CHAPTER III
MECHANICAL PROPERTIES OF WOOL FIBRES

3.1
THE LONGITUDINAL EXTENSION
STUDY OF WOOL FIBRES

Wool has two structures, \( \alpha \) and \( \beta \). The unextended fibre shows an \( \alpha \)-pattern, whereas 100\% (or more than 30\%) extension leads to a \( \beta \)-pattern. The results of extension study may be interpreted in terms of structure and morphology of wool.

3.1.1
Stress-Strain Study of Wool Fibres

The longitudinal extension study dates from Harrison's work(185). The general feature of the longitudinal extension of different wool fibres is the same (Fig. 17A). There are three types of study in general - (i) the rapid rate of loading, (ii) the constant load study, and (iii) the slow rate of loading. In the last, the study consists of the extension at equilibrium position and requires longer time for study. Since, the fibre attains an equilibrium state, the changes occurring will be at completion and hence, the reproducibility of the same fibre is not possible. In the rapid rate of loading a reproducibility is observed. In case of constant load, the fibre is extended rapidly after the
application of load and then fibre creeps slowly because of the variation in the stress. This has been studied by many workers under varying conditions and interpreted in terms of structural deformations either due to bond breaking or in two-or three-phase model. A complete satisfactory interpretation in terms of molecular structure is not yet achieved.

When the fibre is stretched to less than 30% extension and released in water for sufficiently longer time, the load-extension curve is found to be reproducible (185). This indicates existence of a definite mechanism in extensibility. If the extension is more than 30%, the released fibre does not show reproducibility although the feature of the curve is the same (35), as the wool structure is damaged. The load-extension study helps to identify any damage to wool fibre as well as the changes in the properties by the chemical modifications (187).

In load-extension study, the surface area of the specimen at the point of load applied is a more important factor. In case of wool, the diameter of the fibre not only varies from sample to sample, but also from tip to root of the same fibre. This variation makes the load-extension study, in which single fibres are used, more statistical and less conclusive. In most of the cases, care is taken to choose fibre of uniform diameter and of the same breed or lot.
In general, all curves of the extension study exhibit three distinctive regions - (i) Hookean region, (ii) Yield region and (iii) Post-yield region. Besides the diameter of fibres other factors influencing the load-extension curve are time, humidity and temperature(188). Most of the wool has crimp-ness. Certain amount of extension is necessary to decrimp and then starts the stress-strain curve. As stress increases, there is a straight line upto 2% extension parallel to stress axes. This part obeys Hook's law and is called 'Hookean region'. After this, the fibre extends much rapidly as stress increases upto 25% extension. This part is 'Yield region'. In the post-yield region, the fibre stiffens with increase of extension. The ratio of the slopes of these three regions are 100:1:10.

The point where the decrimping of the fibre ends is called the 'zero-strain point' (point A). Fibres swell in water longitudinally by 1-2%. Because the extent of longitudinal swelling is dependent on R.H., the zero-strain point also varies with relative humidity (R.H.). The intersection of Hookean line and yield line (point B) is independent of relative humidity and hence of the position of point A and temperature upto 130°C. Young's modulus in the Hookean region is of the order of \(10^{10}\) dynes/sq.cm. It increases with increase in relative humidity. The ratio of wet to dry fibre value is 2.7(189). The relation between the relative humidity and Young's modulus is non-linear, but the stress at point B varies with
relative humidity linearly. In addition, the modulus is a linear function of logarithm of rate of extension (190, 191). With increase in temperature, the modulus decreases and near about 130°C the Hookean region and hence modulus disappears completely. The fibre shows a $\beta$-pattern (192). As the humidity increases the Hookean region decreases and at saturation it will be one quarter of the length of the dry state. The extension of dry fibre above 30% extension is not possible. The linear part between 3-20% extension (E to C) is called yield region. The order of the modulus is $10^8$ dynes/sq.cm. and is a function of cross-sectional area (193). For a uniform cross-sectional area, the modulus decreases rapidly between 0-40% R.H. and thereafter decreases slowly. The stress relaxation at a given time, in wool, varies linearly with the logarithm of straining rate and is independent of the fibre extension in the yield region. Bull and Gutman (49) consider the yield region extension as a gel-sol transformation. Above 30% extension (i.e. point C), the region is post-yield region. The fibre becomes stiff and extension will be less with the load applied. The modulus is of the order of $10^5$ dynes/sq.cm. This is a function of relative humidity, temperature and rate of extension. As relative humidity and temperature increase, the region becomes less distinct from that of yield-region. Relative humidity over the whole range (0 to 100%) affects the modulus by 15% increase, whereas temperature effect is two-to three-fold change. The rate of
extension too changes the modulus by 25\% (194). The position of the point C is constant up to 50° C, then increases with increase in temperature (195). Point C is a function of rate of extension, the lower the rate the higher the drift. The mechanism of extension in the post-yield region has been explained by thiol-disulphide interchange mechanism.

3.1.2
Fibre Extension and Energy

Elasticity depends on inter-molecular attractions. On stretching the elastomer and hence the bonds, the potential energy increases. Such substances have a positive coefficient of thermal expansion. On warming the stretched fibre, the tension decreases. Wool and other keratins have a positive coefficient of thermal expansion, even when all disulphide bonds are broken (196). The mathematical formula which expresses the restoring force in terms of energy is given by

\[ K = \left( \frac{\partial U}{\partial \ell} \right)_f - T \left( \frac{\partial S}{\partial \ell} \right)_T \]

\[ = \left( \frac{\partial U}{\partial \ell} \right)_f + T \left( \frac{\partial S}{\partial \ell} \right)_T \]

where \( K \) is the restoring force at length \( \ell \), \( U \) the internal energy, \( T \) absolute temperature and \( S \) entropy. The entropy contribution to \( K \) is very small in case of wool (197, 198).

When hydrogen bonds are broken, by stretching in phenol, the coefficient of thermal expansion is found to be negative.

When the fibres are heated in the extended state, and the
disulphide bonds are broken, the K value, is found to be negative. These indicate that the elasticity of the α-structure is due wholly to internal energy and the dis-oriented β-structure is due to entropy. Since, the study is on non-equilibrium systems, the correlation between elasticity and coefficient of thermal expansion is objectionable (199).

3.1.3 Fibre Extension and Structural Changes

Shorter (200) was the first to propose a mechanical model to wool fibre on the basis of the elasticity of the fibre. The model proposes three sets of elements in the fibre - (i) elastic elements which extend and contract freely, coupled to, (ii) elastic elements which are impeded in their extension and contraction by, (iii) elements which act as a resistant medium. Since, wool, with a definite cellular structure, is insoluble in water, the gel structure failed to explain some of the elastic properties.

Since, the extension at point B is independent of temperature and humidity, and after extension, the fibre remains permanently more extensible at the tension, Speakman (201) proposed a model of two gels arranged in parallel, instead of two phase gel structure - (i) the petrified gel consists of an elastic wall enclosing a fibrillar structure, which is not in physical equilibrium with a viscous phase, (ii) the other gel, which fills the interstices of the petrified
gel, is gelatinous and capable of reversible solution in and deposition from water.

When a wool fibre is stretched in water, two types of relaxation occur (202). During the first ten seconds a rapid relaxation occurs due to secondary bond breakage. Then because of disulphide bond fission, a slow relaxation over a greater period of time occurs.

According to Astbury and Woods (35), the rapid loading in water is largely confined to the amorphous region, i.e. sol-gel transformation. Above 20% extension, the molecular transformation takes place. Though $\alpha \rightarrow \beta$ transformation is far from 30% extension, because of the relaxation under stress, the transformation may be enhanced in the stretched fibre. In the extended state of the fibre, the folded configuration opens. In the later stage, due to the new bond formation, not as perfect as in the original state, the fibre loses its strength (203).

Though the rupture of disulphide bonds has been proposed (204-207) to explain, Phillips et al. failed to detect any change in cystine content (122, 208).

The dry strength of the fibre is largely due to the number of peptide bonds and decreases with decrease in peptide bonds. The dry fibre tensile strength is more than that of wet fibre. The swelling in water breaks the bonds, usually weak bonds. The wet strength of the fibre is largely due to disulphide bonds and decreases linearly with cystine content (209, 210). The dry fibre strength is independent of disulphide bond breakage upto
-130-

Above 50% disulphide bond breakage, the fibre does not regain its original tensile strength. Probably, internal rearrangement takes place, preventing the regain of strength.

3.1.4 Fibre Extension and X-ray Diffraction

X-ray diagram of keratins (α-pattern) changes only slightly up to 20% extension beyond which the change is rapid. Above 50% extension the change is again negligible (β-pattern). The α → β transformation starts at 20% extension irrespective of the medium, relaxation effects and chemical modifications (191). α → β transformation shows detectable changes at meridional 5.1Å and equatorial 4.65Å and 9.8Å reflections.

Bendit (43) revealed that:

1. The change in X-ray diffraction diagram starts at 5% extension;
2. There is no rapid change in intensity between 30 to 50% extension;
3. Low humidity and low-temperature extension accelerates the α → β transformation;
4. At 20°C and 50% R.H. for extension from 0 to 20%, the decrease in 5.1Å reflection is not accompanied by a related increase in 4.65Å reflection;
5. X-ray diffraction pattern before and after relaxation revealed no significant change in the intensity of 9.8Å and 5.1Å. But, 4.65Å intensity increased markedly.
3.2
SET/SUPERCONTRACTION STUDY OF WOOL FIBRES

In the chemical structure of wool keratin, the peptide chains are cross-linked by polar and covalent bonds. When a reagent is used to break some of these bonds, the structure tries to converge into a configuration of minimum energy and the new structure may have a shorter length than the original. The fibre is then said to be 'contracted'. On the other hand, if the reagent, in addition to certain bond breakage, builds up new bonds under the deformed condition, which in turn gives an elongated structure of longer length, the fibre is said to be 'set'.

3.2.1
Supercontraction and Set

When a fibre is extended in water, steamed in the extended state and then released in steam, the final length of the fibre will be either less or greater than the original length (35). The short timings of steaming in the extended state result in a decrease in the length. This is termed as 'Supercontraction'. During the steaming some of the bonds are ruptured and the structure, because of free movements, tends towards the low energy state and hence contracts. It is unable to form new bonds in a short time, hence the contraction will be retained.

When the fibre is steamed for a longer time sufficient time is available to form new cross-linkages, which will stabilize the extended state. On release, the links retain their positions
and a 'set' results. This is expressed as the percentage increase in length.

Wool fibres on extension in cold water and on drying in the extended state, acquire a 'cohesive set'. On immersion of the set fibres in cold water, the set is lost. In this case, the removal of water, during drying, forms new polar links, which will be in equilibrium with the strained structure. The internal viscosity of the fibre increases. On releasing the fibre in the dried state, an immediate contraction results. After one hour, the fibre attains a cohesive set and then the further change in length will be too small. The latter change is a linear function of logarithmic time. In an immediate contraction, on release, the force of recovery is equal to the force of new bonds formation during setting(211). On immersion in water, the cohesive set fibre loses its set due to the rupture of the newly formed bonds. The viscosity of the fibre decreases.

If the extended fibre, in water, is steamed or boiled in water and released in cold water, some amount of set is retained. This is known as 'Temporary Set'. It is not stable to boiling water. In some cases, the set fibres even on boiling in water for one hour, do retain some amount of set. This is termed as 'Permanent Set'. On continued boiling of the released fibre for a longer time, however, the set decreases(212).
3.2.2 Stress-Strain Curves of Set Fibres

Stress-strain curves of set fibres (Fig. 17B) indicate the modifications taken place while setting and also indicate in what region the changes have occurred. When set fibres are extended an additional region appears in between the Hookean and yield regions(213). As the time of setting increases, the new region extends and finally the Hookean region disappears. During setting some amount of fibre is converted into elastomer. The elastomer may extend more readily than the rest of the fibre, which results in a new region in the curve. This indicates that the elastomer has a small elastic modulus than the rest of the fibre.

The stress required to produce a fixed extension in water decreases with disulphide content due to decrease in stress at the end of the Hookean region(211,214). Even the stress at the end of yield region and at break decreases with decrease in disulphide content. The reduction of disulphides to thiols increases the limit of maximum extension. Thus, changes in the stress-strain curves help in the identification of the changes in the disulphide content.

3.2.3 Chemistry of Supercontraction

In addition to steaming, some of the chemical treatments cause supercontraction of wool keratin. An extended fibre supercontracts in dilute sodium hydroxide. This gives an \( \alpha \)-pattern whereas fibre steamed for a long time gives a disoriented
Fibres soaked in cuprammonium hydroxide solution contract and show a disoriented $\beta$-pattern. The treated fibres on washing with dilute acids, regain their length as well as $\alpha$-pattern(215). Hence, in some cases supercontraction is a reversible process.

Though, the hydrolysis of disulphide bonds has been proposed for the supercontraction phenomena, Phillips et al.(122,208) failed to detect any change in either disulphide content or reactivity towards alkali.

3.2.3.1 Supercontraction and Polar Linkages

Untreated and set fibres contract in phenol, formaldehyde, lithium bromide, etc. Phenol is effective even at room temperature. The temperature at which supercontraction commences is thought to be 'softening point' and it depends on the disulphide content of the fibre(214).

Phenols rupture hydrogen bonds of wool and hence peptide chains become free to contract. The disulphide content before and after the treatment is found to be the same(217). Phenol solutions are only effective in alkaline medium. In alkaline solution a marked decrease in disulphide content is observed(218). So, the rupture of hydrogen bonds alone is doubtful. The alcoholic solution of phenol is ineffective. The ionic
and non-ionic phenols cause supercontraction. Phenolate ion is more effective than unionised form. At low pH values unionised phenol causes contraction. The two forms of phenols have different mechanisms.

Lithium bromide breaks hydrogen bonds and not disulphide bonds. In lithium bromide solution a two stage supercontraction is observed. Aqueous lithium bromide contraction is variable and is between 10-15%. On washing with water, fibre regains the length. The variation may be due to the presence of bromide and Br^- in solution. The supercontracted fibre shows disoriented pattern and does not have optical birefringency. In bromine free lithium bromide solution, at boil, fibre contracts 50% and process is irreversible. The time taken for the contraction depends on the rate of lithium bromide penetration and decreases with rise in temperature.

As temperature decreases, the two stages of supercontraction in lithium bromide become distinctive. Haly and Feughelman suggested that the first stage contraction could be determined by the number of broken strong secondary bonds, whereas the number of disulphide bonds could be accounted for the total contraction. The conversion of 94% disulphide into S-methyl group does not affect the supercontraction. It results in an increase in the first stage contraction with decrease in disulphide content; finally the first stage approaches the total value of contraction at zero disulphide content. The conversion of disulphide into S-CH₂-CH₂-S does not affect
the first stage contraction, but the total contraction decreases with decrease in disulphide content.

Irradiation of wool by ultraviolet radiations ionizes the tyrosine side chains, which favours the breaking of strong hydrogen bonds (225). The iodination of tyrosine side chain, due to bulkiness, retards the second stage supercontraction (225).

Though supercontraction is independent of thiol and disulphide contents, the first stage is dependent on disulphide and acid-labile cross-linkages whereas the second stage, due to the interconversion of thiol and disulphide is independent.

Since, the equilibrium force at a fixed extension, in concentrated lithium bromide solution, is directly proportional to the absolute temperature, the force is solely due to entropic factor (227). In series zone model, it has been shown that in lithium bromide solution, the hydrogen bonds of the two zones have different energies (228).

3.2.3.2
Thiol-Disulphide Interchange

The fibres treated with sodium sulphide, sodium bisulphite, potassium cyanide, silver sulphate, etc., have been found to contract (229). These are all capable of breaking disulphide bonds. Chemical modifications of wool fibres, by virtue of which cross-linkages are produced, lead to a decrease in the supercontraction by sodium bisulphite (185). Deamination of wool enhances the contraction whereas acetylation is without
effect. Since, there is no change in the disulphide content on supercontraction and the second stage is dependent on the disulphide content, the side reactions of disulphides have been ruled out. The mechanism is thought to be thiol-disulphide interchange. Phillips et al. (113, 208) observed that the breaking of type A and not type B of disulphide bonds is essential for contraction and if both break together, the contraction is found to be accelerated.

