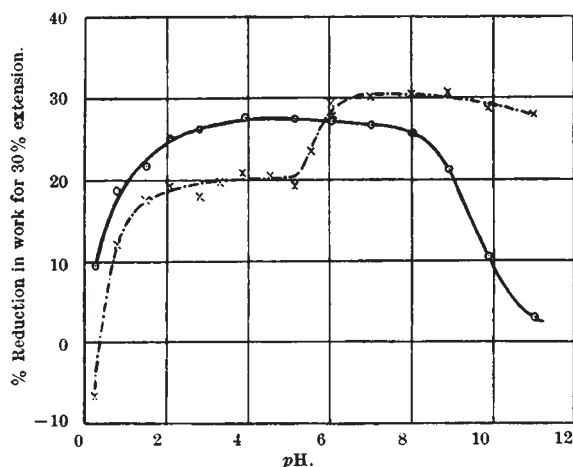


### Constitution of the Keratin Molecule

DURING the past few years, much evidence has been accumulated in support of the view that the free acid and basic side-chains of wool are equivalent and form salt linkages between the peptide chains<sup>1</sup>. Although further proof of the salt linkage hypothesis may seem to be redundant in view of recent determinations of the amounts of aspartic and glutamic acids in wool<sup>2</sup>, a proof based on the properties of deaminated fibres is essential to refute the erroneous conclusions drawn by Sookne and Harris<sup>3</sup> from a study of deaminated wool.

The resistance to extension of keratin fibres in acid and alkaline solutions is less than in water because of the breakdown of salt- and, above pH 10, sulphur-linkages between the peptide chains. A curve illustrating the reduction in the resistance of human hair fibres to extension in buffer solutions of varying pH, as compared with distilled water at pH 5.5, is given in the accompanying graph.



RESISTANCE OF HUMAN HAIR TO EXTENSION IN VARIOUS BUFFER SOLUTIONS; ○—○—○, UNTREATED; X—X—X, DEAMINATED.

The undamaged root ends of human hair fibres were used in preference to wool because of the greater uniformity of the fibres, but the form of the curve, as well as the extent of the pH-stability region, are in conformity with the salt linkage hypothesis. When human hair fibres are deaminated, however, their resistance to extension should be sensibly independent of the acidity of the solution below pH 5, because there are then no salt linkages to be broken by acid. As the curve shows, within small limits, such is the case for single fibres deaminated by two treatments of 24 hours each in 40 c.c. of the van Slyke reagent at 22.2° C. in absence of air.

In terms of the salt linkage hypothesis, too, removal of the basic side-chains by deamination should free a corresponding number of acid side-chains for combination with alkali in the neighbourhood of pH 6. The fibre swelling thereby induced should reduce the resistance to extension, although to a relatively small extent because the reduction is due solely to swelling and not to breakdown of salt linkages. As shown in the graph, the resistance to extension of deaminated fibres decreases sharply between pH 5 and 7, in agreement with theory. Above pH 7, the resistance to extension

is sensibly independent of pH until the sulphur bonds are attacked by alkali.

Thus the elastic properties of deaminated fibres are in strict agreement with the salt linkage hypothesis. The corresponding titration curve for deaminated human hair is now being determined.

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Jan. 24.

<sup>1</sup> Speakman and Hirst, *Trans. Far. Soc.*, **29**, 148 (1933); Speakman and Stott, *Trans. Far. Soc.*, **30**, 539 (1934); Speakman and Townend, *Trans. Far. Soc.*, **32**, 897 (1936); Speakman, *J. Soc. Dyers and Colourists*, **52**, 423 (1936); McMahon and Speakman, *Trans. Far. Soc.*, **33**, 844 (1937); Speakman and Townend, *NATURE*, **139**, 411 (1937).

<sup>2</sup> Speakman and Townend, *NATURE*, **139**, 411 (1937).

<sup>3</sup> *Bureau of Stand. J. Res.*, **19**, 535 (1937).

### A Novel Type of Isomerism in a Co-ordination Compound of Copper

IF a warm alcoholic solution of cupric chloride is treated with diphenyl methyl arsine and allowed to stand overnight, two crystalline species (brown and blue) of identical composition ( $\text{Cu}_2(\text{Ph}_2\text{MeAs})_2\text{Cl}_2$ ) are deposited. The separation of these two substances has already been described<sup>1</sup>. At that time the evidence put forward was insufficient to show whether the two compounds were really isomeric or not. Recently, however, it has been found that the two compounds are appreciably soluble in nitro-benzene, in which solvent the molecular weights of the two are of the same order (brown 878, blue 786). One form is therefore not a polymer of the other. Furthermore, these values, although somewhat lower than the theoretical (986), support the view that each form is binuclear.

The brown form dissolves in thoroughly dried nitro-benzene to give a brown solution. This solution is quite stable at low temperatures and will deposit the brown crystals when cooled sufficiently; but if it is heated to 150° (or more) the brown colour will, during the course of half an hour, change to a greenish blue. The greenish blue solution will deposit crystals of the blue form on cooling. There is nothing to indicate that one form is a hydrate of the other. The fact that solutions of each form in the same solvent are differently coloured rules out the possibility of dimorphism. In confirmation of this it may be noted that the two forms behave differently towards ammonia and pyridine.

All the evidence available points to the conclusion that the two forms are isomers. Of the two, the brown form is the more stable. Even in the dry state the blue form has been found to revert to the brown over a period of several months. As would be expected, the transition of the blue to the brown form is more rapid in nitrobenzene solution. At room temperature, both forms are stable insofar as they show no tendency to lose the arsine even on long standing.

In order to account for the existence of two isomeric forms, the following structures attributing tetrahedral co-ordination to  $\text{Cu}^{\text{I}}$  and square co-ordination to  $\text{Cu}^{\text{II}}$  are suggested:

