inside the fibre, and the two attempts[1,2] which have so far been made to derive quantitative theoretical expressions for the titration curves have not, therefore, been based on the Donnan theory of membrane equilibrium. The purpose of this paper is to show that the internal hydrogen ion concentration, which is incapable of direct measurement, can be calculated, and that the Donnan theory is capable of giving a more precise interpretation of the titration curves than the expressions derived from other considerations by Steinhardt and Harris[1] and Gilbert and Rideal[2]. As a basis for subsequent discussion, the work of these authors must now be reviewed.

(1) The Steinhardt and Harris Theory[1]

Steinhardt and Harris assume that wool can combine with protons and anions in accordance with the following equations—

$$W^{\pm} + H^+ \rightleftharpoons WH^+ \quad (K_H)$$
$$W^{\pm} + Cl^- \rightleftharpoons WCl^- \quad (K_A')$$
$$WH^+ + Cl^- \rightleftharpoons WHCl \quad (K_A)$$
$$WCl^- + H^+ \rightleftharpoons WHCl \quad (K_H')$$

where $W^{\pm}$ may be interpreted more precisely as $H_3\overset{+}{N}\cdot R\cdot COO^-$, WH^+ as $H_3\overset{+}{N}\cdot R\cdot COOH$, WCl^- as $ClH_3N\cdot R\cdot COO^-$, and $WHCl$ as $ClH_3N\cdot R\cdot COOH$. Despite the fact that the last two compounds are salts, the authors assume that the above equilibria are governed by the law of mass action, and derive the following expression for the fraction θ of the wool combined with acid in terms of the activities of the hydrogen and chloride ions and the dissociation constants of the postulated equilibria—

$$\theta = \frac{[WHCl] + [WH^+]}{[WHCl] + [WH^+] + [WCl^-] + [W^{\pm}]} = \frac{1}{1 + \dfrac{K_H'(a_{Cl} + K_A')}{a_H(a_{Cl} + K_A)}} \quad \text{(i)}$$

When wool is titrated with pure acid in absence of salt, Steinhardt and Harris put $a_H = a_{Cl}$ in equation (i) and obtain—

$$\theta = \frac{1}{1 + \dfrac{K_H'(a_H + K_A')}{a_H(a_H + K_A)}} \quad \text{(ii)}$$

The values they selected for the three dissociation constants gave only approximate agreement between the theoretical and experimental titration curves. Far more precise agreement is obtained, as shown in Table I, when four experimental points are used to calculate the values of K_H', K_A', K_A, and the limiting combining capacity for acid.

Speakman and Hirst's[3] and Speakman and Stott's[4] earlier data for the titration of wool with hydrochloric acid can be shown to fit a curve representing the back-titration of a weak acid with a pK value of $2{\cdot}18 \pm 0{\cdot}04$. It is not surprising, therefore, that equation (ii) is able to represent the course of the titration, since our calculated values of K_A' and K_A are so small and their effect is only slight. To some extent they compensate for the arbitrary corrections which Steinhardt and Harris applied to their data.

TABLE I

		Steinhardt and Harris	Peters and Speakman
Limiting combining capacity for acid (m-equiv./100g. dry wool)		82·0	86·0
	K_H'	$6{\cdot}3 \times 10^{-5}$	$6{\cdot}2 \times 10^{-3}$
	K_A	—	$8{\cdot}0 \times 10^{-4}$
	K_A'	0·35	$2{\cdot}0 \times 10^{-4}$

	Combined Acid (m-equiv./100g. dry wool)				
	(*a*)	(*b*)	(*c*)	(*b* − *a*)	(*c* − *a*)
*p*H	Found	Calculated (S. & H.)	(P. & S.)		
0·447	86·8	82·0	84·5	−4·8	−2·3
0·635	83·8	82·0	83·8	−1·8	0·0
0·792	83·6	81·9	82·8	−1·7	−0·8
0·813	80·5	81·9	82·7	+1·4	+2·2
0·814	82·9	81·9	82·7	−1·0	−0·2
0·918	81·3	81·9	81·8	+0·6	+0·5
1·087	76·2	81·7	80·0	+5·5	+3·8
1·125	78·9	81·7	79·5	+2·8	+0·6
1·470	76·8	80·5	72·9	+3·7	−3·9
1·663	67·6	78·3	67·3	+10·7	−0·3
1·711	65·2	77·5	65·7	+12·3	+0·5
1·741	63·1	76·9	64·6	+13·8	+1·5
1·931	57·4	70·7	57·2	+13·0	−0·2
2·061	51·0	63·5	51·5	+12·5	+0·5
2·228	44·5	50·3	44·0	+5·8	−0·5
2·340	38·5	39·9	39·0	+1·4	+0·5
2·451	34·8	29·7	34·3	−5·1	−0·5
2·726	25·1	11·3	24·2	−13·8	+0·9
3·039	16·6	3·0	15·9	−13·6	−0·7
3·272	11·4	1·0	11·6	−10·4	+0·2
3·620	6·7	0·2	7·2	−6·5	+0·5
3·844	4·5	0·1	5·1	−4·4	+0·6
4·198	2·7	0·0	2·8	−2·7	+0·1
4·414	1·7	0·0	1·8	−1·7	+0·1
4·740	1·2	0·0	0·9	−1·2	−0·3
5·145	0·4	0·0	0·4	−0·4	0·0

There is, however, very poor agreement between theory and experiment for titrations carried out in presence of potassium chloride, added in amounts sufficient to keep the chloride ion concentration constant. Under these conditions, equation (i) takes the form—

$$\theta = \frac{1}{1 + \dfrac{K}{a_H}} \quad \text{(iii)}$$

where K is a complex function of the salt concentration, which decreases as a_H increases and tends towards the limiting value K_H'. But equation (iii) has the same form as that for a simple monobasic acid, and the slope at the mid-point—

$$(dpH/d\theta)_{\theta = 0{\cdot}5}$$

should, therefore, be − 1·737. The actual slope is − 3·9 when the anion concentration is molar. Similarly, according to Steinhardt and Harris's approximate form of equation (ii), viz.—

$$\theta = \frac{1}{1 + \dfrac{K_H'K_A'}{a_H^2}}$$

the slope at the mid-point in absence of salt should be − 0·869, but the observed slope is − 1·9*. In both cases, therefore, the observed values are more than double the calculated values. To overcome the difficulty, Steinhardt and Harris adopt the naive procedure of "permitting the concentrations to enter the equation as square root terms". No theoretical justification for this device is offered by the authors, and it seems clear that the failure of the theory is due to the erroneous assumption

* Using the exact form of the equation and the constants given in Table I, the calculated slope is − 1·926.

that the simple law of mass action is obeyed in the ionisation of salts.