N-ethylmaleimide treated fibres show a decrease in thiol content as well as slow contraction in phenol and aqueous lithium bromide solution (230). The presence of bromine, which reacts with thiol groups, inhibits the second stage of supercontraction. If the disulphide is converted into S-methyl, \(-S-\mathrm{CH}_2-\mathrm{CH}_2-S\) groups, there is no effect of bromine. This concludes that thiol-disulphide interchange facilitates the supercontraction.

Though chlorine dioxide and nitrous acid oxidize cystine to cysteic acid, chlorine dioxide does not cause supercontraction, whereas, nitrous acid increases (50). Alexander (231) believed this to be due to the degradation of wool by nitrous acid. But chlorine dioxide pretreated wool supercontracts in water, dilute hydrochloric acid, 50% urea and sodium sulphite solutions. The oxidizing agents help in breaking the stronger bonds and hence enhance the supercontraction. The effect of oxidizing agents for the completion
of supercontraction, reveals that more than 70% disulphide bonds are broken.

3.2.4 Chemistry of Setting

When the stretched fibre is steamed for a longer time, set results. Different types of fibres have different ability to set. The fibres which set readily are, however, not those which supercontract more. These variations are associated with their chemical compositions (232), especially in the cortical regions. During steaming or boiling in water of the stretched fibre, the cross-linkages are hydrolysed and due to the constrained force, the free structure coils up and tends towards the configuration of minimum energy. During the prolonged steaming, the free radicals of the hydrolysed linkages, due to structural coiling, come across a number of other free radicals, thus facilitating the new linkage formation. Since, the force of bond formation is opposite to the force of contraction, some extra energy is required to overcome this force in addition to energy of bond formation. The extended state of the fibre structure helps in forming new bonds. Thus, the formation of new configurations, depending on the new linkages formed, gives varying amount of set to the fibre. Since, the wool structure consists of disulphide and polar linkages, the mechanism of setting was explained in terms of these two separately. But at present none of these explains the mechanism satisfactorily.
3.2.4.1

Thio-disulphide Interchange

The low temperature setting of wool fibres by the rupture of disulphide linkages and reformation of disulphide bonds led to the concept of thiol-disulphide interchange as the mechanism of setting(233). In addition to this, the following factors support this mechanism:

(i) The hydrolytic fission of disulphide bond is a reversible process. The reformed cystine may be responsible for the set(234).

(ii) Wool on long time exposure to atmosphere has been found to lose sulphur as well as the ability to set(235). Similarly, the baryta treated wool has decreased sulphur content and ability to set.

(iii) Fibres dyed with high affinity dye have no ability to set. Deamination by nitrous acid or blocking of amino groups by bulky side chains like 2,4-dinitro-fluorobenzene impair the ability to set.

(iv) The study of setting with pH variation showed that the setting started above pH 6, attained a maximum at pH 9.2 and then decreased with increase in pH. The hydrolysis of disulphide bond is more in alkaline region of pH and increases with increase in pH. Above pH 10, the breakdown of peptide linkage complicates the mechanism. At pH 9.2 the thiol group dissociates, which favours the interchange mechanism and hence the maximum setting at pH 9.2 is observed.
(v) Reduced wool forms stable cross-links with alkyl-dialdehydes, mercuric compounds, formaldehyde and stabilizes the wool structure (185).

\[
\begin{align*}
R-S-S-R & \xrightarrow{\text{Reduction}} 2R-SH \\
R-SH & \xrightarrow{\text{HCHO}} R-S-CH_2-S-R \\
R-SH & \xrightarrow{\text{HgCl}_2} R-S-Hg-S-R \\
R-SH & \xrightarrow{(\text{CH}_2)_n} R-S-(\text{CH}_2)_n-S-R
\end{align*}
\]

(vi) Phillips (122) failed to detect significant changes in amino nitrogen, increase of thiol groups or the formation of aldehyde in alkali treated wool.

(vii) The slow rate of lanthionine and \( \alpha \)-amino acrylic acid formation rules out the side reaction of disulphide bonds during setting (212).

According to Speakman (229), the mechanism of setting is an initial breakdown of disulphide bonds into sulphenic acid or aldehyde, then the rearrangement of the chain and finally formation of cross-links with amino groups.

\[
\begin{align*}
R-\text{CH}_2-S-S-\text{CH}_2-R & \xrightarrow{\text{H}_2\text{O}} R-\text{CH}_2-SOH + R-\text{CH}_2-SH \\
R-\text{CH}_2-SCH & \rightarrow R-\text{CHO} + \text{H}_2\text{O} \\
R-\text{CH}_2-SCH + \text{NH}_2R & \rightarrow R-\text{CH}_2-SHNR \\
R-\text{CHO} + \text{NH}_2R & \rightarrow R-\text{CH}_2-\text{CH}=\text{NR}
\end{align*}
\]

Since, quinone treated fibres fail to take set in 0.05M borax solution (i.e. pH 9.2) and at pH 1, all basic side
groups being combined with acid, the untreated fibre fails to take set, it was thought that the basic side groups of arginine and lysine of wool take part in the new cross-link formation, which are responsible for the permanent set. The formation of sulphenamide (\(-S-NH-\)) linkage is favoured by a number of other properties like:

(a) the chemistry of disulphides shows the presence of sulphenamide linkage,
(b) the irreversibility of set in acid or alkali shows the formation of a new stable cross-link,
(c) the fibres, set in boiling sodium bisulphite solution, do not contract,
(d) though the colour reaction of sodium nitroprusside failed to detect the sulphhydryl groups due to slow penetration and quick colour fading, Feigl’s catalytic sodium azide and iodine reaction (236) showed the presence of large number of thiol groups,
(e) the superiority of sodium bisulphite, as a setting agent, supports the mechanism as,

\[
\begin{align*}
R-S-S-R + NaHSO_3 & \rightarrow R-SNa + R-S-SO_2H \\
\text{or} & \quad R-SH + R-S-SO_3Na
\end{align*}
\]

\(R-SO_3Na(\text{or } H)\) being acidic, reacts with basic side chain groups.

\[
\begin{align*}
R-SO_3Na + H_2N-R & \rightarrow R-3-NH-R + NaHSO_3 \\
R-SO_3H + H_2N-R & \rightarrow R-3-NH-R + H_2SO_3
\end{align*}
\]
(f) The low temperature setting too showed the formation of S-NH-bond (233).

Phillips et al. (208) found that S-cysteine sulphonate groups of wool treated with sodium bisulphite did not react with methylamine. 6N hydrochloric acid decomposes the sulphenamide groups in many compounds. These show the absence of S-NH group. In addition to these, the analytical investigations of hydrolysates of wool failed to identify such type of links.

The optimum pH for wool-fibre setting is pH 9.2. At this alkalinity, the sulphenic acid, formed by the hydrolysis of d-sulphide bonds, may undergo decomposition into aldehyde.

\[
\text{R-CH}_2\text{-SOH} \xrightarrow{} \text{R-CHO + H}_2\text{O}
\]

This aldehyde reacts with basic side chains to form aldimine (-CH = N-) linkages.

\[
\text{R-CHO + H}_2\text{N-R} \xrightarrow{} \text{R-CH = N-R}
\]

Even the thialdehydes and basic side chains form aldimine linkages. The formation and the explanation of setting mechanism by S-NH show little likelihood of aldimine formation. Even if it forms by the treatment of caustic soda on fibre, the set fibre boiled first with 0.1N hydrochloric acid and then with sodium bisulphite should show more contraction than bisulphite alone, because of the rupture of CH = N-bond. In practice, it is not realised. On the contrary, the caustic soda and baryta treatment of the fibre decreases the set, as the time of treatment increases. Though some investigators...
claim the presence of \(-\text{CH} = \text{N}\)- linkage, so many have objected
the mechanism of \(-\text{S}-\text{NH}\)- and \(-\text{CH} = \text{N}\)-linkage formations.

