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PHYSICS AND CHEMISTRY
of
CELLULOSE FIBRES

with particular Reference to Rayon

BY

P. H. HERMANS

DIRECTOR OF THE INSTITUTE FOR CELLULOSE RESEARCH OF THE A.K.U.
AND AFFILIATED COMPANIES, UTRECHT (NETHERLANDS)



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PHYSICS AND CHEMISTRY
of
CELLULOSE FIBRES

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PREFACE

This book, though written to a practical plan, purports to be neither a technical manual nor a completed scientific treatise on cellulose fibres. Its aim is a narrower one.

Hitherto the ever-progressing synthetic fibre industry has almost invariably developed its technical processes on a purely empirical basis, though with the aid of scientific methods and expedients. Yet for many years the only research work intensively pursued was that falling under the head of applied research. This was due to the fact that, at the end of the 19th century, when the artificial fibre industry first came into being, fundamental knowledge of the physico-chemical constitution of cellulose and other native materials was entirely lacking. Scientific progress in this difficult subject began far later and at first was unable to keep pace with industrial development. The latter, sustained by enormous capital outlay, was committed to purely practical and semi-scientific work for utility purposes and left the results of the slow, up-hill work of intrinsically scientific research in the shade.

Every cellulose expert knows that, up to the present, the results of academic cellulose research have, with few exceptions, had little fundamental bearing upon the technical developments; accordingly, their practical value has on the whole been held in little esteem by the artificial silk trade. Some of the big industrial concerns which, in the early days, had at great expense put scientific research in hand, afterwards withdrew their support.

This state of affairs will nevertheless change in time, even in the synthetic fibre industry, and in the long run technical progress will be stimulated by scientific advance. Nor should this time be very far distant. Quite recently the industry has been displaying renewed interest in fundamental research; the beginnings of a noteworthy technical development of wholly synthetic textile fibres, indisputably originating in purely scientific research, are already discernible. There are also signs in the field of artificial cellulose fibres — particularly in that of staple fibre — that actual technical progress has been made thanks to the fact that the results of research carried out for purely scientific reasons were successfully put to practical use.

Though already so widespread, enormous development would seem to await the staple fibre industry which, possibly even more so than the artificial silk industry, imposes upon technical science the task of manufacturing

fibres equalling, if not surpassing, natural fibres in quality. Besides systematic, empirical trial, this will call with ever-increasing urgency for deeper knowledge of the inner structure of the fibres and its relation to the textile properties or practical utility of the product. It is no mere coincidence, therefore, that the industry, and the staple fibre industry in particular, should be evincing renewed interest in pure scientific research.

The author, who has himself had fifteen years' practical experience as Chief Chemist in the artificial silk industry, has endeavoured in this book to present a comprehensive treatment of those results and views of purely scientific cellulose research which seem to him, from the technical standpoint, the fundamentals and the most important equipment for further scientific penetration into technical thought and research on this subject. A certain bias in choice of matter was unavoidable, especially as particular consideration had to be given to work carried out by the author himself and his associates when dealing with a not inconsiderable part of the subject matter of a novel nature, chiefly in Parts II and III of the book. Many observations, hitherto unpublished owing to the war, have been incorporated. A great deal of space has been devoted to the processes of solution and swelling, which until recently were not clearly understood. The author has endeavoured to deal with these processes in the light of the latest ideas on physico-chemical grounds, avoiding the now obsolescent colloid-chemical terminology.

In the difficult but important chapters on gel formation and deformation processes the author has not hesitated to discuss at lenght various theoretical models. Although these are no doubt still seriously deficient, the propositions in question may form the basic material from which the elements of improved and further developed conceptions will grow. Without doubt, however, future developments will entail many changes.