(2) The Gilbert and Rideal Theory[2]

A more successful attempt to derive expressions for the titration of wool with acids in presence and absence of salts is due to Gilbert and Rideal. In accordance with the salt-linkage theory, the numbers of positive and negative sites in the fibre are taken to be identical, and it is assumed that "an anion is free to occupy any positive site, irrespective of whether or not the positive site is next to a carboxyl group that has been neutralised by a proton". Anions and protons are thus regarded as being adsorbed independently, except in so far as they influence one another through their contribution to the net charge of the fibre. It is argued that anions and protons must be adsorbed in equal numbers, because the electrostatic potential, developed by unequal adsorption, would itself prevent further selective adsorption.

On the basis of these premises, Gilbert and Rideal derive an expression for the titration of wool with acids by a method which follows closely that adopted by Donnan and Guggenheim[5] in deriving the exact thermodynamic equation governing a membrane equilibrium. Since the latter forms the main theme of this paper, the derivation of the Gilbert and Rideal equation must be summarised, so that the similarities and dissimilarities between the two theories can be indicated.

The chemical potential μ_H of the hydrogen ions in solution is, of course, given by the equation—

$$\mu_H = \mu_H^\circ + \boldsymbol{R}T \ln a_H \qquad \text{(iv)}$$

where μ_H° is the partial molar free energy of hydrogen ions at unit activity, and a_H is the activity at some other concentration. At equilibrium, the chemical potential of the ions in the fibre must equal that of the corresponding ions in solution. The relationship between μ_h, μ_h° the standard free energy of the hydrogen ions adsorbed by the fibre, θ_H the fraction of the total sites occupied by hydrogen ions, and ψ the electrostatic potential was obtained by the doubtful procedure of introducing the term $\psi\boldsymbol{F}$ into the Fowler and Guggenheim[6] equation for the adsorption of molecules—

$$\mu_h = \mu_h^\circ + \boldsymbol{R}T \ln \frac{\theta_H}{1-\theta_H} + \psi\boldsymbol{F} \qquad \text{(v)}$$

Equating (iv) and (v) and writing $\Delta\mu_H$ for $\mu_h^\circ - \mu_H^\circ$ it is found that—

$$\boldsymbol{R}T \ln \frac{a_H(1-\theta_H)}{\theta_H} = \Delta\mu_H + \psi\boldsymbol{F} \qquad \text{(vi)}$$

The corresponding equation for a univalent anion X is—

$$\boldsymbol{R}T \ln \frac{a_X(1-\theta_X)}{\theta_X} = \Delta\mu_X - \psi\boldsymbol{F} \qquad \text{(vii)}$$

Assuming that $\theta_X = \theta_H$, and eliminating $\psi\boldsymbol{F}$ by adding (vi) and (vii), the following equation for the titration curve is obtained—

$$\boldsymbol{R}T \ln \frac{a_H a_X(1-\theta)^2}{\theta^2} = \Delta\mu_H + \Delta\mu_X \qquad \text{(viii)}$$

Hence $$\sqrt{a_H a_X}\frac{(1-\theta)}{\theta} = K \qquad \text{(ix)}$$

where $$2\boldsymbol{R}T \ln K = \Delta\mu_H + \Delta\mu_X$$

and the square root term appears without the arbitrariness of Steinhardt and Harris. In this respect, therefore, the Gilbert and Rideal theory is clearly superior. Further, equation (ix) is highly successful in predicting how the course of the titration is affected by the presence of a salt (potassium chloride). When no salt is added, $a_H = a_X$ approximately, and the equation takes the form of that for a simple monobasic acid with a slope of $-1{\cdot}737$ at the mid-point. When a_X is kept constant by adding potassium chloride, the slope should be $-3{\cdot}474$. Both the predicted slopes are in very much closer agreement with the observed values of $-1{\cdot}9$ and $-3{\cdot}9$, respectively, than are those calculated from the Steinhardt and Harris equations. Further, the linear dependence of the pH at the mid-point on the logarithm of the anion concentration, as well as the unit slope of the graph, is given by equation (ix), for when $\theta = 0{\cdot}5$—

$$a_H a_X = K^2$$

or $$p\mathrm{H} = \log a_X - 2\log K \qquad \text{(x)}$$

Although the Gilbert and Rideal theory is so much superior to that of Steinhardt and Harris in all these respects, it suffers from a number of limitations. For example, equation (x) suggests that there is no limit to the displacement of the pH of the mid-point of the titration curve as the concentration of salt is increased, whereas the graph of the pH at the mid-point against the logarithm of the chloride concentration is linear only over a range of low chloride concentrations and decreases rapidly in the neighbourhood of 1·0N. Although the relationship is improved by using activities instead of concentrations, as required by equation (x), the main discrepancy persists because the titration curves must pivot about pH 6·5, approximately. This fixed point, and the maximum slope of $-3{\cdot}474$, set an upper limit to the displacement at pH 4·8. Further, equation (viii) predicts a linear relationship between $\log[\theta/(1-\theta)]$ and pH, but sigmoid curves are, in fact, obtained.