According to Caldwell et al. (237), the mechanism of setting
in boiling water and bisulphite solution is the same and set
results due to conformational changes in the polypeptide
structure. Due to hydrolysis of disulphide, thiols will
result and the increased concentration of thiols favours the
thiol-disulphide interchange, which brings the polypeptide
chains to a stable configuration. Rebenfeld (238) gave the
interchange as:

\[
\begin{align*}
\text{R-S-S-R} + \text{H}_2\text{O} & \quad \rightleftharpoons \quad \text{R-SOH} + \text{R-SH} \\
\text{R-SH} & \quad \rightleftharpoons \quad \text{R-S}^- + \text{H}^+ \\
\text{R}'-\text{S-S-R'} + \text{R}^- & \quad \rightleftharpoons \quad \text{R}'-\text{S-S-R} + \text{R}'^- \\
\text{R-S-S-R} + \text{R}'^- & \quad \rightleftharpoons \quad \text{R-S-S-R'} + \text{R}^- 
\end{align*}
\]

The study of set on modified wool fibres (239) showed that in
absence of reducing agents, at pH 5, thiol-disulphide inter­
change took place and in presence of reducing agents
\(\beta\)-keratin formation might take place. At pH 9, new cross-
linkages form. According to Feughelman (240), the rupture
and the reformation of disulphide bonds under stress is
confined to the matrix, without change in length. If the
\(\alpha\)-structure is partly or wholly affected, the change in
length does occur. Though, thiol-disulphide interchange
seems to be the mechanism of setting, the exact nature of
reaction is still unrevealed.
3.2.4.2
Polar Linkages

When Speakman and co-workers thought the mechanism of setting as the thiol-disulphide interchange, other group of investigators thought it to be due to polar linkages, especially hydrogen bondings(113,241,242).

The set fibre in saturated urea is found to regain its original length, when the setting is restricted to few minutes; the set $\alpha$-crystallite changes into $\alpha$-form in urea solution(242). Sodium hydroxide, lithium bromide set fibres recovered partially in 100% formic acid and 100% in cuprammonium hydroxide irrespective of setting time(243).

The investigation of Farnworth(244) reveals that the set of the untreated fibres can be destroyed by lithium bromide and hot formic acid completely, whereas cold formic acid removes partially. The methylated (-SCH$_2$) fibre takes set immediately in boiling water and the hydrogen bond breaking reagents can destroy the set. Since, sulphenimide (-S-NH-) formation is impossible, in this case, hydrogen linkages are responsible for the set. The total loss of 5% disulphide is thought to be due to the reactivity of lithium bromide and formic acid.

The low temperature setting gave another supporting evidence for the hydrogen linkage mechanism. The fibre set at any temperature in any reagent is found to lose set in the same reagent at higher temperatures ($>$ 20°) than the setting.
temperature. The same fibre can be reset and redestroyed and hence forms a cyclic process. Since, the sulphenimide (-S-NH-) formation is irreversible, hydrogen linkage can alone explain the cyclic process.

Thioglycolic acid is a specific reagent for the reduction of cystine to thiols. The thiols so formed do not react with amino groups and hence -S-NH- formation is not possible. But, the setting is too rapid. The effect of thioglycolic acid is more at pH 9.2, the rate of set too found maximum at pH 9.2. In case of sodium borate at pH 9.2, the rapid rate of set decreases with time due to the reoxidation of thiols. So, thioglycolic acid reduction and set rules out the formation of sulphenimide (-S-NH-) linkage.

The work of Feughelman et al. (245) supports the view of Farnsworth. They conclude that the energy of polar bonds is distributed over a wide range so that some are released in cold water and others in lithium bromide at higher temperatures. The tyrosine group, during dissociation transfers excess energy to the neighbouring strong hydrogen bonds, which break and hence facilitate the setting. When the tyrosine is blocked by iodination, nitration or some bulky side chain, both the ability to set and the second stage of supercontraction are inhibited (245). The ultraviolet irradiation accelerates the second stage supercontraction and setting. The crystallinity decreases. Similar effects on egg albumin show the rupture of hydrogen bonds.
The reactivity of 1 flouro-2:4 dinitrobenzene on the stretched and unstretched fibres reveals the steric effect(247). The bulky side chain of the reagent hinders the movement of the chains thereby affecting either hydrogen linkage mechanism or disulphide bonding mechanism of set.

Wolfram showed that during setting the breakdown of disulphide linkage is at much smaller scale. Jenkins and Wolfram(248) think that the stress relaxation at boil is not only due to the chains unfolding but also due to the slip relative to each other. The X-ray study of setting at boil and then treating the set fibre with formic acid reveals that at low disulphide content the initial α-pattern changed to β-form on setting, which on formic acid treatment changed into diffused α-pattern, whereas at the high disulphide content, fibre gives α-, β- and ordered α-forms respectively. This explains that in the low disulphide content fibres, the chains slip over each other, whereas in high disulphide content slipping is forbidden due to large disulphide linkages and the set is due to polar linkages.

3.3 MECHANICAL MODEL OF WOOL FIBRE

Though wool structure, as determined from the study of X-ray diffraction, infrared, etc., satisfactorily explained the observed patterns, it failed to interpret the rheological properties. The study of electron microscopy, stress-strain curves, and set/supercontraction made it necessary to adopt
a new model for wool. Idealised mechanical models of Shorter (249) and Berke and Helsey (250) failed to explain the properties of wool. At present series-zone model is most favoured.

3.3.1 Model of Mandelkern et al. (251)

This model consists of an uniformly cross-linked matrix with the microfibrils in parallel along the fibre axis. Since, in the yield region the unfolding of matrix encounters negligible resistance, the constant stress is due to $\alpha$- and $\beta$-phases in equilibrium and gives the difference in the free energy of the two phases (252). The extension determines the proportion of $\alpha$- and $\beta$-phasess. At the end of the yield region, the network of matrix vanishes and in post-yield region with increase of stress, extension occurs. Though this model explained most of the observed things, it is very unlikely to have at 33% extension, a complete extended matrix and an unextended microfibrils in the immediate vicinity.

3.3.2 Series-Zone Model

The turn over point of yield to the post-yield region, is constant at about 30% extension up to 40°C. This temperature is identified as a second order transition temperature in strained wool, when the bond breaking starts. Any physical or chemical treatment alters the transition temperature. An increase in the transition temperature results in an increase in the second stage supercontraction in lithium bromide and
A. FEUGHELMAN MODEL.

Series Zone Model.

Distribution of disulphide in the matrix.

B. MUNAKATA MODEL.

Zone model.

Slacked state.

Stretched state with reagent attack.

Simple rheological model of wool.
vice-versa. From the study of mechanical properties of supercontracted fibres, Feughelman and Haly proposed a series-zone model consisting of two types of zones in microfibrils along the fibre axis differing in their thermal stability (Fig. 18A).

Since, the matrix is an easily penetrable component, it is the first to be weakened by the treatments. The microfibrils may be either non-penetrable, or one group penetrable in zones. The first-stage supercontraction in htr results in 15% contraction and the longitudinal modulus is decreased by a factor of 100. Since, the microfibrils are responsible for the modulus, the compression of microfibrils by non-penetration or one group penetrable zone is ruled out. If in the fibre structure, some of the zone microfibrils are weakened by zone penetration and contracted, the longitudinal modulus of the supercontracted fibre would be a mean of extensibility of the contracted zone of the microfibrils and the matrix. Hence, a relatively low value of modulus is expected and that is the result.

The microfibrils are divided into X and Y alternative zones along the fibre axis. X zones are easily penetrable. From the first and the second stage supercontraction, consideration of an increment in the length of contraction gave the proportion of X and Y zones as 35% and 44% of the microfibrils respectively. This explains the feature of stress-strain curves. Upto 30% extension only X-zones are extended and the
steric hindrance of the point B is released as the temperature is raised above $50^\circ$C. The reversibility of properties between 0-30% extension reveals that X-zones are reversible in character.