As the author has made a point of dealing circumstantially with those subjects only which have never been clearly presented before, or which undeniably fitted within the framework of the whole, he has passed over the scientific foundations of the methods for the preparation of spinning solutions and of the dyeing and finishing processes (except for viscose manufacture), which have been so ably dealt with in other works *(O. Faust, W. Weltzien, H. Mark, E. Valkó,* and *J. Chwala).*

The author's aim in writing this book will have been attained if it strengthens the bonds between technical science and research, and proves an incentive to the industry to further research, not only applied, but also fundamental research. To enhance it as a book of reference for further research into the subject matter, care has been taken to quote freely and refer to many authors. Nevertheless, the literature is so extensive that it is quite impossible to do justice to everyone. Any suggestions in this or any other direction will be welcomed by the author.

POSTSCRIPT

The manuscript of this book was all but completed by the end of 1941. Its publication was delayed by the war. The author has endeavoured to take account of the recent literature to which he had access up to the end of 1947. Unfortunately, not all the English and non-European literature which appeared during the war was accessible to him and some may appear to the reader to have been neglected. The author would be grateful to his colleagues abroad if they would assist him in making up the arrears.

The work carried out in 1943-1944 by the author and his associates under the ægis of the Institute for Cellulose Research, founded at Utrecht in 1942, necessitated some considerable revision of Parts II and III. The author's acknowledgements are due to Doctors *J. J. Hermans, D. Vermaas,* and *A. Weidinger* for their valuable contributions to this work. Many of the experimental investigations referred to in Part III and carried out in large part by *Dr. Vermaas,* have not yet been published elsewhere. It is the author's pleasant duty to point out, therefore, that the consequent inconspicuousness of this researcher's name in the text and in the register of authors stands in no relation whatever to the importance of his contribution to that work.

The author wishes to express his gratitude to the Management of the A.K.U. (Algemeene Kunstzijde Unie, N.V.) and affiliated companies for permission to publish a considerable portion of the work done at their expense in 1943 and following years.

He is further indebted to Miss M. Hollander for her conscientious and painstaking devotion to the difficult task of translation, to Miss M. E. van Ravenswaay for her valuable assistance in the preparation of the manuscript and proof-reading, and to Dr. P. Platzek for making the subject index.

ERRATA

p. 61. Cancel line 22 from top and substitute by:

"between the ultimate gain in entropy when calculated per unit of weight for a monomer and its polymer. (If calculated per mole the entropy gain is greater in the case of the polymer; cf. p. 62)".

p. 62. Insert at the end of § 6.1:

"Finally it is recalled that in solutions the molecules of the solvent which are close to that of the solute may have an orientation with respect to the latter, particularly if polar forces come into play (see Fig. 27). Effects of this kind which diminish the degree of randomness will have a bearing on the entropy of mixing".

p. 369 and 370. It was later discovered that the zinc-free bath referred to did contain a very small amount of zinc ions owing to impurities.

p. 441. The ordinate in Fig. 183 does not indicate % H_2O but the number of drying and re-wetting cycles

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INTRODUCTION

The scientific analysis of natural and artificial cellulose fibres begins with an enquiry into their "structure", i.e., the nature and arrangement of the elementary units and the forces operative between these.

It is commonly allowed that the problems of spatial configuration — in other words, problems of a geometrical nature — confronting scientific research into structure are usually less difficult than those presented by the forces acting between the particles. The same applies to static and statistical problems, on the one hand, and dynamic problems on the other. The supreme difficulty is the quantitative consideration of forces operating between the particles.

Modern chemistry is fairly well informed on the geometrical structure of many molecules, even of complicated organic substances; likewise, it has extensive knowledge of the spatial structure of crystals. But the difficulties increase enormously as soon as it becomes a matter of a quantitative comprehension of the interatomic and intermolecular forces, the interpretation of chemical reactions and other dynamic processes.

Similarly, the deformation processes of solid and liquid systems present many theoretical difficulties, for here again the forces between the particles have to be taken into account.

In many respects the current theories on the fluid and the solid state are still imperfect and are only in their infancy where systems of complicated structure are concerned, such as we have to deal with in the difficult subject of substances of high molecular weight.