It seems probable, therefore, that the limitations of the Gilbert and Rideal theory are connected fundamentally with the assumption that the anions of the combined acid occupy positively charged sites in the fibre. Besides implying the formation of the electronically impossible compound $R{\cdot}NH_3Cl$, Gilbert and Rideal's treatment can be criticised on the ground that the Fowler and Guggenheim equation for the adsorption of molecules cannot be extended to the adsorption of ions simply by the addition of the term $\psi\boldsymbol{F}$ (equation v). Like Steinhardt and Harris, too, Gilbert and Rideal assume (equation vii) that combination with anions is governed by the simple law of mass action. All these assumptions are, however, unnecessary if combination is examined in terms of the Donnan theory of membrane equilibrium.

(3) The Donnan Membrane Equilibrium

The combination of gelatin with acids and the consequent changes in swelling have been satisfactorily interpreted by Procter[7], and Procter and Wilson[8], in terms of the Donnan theory of membrane equilibrium. Loeb[9] subsequently extended the treatment to proteins in general, and Elöd and Silva[10] attempted to obtain a quantitative interpretation of the dyeing of silk and wool with acid dyes, as well as the tanning of collagen, by means of the Donnan equations. There are, however, serious errors in Elöd and Silva's treatment, and they overlooked the importance of the difference between the internal and external *p*H values, which was emphasised by Speakman and Hirst[3]. Using a model which they regard as intrinsically unreal, Steinhardt and Harris[1] also attempted to interpret the combination of wool with acids in terms of the Donnan theory. Only limited agreement with the requirements of the data was obtained, and they were thus led to prefer the theory which has already been outlined.

The chief obstacle to the successful use of the Donnan theory to obtain a quantitative interpretation of the combination of wool with acids is the lack of any satisfactory method of measuring the *p*H within the fibres. The internal *p*H can, however, be calculated, as is shown below.

(*a*) GENERAL

When isoelectric wool is immersed in a solution of an acid, protons combine with the R·COO$^-$ groups and the state of the fibre at equilibrium is represented by the following diagram, where the term "internal phase" is intended to represent the solution associated with the fibre, most of it being internal, though some is associated with the outer surface. In order to generalise the treatment, the acid is represented as H_zX. The bracketed quan-

Internal Phase		External Phase	
–COOH	$[A\theta]$		
–COO$^-$	$[A(1-\theta)]$		
–$\overset{+}{N}H_3$	$[A]$		
H^+	$[h]$	H^+	$[H]$
$H_nX^{(z-n)-}$	$[u]$	$H_nX^{(z-n)-}$	$[U]$
X^{z-}	$[x]$	X^{z-}	$[X]$

tities in the diagram represent the molar concentrations of the several ions in the internal and external phases, which are assumed to have volumes v and V respectively, while θ is the fraction of the R·COO$^-$ groups which have combined with protons. As a result of combination, the fibre itself is positively charged, and the potential, which influences the diffusion of ions into the fibre, is assumed to be uniform throughout the volume v.

According to Donnan and Guggenheim[5], the electrochemical potential of the hydrogen ions in the external phase is given by the expression—

$$\mu_H = \mu_H^\circ(T) + \boldsymbol{RT} \ln H + \boldsymbol{RT} \ln \gamma_H + P\overline{V}_H \quad \text{(xi)}$$

where $\mu_H^\circ(T)$ is dependent only on the temperature, γ_H is the activity coefficient and $\overline{V}_H$ is the partial molar volume of the hydrogen ion at a pressure equal to the mean pressure of the two phases.

Similarly, the electrochemical potential of the hydrogen ions in the internal phase is—

$$\mu_h = \mu_h^\circ(T) + \boldsymbol{RT} \ln h + \boldsymbol{RT} \ln \gamma_h + p\overline{V}_H + \psi\boldsymbol{F} \quad \text{(xii)}$$

At equilibrium, the chemical potentials of the two phases must be equal, and since they differ only because of the electrostatic potential and the difference in pressure, we may assume that

$$\mu_h^\circ(T) = \mu_H^\circ(T)$$

This relation enables (xi) and (xii) to be combined to give

$$\boldsymbol{RT} \ln \frac{\gamma_H H}{\gamma_h h} + (P-p)\overline{V}_H = \psi\boldsymbol{F} \quad \text{(xiii)}$$

If the activity of the water in the two phases is represented by W and w, and its partial molar volume by $\overline{V}_W$ at a pressure equal to the mean of P and p, then—

$$\boldsymbol{RT} \ln w + p\overline{V}_W = \boldsymbol{RT} \ln W + P\overline{V}_W \quad \text{(xiv)}$$

whence

$$P - p = \frac{\boldsymbol{RT}}{\overline{V}_W} \ln \frac{w}{W} \quad \text{(xv)}$$

Inserting this in equation (xiii), we obtain the expression—

$$\boldsymbol{RT} \ln \frac{\gamma_H H}{\gamma_h h} + \boldsymbol{RT} \frac{\overline{V}_H}{\overline{V}_W} \ln \frac{w}{W} = \psi\boldsymbol{F}$$

from which

$$\frac{\gamma_H}{\gamma_h} \left(\frac{w}{W}\right)^{r_H} \frac{H}{h} = \lambda \quad \text{(xvi)}$$

where r_H is the ratio of the partial molar volumes of the hydrogen ion and water, and $\lambda = e^{\psi F/RT}$.