The extension of a fibre in water will produce a stress in the fibre due to the strain in the microfibrils as well as due to the cross-links and steric factors of the matrix. At any temperature, the behaviour of the matrix either as a rigid glass or as visco-elastic material depends on the critical disulphide concentration. Feughelman(254) in terms of series-zone model, gave the distribution of disulphides as shown in Fig. 18A. He plotted the disulphide density against the microfibrillar axis at different temperatures. At any temperature $T_1$, the critical disulphide concentration is defined as $AB$ or $CD$ as $Y$-zone and $BC$ as $X$-zone. Then the temperature is raised to $T_2$, $Y$-zone diminishes and $X$-zone enlarges. At any fixed disulphide content, the concentration of $X$-zone and the slope of the post-yield region must be uniquely related. The results reveal that most of the disulphide is concentrated in $Y$-zones and the product of the disulphide content of $Y$-zone and the slope of the post-yield region are directly proportional to the total disulphide content. This holds good only upto 30% disulphide less than the normal fibre content.
The microfibrils are embedded in the matrix along the fibre axis and when fibre is stretched both behave mechanically in parallel. As in Tougelman's model the microfibrils consists of two alternatively situated zones called $E$ and $P$ zones (Fig. 18B). The elastic $E$ zone consists of helices which can be reversibly stretched into a random coiled state in water at room temperature. The influence of mechanical properties on $E$ zone is very small. The non-elastic $P$ zone consists of helices with disulphide linkages.

The chemical treatments in the stretched state break the disulphide linkages in the matrix and due to the stress relaxation the stress reduces to zero. The force will reach the equilibrium force of the $E$-zone. The continued treatment, enhances the reaction at the surface of the crystalline phase. When the rupture of disulphide links of $Y$-zones ensues an irreversible extension of $P$ zones starts and will be enhanced due to the contraction of $E$ zones.

The X-ray study of relaxation of the stretched fibre (255) shows an increase in the $\alpha$, $\beta$-reflection intensities, which is due to the recovery of $E$ zones and crystallization of $P$ zones. In the set fibre, the contraction of $P$ zone is restricted by the interaction of neighbouring chains. The stability of set depends on the number and strength of the reformed bonds and steric hindrance.
Thus, the mechanism of setting can be explained as the rupture of cystine linkages, which hinder the P-zone stretch, the rupture of hydrogen bonds of the backbone and side chains and their reformation, which retains the elongated state. The supercontraction of the set fibre, under severe conditions like concentrated solutions of urea and lithium bromide, is due to the rupture of reformed bonds and the greater contractile force than the force of stretched F zone. Because of the bulky side chains, the contracted fibre never returns to the highly ordered α-helices.

According to Pauling and Corey(55), the helix structure is AB₈ rope alignment. Since microfibril is of 50 Å diameter(257), there will be 20-30 component helices. Since the tensile strength of the stretched-steamed fibre is greater than the slacked-steamed fibre(258) it appears that P-zones of one strand are adjacent to the P-zones of another strand, thereby protecting the disulphide breaking of P-zones. This alignment too explains why the yield strain of the set fibre in water is twice the setting strain.

Recently, on the basis of stress-strain study on fibres of reduced-alkylated disulphide bonds, Crewther(259) has given a model of the cross-linked high sulphur fraction, existing as globular protein in the matrix, bound to the microfibrils by alternatively polar or disulphide bonds. This has a series-zone effect.
In 1958, Menefee(250) proposed a revised model viz.,
honeycomb model to account for the wool properties. The
fibre cortex consists of two axially parallel elements:
(a) the microfibrils are made up of low-stability \( \alpha \)-keratin,
and (b) the matrix consists of partly high-stability
\( \alpha \)-keratin and partly amorphous protein. The fibre is resis-
tant to spontaneous length-wise changes. On extension,
\( \beta \)-keratin results from \( \alpha \)-keratin as well as from amorphous
protein. Because of the greater modulus of the matrix, the
tensile properties result, whereas the results of compression
are due to low modulus microfibrils.

Recently, Chapman(261) proposed a model based on parallel
two-phases, to account for the stress-strain behaviour. The
model consists of a parallel assembly of \( \alpha \)-helical, crystal-
line microfibrils embedded in less orderly matrix. These
microfibrils are connected mechanically with the matrix
through a number of covalent bonds. Though, these are not
necessarily at definite intervals, they are assumed to be so.
The microfibrils and the matrix have separate and independent
stress-strain curves. In the initial stage of extension the
microfibrils are extended to a length more than that of
point B. During extension some amount of \( \alpha \)-form is con-
verted into \( \beta \), which tries to bring down the real extended
length. The \( \alpha - \beta \) conversion finally attains an equili-
brium position, which is nothing but point B. At this stage,
though the stress remains constant, the conversion of \( \alpha \)-to
\( \beta \)-form is continued and thereby a plateau with constant
FIG. 19

CURVE OF FUNDAMENTAL UNIT
CURVE OF MATRIX
CURVE OF MICROFIBRIL

STRESS

STRAIN %.
stress results i.e., BC. At C all will be in $\beta$-form and after C, the curve is due to extension of $\beta$-phase (Fig. 19).

The study of set/supercontraction of different fibres (232) reveals that the low-temperature set results due to the changes in the non-helical zones, adjacent to the more labile $\alpha$-helices. Any change in the $\alpha$-helices requires the elimination of non-helical zones. So, non-helical zones stabilize the $\alpha$-helices by two ways. The non-helical zone is thought to be of: (i) $X_1$ zones which stabilize the $\alpha$-helices and extend on deformation up to 10%, (ii) $X_2$ zones connected to $\alpha$-helices by disulphide linkage and can extend on deformation up to 30%, and (iii) $X_3$ zones, with more concentration of disulphide bonds, are surrounded by rigid $\alpha$-helices. These are extended beyond 30% deformation.

All these proposed models explain the properties, none of them, however, has given a detailed information about the molecular organization.

Although set/supercontraction characteristics of keratin fibres have been widely studied over a period of years, mechanisms involved have not been as yet wholly understood. It is believed that when the fibre either supercontracts or acquires set a number of changes may take place. For example, (a) formation of aldimine and silphenimide linkage, (b) rupture and re-formation of hydrogen bonds in more stable configuration,
(c) re-formation of disulphide bonds broken while setting,
(d) thiol disulphide interchange, etc.

There is little doubt that mechanism of setting is quite complex and that changes taking place may depend on the media in which fibres are allowed to supercontract or acquire set. So far it has been observed that fibres can be set in alkaline, reducing, and even strongly acidic oxidising media. The study of the ability of keratin fibres, either untreated or suitably modified, to take set in different media, has been very useful in elucidating the changes taking place during certain chemical treatments. In the present investigation also, it was decided, therefore, to examine the setting characteristics of fibres treated in salt solutions in a systematic manner to obtain an insight into the nature of mechanism/mechanisms involved.
3.4
EXPERIMENTAL TECHNIQUES

3.4.1
Preparation of Samples

Purified-conditioned wool (as in 2.7.1) was equilibrated with 0.05N aqueous cupric chloride at 50°C for 24 hours. The equilibrated fibres were washed thoroughly with distilled water and air-dried.

For the study of load-extension and reflectance spectra, samples at different pH were prepared by equilibrating purified wool with cupric chloride solution of various pH values for 24 hours at 50°C. The equilibrated samples were washed thoroughly with distilled water, air-dried and conditioned over saturated sodium nitrite solution at room temperature.

3.4.2
Measurement of Permanent Set and Supercontraction

Care was taken to choose more or less uniform cross-sectional area fibres, for the experiment. About 4-5 cm length fibres were mounted on the stainless-steel frames and kept immersed in distilled water, prior to the start of the experiment. With the help of travelling microscope, a just-taut length of the fibre was taken and then stretched by 40% of its initial length. The frame was immediately transferred to the boiling setting solution and boiled for different time intervals. Frames were removed from the solution, fibre was released and washed thoroughly with distilled water and then...
transferred to boiling distilled water, where it was boiled for one hour in released condition. After cooling in cold distilled water, the wet taut length was measured and fibre was allowed to air-dry. Finally, the dry length was too recorded. The percentage of set or supercontraction was determined using the expression \[ \frac{100(l_i - l_f)}{l_i} \] where \( l_i \) is the initial length and \( l_f \), the final length. In each experiment minimum 4-5 fibres were tested.
3.5 LOAD EXTENSION STUDY OF CUPRIC CHLORIDE TREATED FIBRES AT VARIOUS pH VALUES

The samples were equilibrated with 0.05N cupric chloride at different pH values of solutions and prepared as described in 3.4.2.2 and conditioned at 64% R.H. at 27°C. The conditioned wool fibres were mounted on card-board paper such that the fibre length was 1 cm. These were mounted on Instron tensile tester and the automatic load-extension graphs were recorded, rate of extension being 100% per minute. For each sample 30 fibres were tested. From these graphs, the breaking extension, force at 30% extension and stress at 30% extensions were recorded. From these data, breaking extension percent, was calculated. In the Hookean region, at 0.5% extension, the force and extensions were noted for all samples and Young's modulus was calculated. The values of breaking extension percent, force at 30% extension, stress at 30% extension and Young's modulus are tabulated in Table XIII.