Once again, the geometrical side of the problem, i.e., the question of the spatial arrangement of the elementary particles and the modifications brought about by exterior forces, is the easier of approach, wherever an arrangement is capable of being expressed statistically, as in the case of solids. Difficulties arise, however, the moment an attempt is made to probe into the play of the forces between the particles, the nature of their interdependence and their reciprocal influence and into the dynamics of the processes, either in the gel or in the colloidally dissolved state. We shall ever and again be meeting this peculiarity.

Cellulose is a substance formed by living Nature. We shall not concern ourselves with its origin and deposition in plants or by the activity of micro-organisms. In this book we shall regard it as the raw material for technical processing to artificial objects and derivative products. For this purpose we

have it, almost without exception, in the form of fibre from various different sources and, when manufacturing artificial textiles, our object must always be to equal, or surpass, those natural fibres which are best suited to textile use. As a rule, the investigation into the chemical structure of simple substances closes with the enquiry into the molecular structure and the crystal structure, but in our case the criterion for the properties and usefulness of the material is the structure of the whole organised cellulose fibre, both its molecular and its superimposed supermolecular structure. Consequently, the first task in the investigation of this raw material is to discover the geometrical plan, right from the atoms up to the macroscopic fibre, for which not only chemical, but also physical methods of research have to be applied. Another task for research on artificial fibres produced from cellulose is to find out what are the processes that take place in the dispersion of the raw material to the spinning solution and upon the reassociation of the dispersed particles to form artificial fibre.

It is possible in the present stage of our knowledge to present a fairly clear picture of fibre structure which, although needing completion in many respects, may broadly represent the true facts. This picture has been growing gradually, chiefly in the last 25 years, out of the combined results of organic-chemical and physical investigations. This development and its results will be outlined briefly in the first and second parts of this book.

For practical reasons the book has been divided into three parts. The First Part deals with the general principles of the subject not directly connected with the specific form of the *fibre*. It is concerned primarily with the molecular and super-molecular structure of cellulose in general, with the properties of the cellulose molecule and with the methods used to determine the size of the molecule. This is followed by a chapter on cellulose solutions and gels and, lastly, there is a chapter on the material resemblances and distinctions between native and recovered cellulose.

The Second Part treats the morphology and the general physical and chemical behaviour of cellulose in the form of fibre. In the Third Part an attempt has been made to coordinate the material so far known (admittedly still very inadequate) on the scientific principles and methods of attacking the problem of the genesis of artificial fibres from cellulose solutions.

FIRST PART

CONSTITUTION, CRYSTALLINITY, MICELLAR STRUCTURE, MOLECULAR WEIGHT, CHEMICAL BEHAVIOUR AND DISPERSION OF CELLULOSE

I. MOLECULAR MODEL, CRYSTAL STRUCTURE AND MICELLAR CONSTITUTION OF CELLULOSE

§ 1. THE THEORY OF CHAIN MOLECULES

The elementary composition of purified cellulose has long been known to approximate fairly closely the formula of an anhydrohexose, i.e., $C_6H_{10}O_5$. The first task was to establish the molecular constitution of the substance by the methods of organic chemistry and then to endeavour to account for its peculiar properties. The presence of three alcoholic hydroxyl groups per C_6 was inferred from the ready formation of tri-esters of the composition $C_6H_7O_2(OR)_3$.

Since the time of *H. Braconnot* [1] it has been known that appreciable amounts of glucose are obtained by the hydrolysis of cellulose with acids; *E. Flechzig* [2] and later *R. Willstätter* and *L. Zechmeister* [3] found that something only a little short of the theoretical yield of this sugar could be obtained and *G. W. Monier-Williams* [4] attained a 91 per cent yield in his crystalline glucose preparation from cellulose.