The corresponding equation for an anion having z charges is—

$$\frac{\gamma_X}{\gamma_X} \left(\frac{W}{w}\right)^{r_X} \frac{x}{X} = \lambda^z \quad \text{(xvii)}$$

Hence the equations for the equilibrium for any pair of ions can be written in the form—

$$\lambda^z = \left(\frac{H}{\gamma_0}\right)^z = \frac{x}{X}\gamma_z = \ldots \quad \text{(xviii)}$$

where $\gamma_0 = \frac{\gamma_H}{\gamma_h}\left(\frac{w}{W}\right)^{r_H}$ and $\gamma_z = \frac{\gamma_X}{\gamma_X}\left(\frac{W}{w}\right)^{r_X}$

The condition that both phases must finally be electrically neutral provides two further equations—

$$A\theta + h = zx + \Sigma(z-n)u \quad \text{(xix)}$$

and

$$H = zX + \Sigma(z-n)U \quad \text{(xx)}$$

Since the amount a of acid combined with the fibre is usually calculated by subtracting the residual acid from the amount originally added, with the assumption that, at equilibrium, the concentration of free acid is the same inside and outside the fibre,

$$\begin{aligned} a &= v(A\theta + h + \Sigma nu) + V(H + \Sigma nU) \\ &\quad - (V+v)(H + \Sigma nU) \\ &= v(A\theta + h + \Sigma nu - H - \Sigma nU) \end{aligned} \quad \text{(xxi)}$$

Using equations (xix) and (xx), equation (xxi) may be rewritten—

$$\frac{a}{v} = z(x - X) + z\Sigma(u - U)$$

or, using equations (xvi) and (xvii) in the abbreviated form (xviii)—

$$\frac{a}{zv} = \left(\frac{\lambda^z}{\gamma_z} - 1\right) X + \Sigma\left(\frac{\lambda^{z-n}}{\gamma_{z-n}} - 1\right) U \qquad \text{(xxii)}$$

This equation assumes the following relatively simple form for strong acids, i.e. when the undissociated forms are absent—

$$\frac{a}{v} = \left(\frac{\lambda^z}{\gamma_z} - 1\right) zX \qquad \text{(xxiii)}$$

and, since $H = zX$ in absence of salt, equation (xxiii) can be rearranged as follows—

$$p\mathrm{H}_{\mathrm{int}} \simeq \frac{z+1}{z} p\mathrm{H}_{\mathrm{ext}} + \frac{1}{z}\log\left(\frac{a}{v} + H\right)\gamma_z \qquad \text{(xxiv)}$$

Apart from γ_z and v, equation (xxiv) contains only quantities which are determined by external conditions and accessible to direct experimental determination. A value for v was obtained from King's[11] data for the densities of dry and saturated (33% regain) wools, viz. 1·3065 and 1·266 g. per c.c. respectively. From these values it can be shown that the 33 g. of water adsorbed by 100 g. of dry wool at saturation occupy 28·51 c.c., and it will be assumed that this volume of water is free. In applying equation (xxii) to different acids, it is also assumed that the volume of free water is increased by the swelling which the fibres undergo in acid solutions. Speakman and Stott's[12] data were used. If, instead of the volume of free water calculated from King's data, Hailwood and Horrobin's value[13] for the amount of water which does not form "hydrates" with the wool is used, the results of the following calculations are not modified to any significant extent, because it is the logarithm of the volume which is used. The general validity of equation (xxii) will now be tested in three cases.

(*b*) QUANTITATIVE

(i) HYDROCHLORIC ACID— Putting $z = 1$ in equation (xxiv), we obtain the expression—

$$p\mathrm{H}_{\mathrm{int}} \simeq 2\, p\mathrm{H}_{\mathrm{ext}} + \log\left(\frac{a}{v} + H\right)\gamma_1 \qquad \text{(xxv)}$$

or, to a close approximation

$$p\mathrm{H}_{\mathrm{int}} \simeq 2\, p\mathrm{H}_{\mathrm{ext}} + \log\frac{a}{v}\gamma_1 \qquad \text{(xxvi)}$$

As has already been indicated in connection with equation (xviii), γ_z is a complex quantity. In applying the above equations to the combination of wool with hydrochloric acid, it has been assumed that the partial molar volume of a chloride ion is not significantly different from that of a water molecule, i.e. that $r_{\mathrm{Cl}^-} = 1$; and that the activity of the water is the same in both phases, i.e. that $W/w = 1$; while the activity coefficient ratio $\gamma_{\mathrm{X}}/\gamma_{\mathrm{X}}$ was calculated in three ways—

As a rough approximation (i), the ratio of the activity coefficients was first taken as unity, thus enabling an approximate value for the activity coefficient in the internal phase to be interpolated from the tables of Harned and Owen[14] for hydrochloric acid. The value of λ was then recalculated using this activity coefficient, and the process repeated until a constant value was obtained. A second series of calculations (ii) was then made, using Harned and Owen's tables for the activity coefficient of potassium chloride at a concentration equal to a/v, as an approximation to the effect that the $-NH_3^+$ groups might have. Finally, in a third series of calculations (iii), all activity coefficients were assumed to be unity, implying, with the assumptions already made, that $\gamma_z = 1$. This is not so unreasonable an approximation as might at first sight appear, because the variation with concentration of the mean activity coefficient of most uni-univalent salts is of the same order as, but in the opposite direction to, that of the activity of water in solutions of the same salts. There is, therefore, less variation in the product than in either separately.