Because of the variations in the diameter of the fibres, and most probably due to less test numbers, there is no regularity in the results tabulated. These statistical results merely gave qualitative results and are not conclusive in any sense.

The sample of untreated wool was equilibrated at pH 5.20 under identical conditions of the experiment, in deionized water. This was treated as a standard for comparison. In general, the untreated sample has the minimum values in all data. As
### TABLE XIII
DATA FOR 0.05N CUPRIC CHLORIDE TREATED FIBRES AT VARIOUS pH VALUES

<table>
<thead>
<tr>
<th>Equilibrium pH</th>
<th>Breaking Extension %</th>
<th>Force at 30% Extension (g)</th>
<th>Stress at 30% Extension 10^8 dynes/sq.cm</th>
<th>Young's Modulus 10^10 dynes/sq.cm</th>
</tr>
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<tbody>
<tr>
<td>1.06</td>
<td>77.9</td>
<td>22.2</td>
<td>13.9</td>
<td>2.131</td>
</tr>
<tr>
<td>1.55</td>
<td>73.4</td>
<td>19.8</td>
<td>12.4</td>
<td>1.824</td>
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<td>2.09</td>
<td>76.3</td>
<td>21.9</td>
<td>13.7</td>
<td>2.308</td>
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<td>2.50</td>
<td>58.4</td>
<td>22.6</td>
<td>14.1</td>
<td>2.362</td>
</tr>
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<td>3.20</td>
<td>80.1</td>
<td>23.3</td>
<td>14.4</td>
<td>2.186</td>
</tr>
<tr>
<td>3.50</td>
<td>78.9</td>
<td>24.8</td>
<td>15.5</td>
<td>2.347</td>
</tr>
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<td>3.51</td>
<td>84.5</td>
<td>24.7</td>
<td>15.4</td>
<td>2.285</td>
</tr>
<tr>
<td>3.61</td>
<td>75.9</td>
<td>22.0</td>
<td>13.7</td>
<td>2.100</td>
</tr>
<tr>
<td>3.95</td>
<td>73.8</td>
<td>22.1</td>
<td>13.8</td>
<td>2.074</td>
</tr>
<tr>
<td>4.31</td>
<td>55.5</td>
<td>27.9</td>
<td>17.4</td>
<td>2.300</td>
</tr>
<tr>
<td>6.20</td>
<td>52.7</td>
<td>21.0</td>
<td>15.1</td>
<td>2.022</td>
</tr>
</tbody>
</table>

(un-treated)

Equilibrium pH increases from 1.06, there is an increasing order in force at 30% extension, stress at 30% extension and Young's modulus, with few exceptions. But, in case of breaking extension, there is an initial increase up to pH 3.5 and then a decrease is observed. The Young's modulus is of the order of $10^{10}$ dynes/sq.cm. An increase in the value of young's modulus shows that metal ions adsorbed on the fibre cause an increase in the strength of the wool structure. In fact, the maximum value of Young's modulus, in the studied region, is around pH 4.3 at which maximum amount of cupric ion is absorbed by the fibre.
X-RAY DIFFRACTION STUDY OF TREATED FIBRES

Purified-conditioned wool was equilibrated at 50°C with 0.05N cupric chloride aqueous solution and 0.05N zinc chloride solution at pH 5.0. The equilibrated samples were washed thoroughly with distilled water and air-dried. The air-dried samples and untreated wool fibres were reduced almost to powder form by cutting the fibres with a pair of scissors. The samples were then dried over phosphorus pentoxide for a fortnight. The X-ray diffraction scans of the powdered material were recorded at room temperature. The radial intensity scans were normalized, to equalize the area, between 2θ = 5° and 55°. The normalized intensity was plotted against 2θ and is illustrated in Fig. 20.

The normalized radial intensity scans of wool, wool treated with zinc chloride and with cupric chloride, show three intensity peaks. The peak at 9.6° has maximum intensity. In the case of untreated wool, the three peaks are at 9.6°, 4.44° and 2.15°.

The intensity scan of wool treated with cupric chloride is significantly different from that of untreated wool. The intensity at 2θ = 5° is higher, while the intensity of the first two peaks, i.e., 9.6° and 4.44° are decreased, though the peak positions remain the same as in untreated wool. On the other hand, the intensity of the third peak is greater than that of untreated wool and at the same time the peak is
slightly shifted to a lower value (2.06 Å). At pH 4.4, the amount of adsorbed cupric chloride is quite considerable and consequently the change in the intensity is appreciable. The adsorbed cupric chloride brings about a general reduction in intensity of the two strong peaks which might be due to a redistribution of order in the fibres. Hewell et al. (90) suggest that the fading of the intensity is due to a decrease in the crystallinity by the penetration of copper into the chain bundles. However, by mere decrease in the intensity of the peaks, it is difficult to interpret the results at this stage.

In the case of zinc chloride treated fibres, the intensity scan is almost identical with that of untreated wool. Only a slight decrease in the 9.6 Å peak is observed. This is because the amount of zinc ions adsorbed is small as compared to the adsorbed cupric ions. Consequently, the small amount of adsorbed zinc ions has practically no effect on the structural order of the fibres.
FIG. 22

Reflectance \% vs. Wavelength in \( \mu \text{m} \)

- **NaOH Treated**
- **PH 3.9**
3.7
STUDY OF REFLECTANCE SPECTRA

Wool fibres were treated with cupric chloride solutions at different pH values and samples were prepared as described in 3.4.2.2.

The reflectance spectra of these samples were recorded using Beckmann quartz spectrophotometer, DU-32480. The reference was vitreolite plate. The results are tabulated in Table XIV and illustrated in Fig. 21.

The reflectance study on cupric chloride treated Mohair keratin and cupric-bound methylated Mohair keratin(179) has shown a maximum absorption at 710 m\(\mu\) and 630 m\(\mu\), respectively. The 300-400 m\(\mu\) range was not affected. This was concluded by reasoning two types of binding sites in the keratin.

In the present investigation, the spectra of cupric chloride treated wool shows a maximum absorption at 720 m\(\mu\). This absorption maximum is on the border line between all oxygen ligands and a single nitrogen ligand per cupric ion. The binding of cupric ions to carboxyl groups of the side chains of wool is supported. Since, pK of \(-\text{NH}_3^+\) of the dicarboxylic and diamino acids is 9.5, it is very difficult to account for nitrogen ligand linkage. When the cupric ions adsorbed wool was treated with sodium hydroxide solution at pH 9, cupric ions were not given up, but a colour change (bluish green to reddish brown) occurred. The spectra of this sample did not show either maxima or minima (Fig. 22). This shows that...
**TABLE AIV**

**DATA FOR REFLECTANCE SPECTRA**

**REFERENCE - VITREOLEITE**

<table>
<thead>
<tr>
<th>Equilibrium pH</th>
<th>1.10</th>
<th>2.12</th>
<th>3.15</th>
<th>3.70</th>
<th>3.85</th>
<th>3.95</th>
<th>5.20*</th>
<th>5.90</th>
<th>9.0**</th>
</tr>
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<tbody>
<tr>
<td>Wavelength m(\mu)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>400</td>
<td>51.5</td>
<td>48.5</td>
<td>34.5</td>
<td>28.5</td>
<td>27.5</td>
<td>27.5</td>
<td>55.0</td>
<td>30.0</td>
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<td>450</td>
<td>71.0</td>
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<td>51.5</td>
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<td>70.5</td>
<td>49.0</td>
<td>27.0</td>
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<td>67.0</td>
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<td>61.5</td>
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<td>61.5</td>
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<td>54.0</td>
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<td>-</td>
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<td>-</td>
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<td>75.5</td>
<td>72.5</td>
<td>-</td>
<td>95.0</td>
<td>90.0</td>
</tr>
</tbody>
</table>

* Untreated wool fibres.