One of the decomposition products of the combined acetylation and hydrolysis (acetolysis) of cellulose was the disaccharide cellobiose $C_{12}H_{22}O_{11}$ in the form of its octaacetate. This substance was first discovered by *A. N. P. Franchimont* [5] and was later identified and more closely analysed by *Z. H. Skraup* and *J. Koenig* [6]. As *H. Ost* [7] and *J. Madsen* [8] found, it is formed with a yield of up to 40 per cent but, under the acetolysis, itself undergoes further decomposition. Allowing for this fact, the work of *K. Freudenberg* [9], *P. Karrer* and *Widmann* [10] warranted the conclusion that up to 60 per cent of the cellulose is transformed into cellobiose during acetolysis. *H. Pringsheim* [11] found that the fermentation of cellulose by bacteria likewise produces cellobiose in addition to glucose. Hence the two sugars had to be regarded as constitutional units of the cellulose molecule, but the question as to how these sugar residues are

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1 *H. Braconnot,* Ann. chim., 12, (1819) 172.
2 *E. Flechzig,* Z. physiol. Chem., 7, (1883) 523.
3 *R. Willstätter* and *L. Zechmeister,* Ber., 46, (1913) 2401.
4 *G. W. Monier-Williams,* J. chem. Soc., 119, (1921) 803.
5 *A. N. P. Franchimont,* Ber., 12, (1879) 1941.
6 *Z. H. Skraup* and *J. Koenig,* Ber. 34, 115; Monatsh., 22, (1901) 1011.
7 *H. Ost,* Ann., 398, (1913) 338.
8 *J. Madsen,* Thesis Hannover, 1917.
9 *K. Freudenberg,* Ber., 54, (1921) 767, cf. also: "Tannin, Cellulose, Lignin". Berlin 1932, p. 94.
10 *P. Karrer* and *Fr. Widmann,* Helv. chim. acta, 4, (1921) 174.
11 *H. Pringsheim,* Z. physiol. Chem., 78, (1912) 266.

interlinked has given rise to much discussion and speculation. The most plausible assumption was the presence of hydrolizable, ether-like or glucosidic bonds between the sugar residues, but this left a host of open questions, besides which, without reliable information as to the molecular weight, the number of sugar residues linked by primary valencies remained uncertain. To understand the historical development of the subject, it is necessary to realize that twenty years ago the current concept of very large molecules was by no means self-evident and was, indeed, rejected by many as untenable.

The idea of a chain-like structure was first put forward by *B. Tollens* [12]. Experimental evidence of the chainwise glucosidic interlinking of a great many identical glucose residues to the pattern of the cellobiose bond was first brought to light in an almost overlooked, commendable paper by *J. Böeseken* [13], who demonstrated that the acetyl content of the products precipitated from the reaction at various times during the acetolysis, steadily increased from three acetyl groups per C_6 in cellulose triacetate to five in glucose pentaacetate. The existence of any pre-formed mono- or disaccharide units would in all probability preclude any such gradual increase. On kinetic grounds, *K. Freudenberg* [14] likewise inferred from the yield of cellobiose from acetolysis that a continuous chainlike interlinking of glucose residues by glucosidic bonds of the type occurring in cellobiose was highly probable. At the time, however, this view met with little support and the majority of research workers preferred the assumption of small molecules made up of only a few glucose or cellobiose residues [15].

There were two reasons for this hindrance to progress. Firstly, there was the "colloidal" nature of the substances under examination, involving a confusing variety of peculiar phenomena as yet imperfectly understood, similar to those sometimes observed in inorganic substances of simple composition (e.g., silicic acid, hydroxides of heavy metals, etc.). According to the contemporary views of "colloid chemistry", which at that time was emancipating itself as a new branch of science, a particular state of dispersion was to be presumed rather than a given molecular weight in the classical sense.

Secondly, it was just about 1920 that cellulose and other macro-molecular substances were for the first time subjected to X-ray examination. Its achievements caused much stir and were destined to become of profound importance to cellulose research, but in one respect they were at first misinterpreted.