TABLE II

External *p*H (measured)	Normality of Solution in equilibrium with Wool H	Combined Acid (m-equiv./100 g. dry wool) a	Volume Swelling (c.c./100 g. dry wool) v	Internal *p*H (calculated) (i)	(ii)	(iii)	True Amount of Combined Acid (m-equiv./100 g. dry wool) $\frac{vA\theta}{}$ (i)	(ii)	(iii)
0·36	$5·77 \times 10^{-1}$	75·0	34·3	1·27	0·92	1·16	92·4	87·5	92·4
0·51	—	76·9	—	—	—	1·12	—	—	94·5
0·62	$3·03 \times 10^{-1}$	79·7	34·6	1·74	1·41	1·66	89·7	87·8	89·4
1·10	$9·50 \times 10^{-2}$	79·6	34·8	2·63	2·31	2·58	82·8	82·6	82·8
1·41	$4·48 \times 10^{-2}$	74·7	34·1	3·21	2·93	3·17	76·2	76·2	76·2
1·76	$1·99 \times 10^{-2}$	63·4	33·0	3·81	3·57	3·81	64·1	64·0	64·1
2·41	$4·25 \times 10^{-3}$	33·0	31·6	4·75	4·62	4·84		33·0	
2·53	$3·14 \times 10^{-3}$	28·0	31·4	4·91	4·80	5·01		28·0	
2·71	$2·09 \times 10^{-3}$	19·8	31·1	5·11	5·03	5·22		19·8	
2·94	$1·19 \times 10^{-3}$	14·0	30·7	5·42	5·35	5·54		14·0	
3·38	$4·3 \times 10^{-4}$	4·6	30·0	5·84	5·82	5·95		4·6	
3·53	$3·0 \times 10^{-4}$	4·0	29·9	6·08	6·05	6·19		4·0	
4·33	$4·7 \times 10^{-5}$	0·5	29·0	6·84	—	6·90		0·5	

Exact analysis of the "internal" titration curves is not yet possible because of the difficulty of deducing the expression for the equilibrium between a solid possessing electrically charged groups and a solution containing ions. For present purposes, however, this expression is not required. Taking the limiting acid combining capacities for cases (i), (ii), and (iii) as being 93·5, 88·0, and 95·0 milliequivalents per 100 g. of dry wool respectively, the mid-points of the internal titration curves lie at *p*H 4·35, 4·15, and 4·35, as may be seen from Fig. 1. Since these three values are in such good agreement, it is evident that any uncertainty

The results of these calculations, using the data of Speakman and Stott[4], are given in Table II and illustrated by Fig. 1.

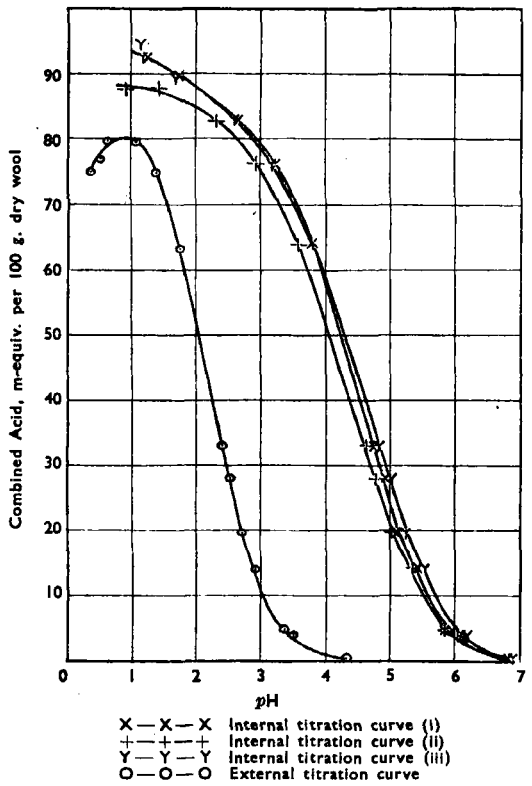

FIG. 1

regarding activity coefficients cannot invalidate the general conclusion that the mid-point of the internal titration curve lies at about *p*H 4·3. For convenience, this value may be referred to as the *pK* value of the carboxyl groups of wool— terminal carboxyl groups of the polypeptide chains as well as the carboxyl groups of aspartic and glutamic acid side-chains— but it should be mentioned that the form of the internal titration curves is not that given by a soluble monobasic acid. A *pK* value of about 4·3 is, of course, to be expected if the combination of wool with acid is due to back-titration of the carboxyl groups of salt linkages, and this agreement between theory and experiment is a first indication of the quantitative validity of the Donnan theory as applied to the combination of wool with acid. Further support for the theory comes from its application to the case of combination with sulphuric acid[4].

(ii) SULPHURIC ACID— Putting $z = 2$ in equation (xxii), we obtain the expression—

$$\frac{a}{2v} = \left(\frac{\lambda^2}{\gamma_2} - 1\right)[SO_4^{--}] + \left(\frac{\lambda}{\gamma_1} - 1\right)[HSO_4^{-}] \quad \text{(xxvii)}$$

At *p*H values well above 1·9, which is the *pK* value of HSO_4^-, the acid is almost completely dissociated into hydrogen and sulphate ions, and equation (xxvii) takes the simpler form—

$$\frac{a}{v} = \left(\frac{\lambda^2}{\gamma_2} - 1\right)H$$

$$\text{or} \quad pH_{int} = \frac{3}{2}pH_{ext} + \frac{1}{2}\log\left(\frac{a}{v} + H\right)\gamma_2 \quad \text{(xxviii)}$$

or, to a close approximation—

$$pH_{int} = \frac{3}{2}pH_{ext} + \frac{1}{2}\log\frac{a}{v}\gamma_2 \quad \text{(xxix)}$$

Only one "internal" titration curve for sulphuric acid was calculated with the help of these equations, because the three calculated curves for hydrochloric acid are in such good agreement. The data were obtained by calculating the concentrations of H^+, HSO_4^-, and SO_4^{--} from the concentration of each solution on the assumption that the dissociation constant of HSO_4^- is 0·01243 at all concentrations. In the calculation of λ, the values of γ_2 and γ_1 were assumed to be unity as in case (iii) for hydrochloric acid. The results are given in Table III and illustrated by Fig. 2.