** Sample of pH 3.90 cupric chloride treated fibre, after treatment with pH 9.0 NaOH for one hour and thoroughly washed with distilled water. **
ions initially adsorbed on the carboxyl groups have changed their binding sites. These may be either disulphide or amino nitrogen or both.
3.8
SET/SUPERCONTRACTION OF WOOL FIBRES

The data obtained are recorded in Table XV to XXI and are illustrated in Figs. 23 to 29.

**TABLE XV**

**SET/SUPERCONTRACTION \% DATA OF UNTREATED FIBRES AT BOIL IN**

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Water</th>
<th>aq.0.05N NaCl</th>
<th>aq.0.05N CuCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.81</td>
<td>+0.47</td>
<td>-0.31</td>
</tr>
<tr>
<td>2</td>
<td>-1.06</td>
<td>+0.47</td>
<td>-2.52</td>
</tr>
<tr>
<td>5</td>
<td>-6.04</td>
<td>-0.27</td>
<td>-1.50</td>
</tr>
<tr>
<td>10</td>
<td>-3.30</td>
<td>+1.95</td>
<td>+0.50</td>
</tr>
<tr>
<td>15</td>
<td>-0.52</td>
<td>+0.85</td>
<td>+2.30</td>
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<td>30</td>
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</tr>
<tr>
<td>60</td>
<td>+14.01</td>
<td>+8.54</td>
<td>+17.54</td>
</tr>
<tr>
<td>120</td>
<td>+18.00</td>
<td>+15.77</td>
<td>+24.38</td>
</tr>
</tbody>
</table>

**TABLE XVI**

**SET/SUPERCONTRACTION \% DATA OF UNTREATED FIBRES AT BOIL IN 0.05N SOLUTIONS OF**

<table>
<thead>
<tr>
<th>Time (mins.)</th>
<th>K.H. phthalate at pH 4</th>
<th>NaCl at pH 4</th>
<th>CuCl₂ at pH 4</th>
<th>ZnCl₂ at pH 4</th>
<th>Borax at pH 9</th>
<th>NaCl at pH 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+0.70</td>
<td>+1.20</td>
<td>+0.60</td>
<td>+2.00</td>
<td>-14.70</td>
<td>-18.40</td>
</tr>
<tr>
<td>2</td>
<td>+0.90</td>
<td>+2.60</td>
<td>+2.90</td>
<td>+1.00</td>
<td>-2.10</td>
<td>-3.00</td>
</tr>
<tr>
<td>5</td>
<td>+0.40</td>
<td>-2.20</td>
<td>+0.90</td>
<td>+0.80</td>
<td>+15.00</td>
<td>0.00</td>
</tr>
<tr>
<td>10</td>
<td>+0.80</td>
<td>-10.60</td>
<td>+1.10</td>
<td>+1.20</td>
<td>+15.50</td>
<td>+10.90</td>
</tr>
<tr>
<td>15</td>
<td>+0.40</td>
<td>-10.60</td>
<td>+1.0</td>
<td>+0.90</td>
<td>+15.80</td>
<td>+15.80</td>
</tr>
<tr>
<td>30</td>
<td>-1.20</td>
<td>-8.50</td>
<td>+1.0</td>
<td>-5.30</td>
<td>+17.00</td>
<td>+19.10</td>
</tr>
<tr>
<td>60</td>
<td>-2.80</td>
<td>-5.50</td>
<td>+1.20</td>
<td>-14.10</td>
<td>+17.10</td>
<td>+19.80</td>
</tr>
<tr>
<td>120</td>
<td>-3.10</td>
<td>+3.40</td>
<td>+13.80</td>
<td>-14.30</td>
<td>+17.50</td>
<td>+20.30</td>
</tr>
</tbody>
</table>
TABLE XVII

SET/SUPERCONTRACTION % DATA OF UNTREATED FIBRES AT BCIL IN

<table>
<thead>
<tr>
<th>Time minutes</th>
<th>0.1 % NaHSO₃</th>
<th>0.05N NaCl</th>
<th>0.05N CuCl₂</th>
<th>0.05N ZnCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>- 0.5</td>
<td>- 8.90</td>
<td>- 8.40</td>
<td>- 5.50</td>
</tr>
<tr>
<td>2</td>
<td>+ 6.0</td>
<td>- 1.00</td>
<td>- 2.80</td>
<td>- 2.00</td>
</tr>
<tr>
<td>5</td>
<td>+19.4</td>
<td>+18.80</td>
<td>+ 7.0</td>
<td>+ 6.40</td>
</tr>
<tr>
<td>10</td>
<td>+20.0</td>
<td>+20.2</td>
<td>+18.70</td>
<td>+12.80</td>
</tr>
<tr>
<td>15</td>
<td>+27.4</td>
<td>+21.8</td>
<td>+21.80</td>
<td>+15.20</td>
</tr>
<tr>
<td>30</td>
<td>+31.2</td>
<td>+26.9</td>
<td>+21.20</td>
<td>+21.40</td>
</tr>
<tr>
<td>60</td>
<td>+31.4</td>
<td>+26.8</td>
<td>+24.80</td>
<td>+25.70</td>
</tr>
<tr>
<td>120</td>
<td>+31.7</td>
<td>+26.9</td>
<td>+27.70</td>
<td>+26.70</td>
</tr>
<tr>
<td>Final pH</td>
<td>~5.5</td>
<td>~5.5</td>
<td>Less than 2.5</td>
<td>~5.5</td>
</tr>
</tbody>
</table>

TABLE XVIII

SET/SUPERCONTRACTION % DATA OF UNTREATED FIBRES AT BOIL IN

<table>
<thead>
<tr>
<th>Time minutes</th>
<th>0.01% HIO₄</th>
<th>0.05N NaCl</th>
<th>0.05N CuCl₂</th>
<th>0.05N ZnCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+ 3.16</td>
<td>- 0.50</td>
<td>+ 0.30</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>+ 0.34</td>
<td>- 1.50</td>
<td>+ 0.60</td>
<td>- 0.80</td>
</tr>
<tr>
<td>5</td>
<td>- 6.21</td>
<td>- 2.27</td>
<td>+ 0.05</td>
<td>- 7.00</td>
</tr>
<tr>
<td>10</td>
<td>- 6.12</td>
<td>- 4.67</td>
<td>- 0.74</td>
<td>- 9.09</td>
</tr>
<tr>
<td>15</td>
<td>- 7.66</td>
<td>- 3.98</td>
<td>0.00</td>
<td>- 7.40</td>
</tr>
<tr>
<td>30</td>
<td>- 5.97</td>
<td>- 5.99</td>
<td>+ 3.20</td>
<td>- 0.80</td>
</tr>
<tr>
<td>60</td>
<td>- 0.04</td>
<td>- 1.65</td>
<td>+ 8.00</td>
<td>+ 2.65</td>
</tr>
<tr>
<td>120</td>
<td>+14.45</td>
<td>+ 2.63</td>
<td>+16.55</td>
<td>+ 6.51</td>
</tr>
<tr>
<td>Final pH</td>
<td>~5.3</td>
<td>~5.3</td>
<td>~5.0</td>
<td>~5.0</td>
</tr>
</tbody>
</table>
### TABLE XIX