TABLE III

External *p*H (measured)	Normality of Solution in equilibrium with Wool *H*	Combined Acid (m-equiv. per 100 g. dry wool) *a*	Volume Swelling (c.c./100 g. dry wool) *v*	Internal *p*H (calculated)	True Amount of Combined Acid (m-equiv. per 100g. dry wool) vA^θ
0·78	$3·16 \times 10^{-1}$	105·5	30·1	1·62	85·2
1·60	$3·39 \times 10^{-2}$	83·5	29·8	2·70	81·3
1·86	$1·89 \times 10^{-2}$	78·8	29·6	3·03	77·7
1·98	$1·41 \times 10^{-2}$	76·5	29·6	3·19	75·7
2·39	$4·86 \times 10^{-3}$	63·5	29·3	3·75	63·4
2·46	$5·18 \times 10^{-3}$	58·4	29·3	3·79	58·1
2·92	$1·41 \times 10^{-3}$	44·8	29·1	4·45	44·8
3·08	$9·55 \times 10^{-4}$	36·7	29·0	4·65	36·7
3·32	$5·37 \times 10^{-4}$	29·2	29·0	4·97	29·2
3·45	$3·89 \times 10^{-4}$	22·5	28·9	5·10	22·5
3·84	—	11·4	28·8	5·36	11·4
3·86	$2·04 \times 10^{-4}$	13·6	28·8	5·45	13·6
4·24	—	5·2	28·7	5·99	5·2
4·50	—	2·2	28·6	6·19	2·2
4·60	$2·51 \times 10^{-5}$	3·0	28·6	6·41	3·0
4·67	$2·14 \times 10^{-5}$	1·1	28·6	6·30	1·1
4·75	$1·78 \times 10^{-5}$	0·4	28·6	6·20	0·4

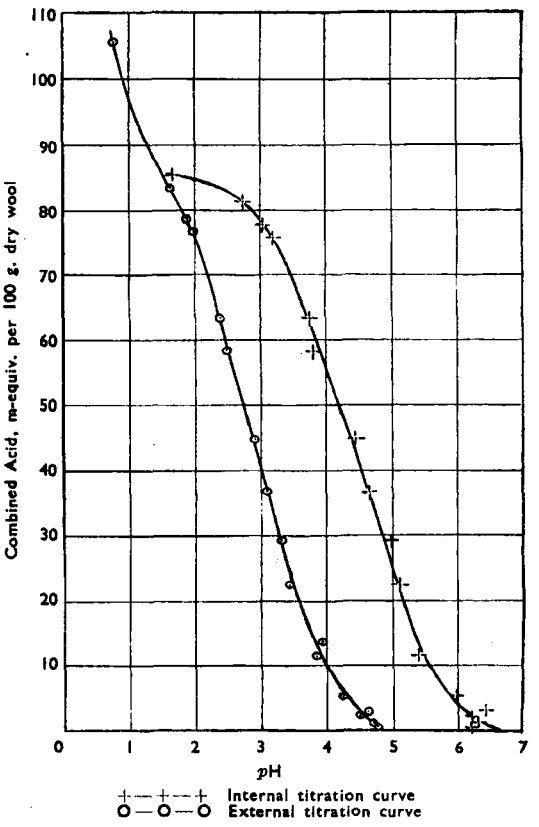

FIG. 2

The pK value derived from the "internal" titration curve is 4·45, in good agreement with the values derived from the "internal" titration curves for hydrochloric acid. Since the "internal" titration curves for hydrochloric and sulphuric acids are in such good agreement, further support is given to the quantitative validity of the Donnan theory. Attention was next turned to the combination of wool with hydrochloric acid in presence of a neutral salt.

(iii) HYDROCHLORIC ACID AND POTASSIUM CHLORIDE— Steinhardt and Harris[1] have determined the titration curves for wool and hydrochloric acid in presence of potassium chloride, the salt being added in amounts sufficient to maintain the chloride ion concentration at different fixed values. As the concentration of potassium chloride was increased, the titration curves were displaced to higher pH values in accordance with the qualitative predictions of the Donnan theory. Steinhardt and Harris, however, attempted to give quantitative expression to the phenomena on a different basis. As has already been indicated, their theory is unsatisfactory, and the purpose of this section of the present paper is to show that a sound quantitative interpretation of the family of titration curves can be obtained in terms of the Donnan theory.

As before, the bracketed letters in the following diagram represent the equilibrium concentrations of the ions in the internal and external phases.

Internal Phase			External Phase	
–COOH		$[A\theta]$		
$-COO^-$		$[A(1-\theta)]$		
$-\overset{+}{N}H_3$		$[A]$		
	H^+	$[h]$	H^+	$[H]$
	K^+	$[x-h-A\theta]$	K^+	$[X-H]$
	Cl^-	$[x]$	Cl^-	$[X]$

In applying equation (xviii) to the family of curves under consideration, it has been assumed that $\gamma_0 = \gamma_z = 1$ because the purpose of the calculations is simply to compare the curves with one another. Making this assumption, it is obvious from equation (xviii) that the ratio λ of the hydrogen ion concentrations outside and inside the fibre is given by the following expressions—

$$\lambda = \frac{H}{h} = \frac{x}{X} = \frac{X-H}{x-h-A\theta} \qquad \text{(xxx)}$$

The relation between the external anion concentration X, the amount of combined acid a, and the external hydrogen ion concentration H is as follows—

$$X\lambda^2 - \frac{a}{v}\lambda = X - H \qquad \text{(xxxi)}$$

It should be noted that this expression, from which λ can be calculated, is slightly different from that which would be obtained from equation (xxi) because of Steinhardt and Harris's assumption that the internal phase contains no acid. As the salt concentration is increased, the value of λ approaches unity, but even when the hydrogen ion concentration is as low as 5×10^{-5} N. and the salt concentration is 1·0 M., the value of λ is 2. For almost the whole range of conditions used by Steinhardt and Harris, therefore, the value of λ is high and equation (xxxi) can be simplified to the approximation—

$$\lambda \simeq \frac{a}{vX}$$

or

$$p\mathrm{H}_{\mathrm{ext}} \simeq p\mathrm{H}_{\mathrm{int}} + \log X - \log \frac{a}{v} \qquad \text{(xxxii)}$$

Using this equation where applicable, and the exact equation elsewhere, the internal pH values have been calculated from Steinhardt and Harris's data. For combination with hydrochloric acid in presence of potassium chloride, the value of v was assumed to be 28·5 c.c. per 100 g. of dry wool, because swelling is depressed by neutral salts and there are no data for the swelling of wool fibres in solutions containing hydrochloric acid and potassium chloride. For combination with hydrochloric acid in absence of salt, the values of v appropriate to the pH values of the solutions were used, just as in the calculation of the data given in Table II. The results are given in Tables IV–VII and illustrated by Fig. 3.

TABLE IV

Combination with Hydrochloric Acid in Absence of Potassium Chloride

External pH (measured)	Combined Acid (m-equiv./100 g. dry wool)	Internal pH (calculated)
0·447	86·8	1·30
0·635	83·8	1·66
0·792	83·6	1·97
0·813	80·5	1·99
0·814	82·9	2·19
0·918	81·3	2·20
1·087	76·2	2·51
1·125	78·9	2·61
1·470	76·8	3·29
1·663	67·6	3·63
1·711	65·2	3·72
1·741	63·1	3·76
1·931	57·4	4·11
2·061	51·0	4·32
2·228	44·5	4·60
2·340	38·5	4·76
2·451	34·8	4·95
2·726	25·1	5·36
3·039	16·6	5·83
3·272	11·4	6·12
3·620	6·7	6·59
3·844	4·5	6·87
4·198	2·7·	7·36
4·414	1·7	7·59
4·740	1·2	8·1
5·145	0·4	8·4

TABLE V

Combination with Hydrochloric Acid in Presence of Sufficient Potassium Chloride to give a Constant Chloride Ion Concentration of 0·04 N.

External pH (measured)	Combined Acid (m-equiv./100 g. dry wool)	Internal pH (calculated)
1·663	67·6	3·44
1·830	66·8	3·60
1·925	65·0	3·68
2·152	60·5	3·88
2·620	50·5	4·27
2·639	50·0	4·28
3·016	40·6	4·57
3·294	35·7	4·79
3·628	28·0	5·02
4·035	22·9	5·34
4·377	17·1	5·55
4·650	14·6	5·76
5·080	10·2	6·03
5·283	8·2	6·14
5·40	6·4	6·15

TABLE VI

Combination with Hydrochloric Acid in Presence of Sufficient Potassium Chloride to give a Constant Chloride Ion Concentration of 0·2 N.

External *p*H (measured)	Combined Acid (m-equiv./100 g. dry wool)	Internal *p*H (calculated)
0·918	81·3	2·07
1·100	79·9	2·25
1·130	79·8	2·28
1·400	78·9	2·54
1·409	78·8	2·55
1·433	77·4	2·57
1·707	77·0	2·84
1·751	75·3	2·86
1·982	73·0	3·09
2·038	74·0	3·15
2·061	70·2	3·15.
2·364	70·1	3·46
2·378	67·0	3·45
2·708	64·1	3·76
2·744	59·5	3·77
2·790	59·4	3·81
3·172	53·5	4·15
3·273	48·7	4·21
3·571	43·5	4·40
3·670	41·9	4·55
3·825	37·2	4·65
4·082	32·0	4·84
4·359	27·9	5·07
4·662	22·4	5·28
4·855	17·7	5·39
5·015	16·8	5·53
5·246	13·1	5·67
5·400	11·2	5·78
5·528	9·9	5·87
5·564	6·7	5·81
5·670	7·8	5·95
5·887	5·4	6·02
5·94	3·0	6·05
6·14	2·3	6·23
6·3	0·2	6·4
6·5	0·2	6·6

TABLE VII

Combination with Hydrochloric Acid in Presence of Sufficient Potassium Chloride to give a Constant Chloride Ion Concentration of 1·0 N.

External *p*H (measured)	Combined Acid (m-equiv./100 g. dry wool)	Internal *p*H (calculated)
0·578	92·0	1·11
0·840	89·0	1·37
1·138	85·2	1·65
1·445	84·0	1·96
1·743	79·4	2·23
2·062	77·7	2·55
3·074	65·2	3·50
4·258	40·3	4·54
4·334	39·5	4·61
4·768	28·8	4·98
5·342	20·8	5·50
5·651	11·9	5·74
5·908	6·5	5·96
6·4	1·3	6·41

As shown in Fig. 3, when the amounts of combined acid are plotted against the calculated internal *p*H values instead of the measured external *p*H values, the four titration curves are unified, as would be expected in terms of the Donnan theory. Further support for the latter is provided by the following considerations—Steinhardt and Harris have shown that when wool is titrated with hydrochloric acid in presence of sufficient potassium chloride to keep the chloride ion concentration constant, there is a linear relationship between the *p*H of half-maximum combination and the logarithm of the chloride ion concentration, when the latter does not exceed about 0·2 N. Such a relationship is to be expected from the approximate equation (xxxii); of the terms on the right-hand side of the equation, Fig. 3 shows that the internal *p*H at which the wool combines with half the maximum possible amount of acid is a characteristic constant, independent of the salt concentration, while the term log (a/v) will be practically constant because a is then half the maximum combining capacity and v changes only slightly with salt concentration. In other words, if $p\mathrm{H}'$ is