**SET/SUPERCONTRACTION % DATA OF UNTREATED FIBRES AT BOIL IN**

<table>
<thead>
<tr>
<th>Time minutes</th>
<th>0.1% HIO$_4$</th>
<th>0.05N NaCl</th>
<th>0.05N CuCl$_2$</th>
<th>0.05N ZnCl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-10.25</td>
<td>-0.51</td>
<td>-3.28</td>
<td>-0.79</td>
</tr>
<tr>
<td>2</td>
<td>-5.50</td>
<td>-14.80</td>
<td>-21.90</td>
<td>-3.70</td>
</tr>
<tr>
<td>5</td>
<td>+2.80</td>
<td>-7.18</td>
<td>-14.40</td>
<td>-2.80</td>
</tr>
<tr>
<td>10</td>
<td>+0.72</td>
<td>+5.24</td>
<td>-14.33</td>
<td>+4.55</td>
</tr>
<tr>
<td>15</td>
<td>+8.03</td>
<td>+3.14</td>
<td>+12.00</td>
<td>+10.25</td>
</tr>
<tr>
<td>30</td>
<td>+10.38</td>
<td>-1.00</td>
<td>-5.11</td>
<td>+3.87</td>
</tr>
<tr>
<td>60</td>
<td>+2.74</td>
<td>-4.23</td>
<td>dissolved</td>
<td>dissolved</td>
</tr>
<tr>
<td>120</td>
<td>dissolved</td>
<td>dissolved</td>
<td>dissolved</td>
<td>dissolved</td>
</tr>
</tbody>
</table>

**Initial pH** ~5.5  
**Final pH** ~2.5

### TABLE XX

**SET/SUPERCONTRACTION % DATA OF FIBRES TREATED WITH 0.05N aq. CuCl$_2$**

<table>
<thead>
<tr>
<th>Time minutes</th>
<th>Water</th>
<th>0.05M K.H. phthalate</th>
<th>0.05M Borax</th>
<th>0.1% NaHSO$_3$</th>
<th>1.0% NaHSO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.06</td>
<td>-0.70</td>
<td>+0.50</td>
<td>-1.08</td>
<td>-0.85</td>
</tr>
<tr>
<td>2</td>
<td>-0.33</td>
<td>+0.43</td>
<td>-0.08</td>
<td>-1.20</td>
<td>+12.18</td>
</tr>
<tr>
<td>5</td>
<td>+0.87</td>
<td>+0.48</td>
<td>-4.25</td>
<td>+2.06</td>
<td>+17.72</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>+0.40</td>
<td>0.10</td>
<td>+3.70</td>
<td>+17.00</td>
</tr>
<tr>
<td>15</td>
<td>-0.04</td>
<td>+0.29</td>
<td>+4.30</td>
<td>+4.89</td>
<td>+19.75</td>
</tr>
<tr>
<td>30</td>
<td>-0.08</td>
<td>+0.50</td>
<td>+3.90</td>
<td>+10.10</td>
<td>+19.50</td>
</tr>
<tr>
<td>60</td>
<td>-0.10</td>
<td>+0.73</td>
<td>+3.34</td>
<td>+17.49</td>
<td>+18.58</td>
</tr>
<tr>
<td>120</td>
<td>5.28</td>
<td>+0.34</td>
<td>-4.57</td>
<td>+22.92</td>
<td>+15.01</td>
</tr>
</tbody>
</table>

**Final pH** ~5.2  
**Initial pH** ~5.2
From these data it is observed that whereas untreated keratin fibres either do not supercontract or supercontract very little in salt solutions as compared to water, they acquire more set in aq. 0.05N copper chloride solution and less set in aq. 0.05N sodium chloride solution when set for a longer time as compared to setting in water alone (Fig. 23). It is evident that keratin fibres when set in water have a transition time of 18 minutes, that is, when set for 18 minutes they neither supercontract nor acquire set. However, in salt solutions, both sodium chloride as well as copper chloride, the transition time is only 8 minutes. This indicates that the presence of salt inhibits the changes promoting supercontraction. On the other hand presence of copper chloride in water enhances the changes promoting set.
When setting characteristics of keratin fibres in salt solutions buffered at pH 4.0 is considered (Fig. 24), it is seen that fibres supercontract in 0.05N sodium chloride and 0.05N zinc chloride solutions at pH 4.0, but they do not supercontract in 0.05N copper chloride solution at pH 4.0. In buffer alone in the absence of salt both supercontraction as well as set are inhibited. There is no doubt that changes involved are quite complex. It is interesting to note that copper chloride and zinc chloride influence the setting characteristics in a different manner. It is clear from Fig. 24 that the curve of sodium chloride lies in between the curves of zinc chloride and copper chloride. In the presence of zinc chloride even after 120 minutes of setting time also, formation of new stabilizing bonds is not favoured, although bond rupture is taking place. Presence of copper chloride, on the other hand, does permit the formation of new stabilizing bonds although only when set for more than 50 minutes.

Thus, at pH 4.0 bond rupture is delayed both in the absence as well as in the presence of copper and zinc chlorides. In case of copper chloride solution, however, ruptured bond elements are able to reunite and stabilize the extended configuration; in case of zinc chloride bond elements are such that no reformation of bonds occurs. It seems that the effect of the presence of sodium chloride in solution at pH 4.0 is only to delay the ability of the fibres to take set. As compared to this, the presence of sodium chloride in a solution buffered
FIG. 25

Set % vs. Minutes

- 0.1% NaHSO₃
- 0.05N CuCl₂
- 0.05N NaCl
- 0.05N ZnCl₂
at pH 9.0 enhances the ability to take set.

When the effects of different salts in presence of reducing agents such as 0.1 % sodium bisulphite are analysed (Fig. 25), it appears that fibres supercontract more when salt is present. However, the amount of set acquired is somewhat less in all the three cases. This probably implies that owing to the presence of salt, thiol-disulphide interchange mechanism is somewhat arrested. It is important to note that in presence of copper chloride, even at pH 2.50, similar phenomenon is observed. Thus, whereas at pH 4.0 in a buffered solution (Fig. 24) copper chloride and zinc chloride behaved differently, in an acidic reducing media their behaviours are akin.

When keratin fibres are set in presence of salts in a 0.01% periodic acid medium, it is clear that copper chloride prevents supercontraction and enhances the ability to take set, whereas, zinc chloride behaves in an exactly opposite manner. The effect of the presence of sodium chloride is similar to that of zinc chloride. Earlier workers in this field have concluded that fibres acquire set in an acidic oxidising media mainly due to the formation of stable salt linkages of the type $-\text{SO}_3^- \ldots +\text{H}_2\text{N}$. If this is so, obviously copper chloride promotes the formation of such linkages by accelerating the oxidation of $-\text{S-S-}$ bonds. Zinc chloride, on the other hand, inhibits the process. This is also supported by earlier observation that in reducing media copper chloride behaves as zinc chloride (Fig. 25).
When 0.1% periodic acid solutions are employed as setting media (Fig. 27) in the presence of sodium chloride and zinc chloride fibres do acquire small amounts of set and then on further increasing the setting time again supercontract; in case of copper chloride the action is so severe that fibre dissolves before acquiring any set due to overall attack on the keratin structure. It may be that formation of cross-links such as $-\mathrm{SO}_2^- \ldots \ldots +\mathrm{H}_3\mathrm{N} -$ is not favoured under more drastic conditions. This also indicates that the mechanism/mechanisms of reactions involved is/are much more complex and that other functional groups are also attacked. It may not be possible to draw any definite conclusions from data collected, although it may be suggested that copper chloride favours oxidative attack on wool whereas zinc chloride does not.

When fibres previously treated with aqueous copper chloride solution are subsequently set in different media (Figs. 28 & 29), it is observed that:

(a) treated fibres do not acquire any set in water at the boil,
(b) treated fibres do not supercontract and acquire less set in sodium bisulphite solution as compared to untreated fibres in sodium bisulphite solution,
(c) treated fibres supercontract somewhat less and acquire slightly higher sets in 0.01% periodic acid solution as compared to untreated fibres,
(d) treated fibres exhibit impaired supercontraction as well as set in borax solution as compared to untreated fibre,
(e) treated fibres do not supercontract or take set readily in boiling water, but such fibres do acquire set in dilute sodium sulphite solution when sodium sulphite solution is concentrated, fibres however, supercontract and break when set for longer time.

From all these it appears that fibres previously treated with copper chloride are more susceptible to an attack of oxidising agents such as periodic acid. When such fibres are set in the solution of borax or sodium sulphite in an alkaline medium, it appears that Cu$^{++}$ ions adsorbed on carboxyl groups shift to -S-S- bonds and nitrogen of amino group and thus impair the ability to take set. The presence of copper ions inside the fibre probably adversely affects the formation of lanthionine in an alkaline medium. There is no doubt that in an acidic and oxidising media the presence of copper ions favours the mechanism involved, whereas, zinc ions inhibit the setting mechanism.