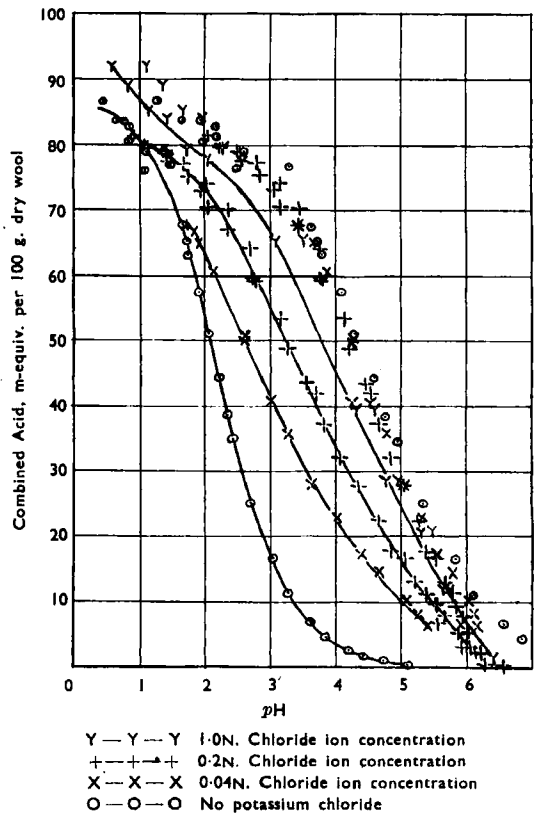

FIG. 3

the external *p*H corresponding to half-maximum combination with acid,

$$p\mathrm{H}' \simeq \log X + \text{constant}$$

The exact equation (xxxi), however, predicts that as the salt concentration is increased, λ decreases and $p\mathrm{H}_{\mathrm{int}}$ approaches $p\mathrm{H}_{\mathrm{ext}}$, so that the graph of $p\mathrm{H}'$ against $\log X$ should asymptotically approach a limiting value, viz. pK_{int}, which is about 4·5. Steinhardt and Harris found this to be the case, and in this respect, therefore, the Donnan theory is superior to that of Gilbert and Rideal, which does not predict the departure from the linear relationship.

Similarly, when wool is titrated with sulphuric acid in presence of sufficient potassium sulphate to give a constant concentration of sulphate ions,

$$p\mathrm{H}' \simeq \frac{1}{2}\log [\mathrm{SO}_4^{--}] + \text{constant}$$

if complete dissociation of HSO_4^- ions is assumed. This approximate equation is obeyed at low concentrations of potassium sulphate, and the large deviations at high concentrations are in exact accordance with the predictions of the Donnan theory.

Finally, reference may be made to the fact that the extent to which amide groups are hydrolysed by hydrochloric acid in twenty-four hours at 22·2°C. has been found[15] to increase with increasing concentration of sodium chloride in solutions of the same external *p*H. This observation is in striking agreement with application (iii) of the

Donnan theory, because the internal *p*H decreases with increasing salt concentration. The so-called "catalysed hydrolysis"[16] of amide groups by acids with high anion affinity is similar in nature, although the closer approximation of the internal and external *p*H values is here due to a different cause. The application of the Donnan theory to acids of this type will be discussed in a later paper.

The authors are indebted to the International Wool Secretariat for grants in aid of this investigation.

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DEPARTMENT OF TEXTILE INDUSTRIES
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(*Received on 24th July* 1948)

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Affiliated Society (this *Journal*, 1949, **65**, 4). The address of the Honorary Treasurer of the Society of Dyers and Colourists of Australia should be c/o Ciba Co. Pty. Ltd., 213 Canning Street, Carlton N 3, Melbourne.

Notes

Proceedings of the Council

At a meeting of the Council, held at the offices of the Society, 32–34 Piccadilly, Bradford, on 15th December 1948, the proceedings included the following items of general interest—

Composition of the Council— It was reported that four Vice-presidents would retire in March 1949, viz. Mr. H. H. Bowen, Mr. W. A. Edwards, Dr. L. L. Lloyd, and Mr. F. Smith; and two Ordinary Members of Council, viz. Mr. F. L. Goodall and Mr. E. A. Swift. Two casual vacancies for Ordinary Members had not been filled in the course of the year, so that nominations for four vacancies for Ordinary Members would be required. Mr. H. Jennison and Mr. J. Barritt were nominated for re-election as Honorary Treasurer and Honorary Secretary respectively.

Wool Dyes Committee— The resignation of Dr. J. F. Gaunt and Mr. J. G. Grundy, and the co-option of Mr. B. Kramrisch and Mr. D. R. Lemin, were reported.

Vat Dyes Committee—The resignation of Mr. J. G. Grundy and the co-option of Mr. F. W. Bradley were reported.

Membership—Twenty-four applications for membership were approved.

Meetings of Council and Committees
January

Council— 19th
Finance— 19th
Publications— 18th
Fastness Tests— 14th (Manchester Sub-committee)
Vat Dyes— 26th
Wool Dyes— 12th
Historical Records— 19th
Annual Reviews of Textile Progress— 12th
Light Symposium— 28th

Relaxation of Controls

The Board of Trade have announced that the Control of Dyestuffs Orders which prohibit the sale and supply of dyestuffs and intermediates except under licence by the Board of Trade have been revoked. These Orders are—

S.R. & O. 1939 (No. 1431)
S.R. & O. 1940 (No. 1836)
S.R. & O. 1941 (No. 171)

The new Revocation Order, Raw Materials (Various Controls) (Revocation) (No. 2) Order 1948, does not affect the regulations governing the import and export of dyestuffs and intermediates, for which licences are still required. It can be obtained through any bookseller or newsagent or from H.M. Stationery Office, Kingsway, London W.C.2 and branches, and came into operation on 1st January 1949.

Textile Machinery Exhibition

An exhibition of textile machinery and accessories, yarns, and fabrics will be held at Belle Vue, Manchester, on 12th-22nd October 1949. The last such exhibition was held in October 1938, so that the first post-war exhibition should arouse considerable interest. Applications for allocation of stands should be addressed to Messrs. *Textile Recorder* Machinery & Accessories Exhibitions Ltd., Old Colony House, South King Street, Manchester 2, the organisers of the exhibition, from whom further information may be obtained.

Textile Research in Spain

The Asociación Nacional de Ingenieros de Industrias Textiles of Barcelona has set up a research section, whose object will be the development of technical textile research. It is hoped to maintain close contact with all similar research institutes, both Spanish and foreign.