The classical optical work of *H. Ambronn* [16] had already made it clear that the existence of orientated, crystalline particles of sub-microscopic dimen-

[12] *B. Tollens*, 1895, cf. "Handbuch der Kohlenhydrate", Leipzig 1914, p. 564.
[13] *J. Böeseken*, Rec. trav. chim., 35, (1915) 320.
[14] *K. Freudenberg*, Ber., 54, (1921) 767; cf. also "Tannin, Cellulose, Lignin", Berlin 1932 p. 94.
[15] For a survey of earlier "cellulose formulae" see: *J. Hibbert*, Ind. Eng. Chem., 13, (1921) 256, 334.
[16] *H. Ambronn*, Ber. Sächs. Ges. Wiss. 63, (1911) 249. Kolloid-Z., 18, (1916) 90, 273. Kolloid-Z., 20, (1917) 173.

sions must be assumed in cellulose fibres. At *Ambronn's* suggestion, *P. Scherrer*[17] X-rayed ramie fibres and was able to confirm the foregoing assumption. The same discovery had already been made by the Japanese investigators *S. Nishikawa* and *S. Ono*[18] and the American *A. W. Hull*[19], but had passed unnoticed. The X-ray spectrography of cellulose was then further developed and made known to a wider public by the work of *R. O. Herzog* and *W. Jancke*[20]. Qualitatively it seemed beyond doubt that the preparations examined actually did contain small latticed particles and that, in conformity with the results recorded by *Ambronn,* those particles were orientated with one of their crystallographic axes parallel to the fibre axis, at any rate in native fibres.

The probable dimensions of the elementary cell of the lattice were calculated for the first time by *M. Polanyi*[21] in 1921, the volume proving to be approximately 700 å. That meant that it could contain exactly four groups of anhydroglucose.

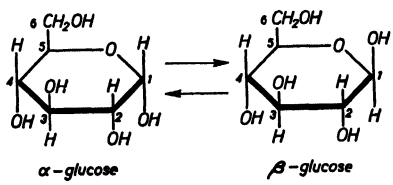
Following the classical concepts of the structure of crystals, it had hitherto always been accepted as a fact, based on earlier investigations applied to crystals of a simple organic substance, that the elementary cell exactly corresponds to the space occupied by a molecule, or a very small group of molecules. Setting aside the unanswered question as to why the polysaccharides could not be obtained in a macrocrystalline form, it was thought that their chemical constitution must be made to fit in with a similar structural scheme and that it could then only be a matter of formulae with 1, 2 or 4 glucose units[22]. Many research workers attached so much importance to this rash conclusion, drawn from the results of the new and promising physical method of investigation, that they went so far as to attribute the peculiar properties of these "polymers" to assumed special, strong associative forces between the "individual groups", i.e., invoking a special theory as to their solid state[23]. The extrapolation of the authenticated classical *Kékulé* doctrine of structure — really so obvious to the organic chemist — was thereby rejected, though it had been suggested and experimentally substantiated in many quarters (e.g., *Böeseken, Freudenberg,* and others) and though *Emil Fischer* had, even

[17] *P. Scherrer,* Private comm. to *H. Ambronn* (1919), cf. *R. Zsigmondy,* "Lehrbuch der Kolloidchemie", 2nd. ed. 1920.
[18] *S. Nishikawa* and *S. Ono,* Proc. Math. Phys. Soc. Tokyo., 7, (1913) 131.
[19] *A. W. Hull,* Physic. Review., 10, (1917) 661.
[20] *R. O. Herzog* and *W. Jancke,* Z. Physik, 3, (1920) 196; Ber., 53, (1920) 2162; Naturwiss., 9, (1921) 320; Cellulose Chemie 2, (1921) 101; Z. angew. Chem., 34, (1921) 385.
[21] *M. Polanyi,* Naturwiss. 9, (1921) 288.
[22] See e.g., *R. O. Herzog,* Naturwiss., 12, (1924) 955.
[23] Cf. *P. Karrer,* Cellulosechemie, 2, (1921) 125; *P. Karrer* and *A. P. Smirnoff,* Helv. chim. acta, 5, (1922) 187; *K. Hess,* Ann., 435, (1924) 1 and Z. angew. Chem. 37, (1924) 903; *H. Pringsheim,* Ann., 448, (1926) 163 and Ber., 59, (1926) 3008; *M. Bergmann,* Ann., 445, (1925) 1 and Ber. 59, (1926) 2973. Thus *M. Bergmann,* Ber. 59, (1926) 2973 speaks of "pseudo-highmolecular substances", *H. Staudinger,* Ber., 59, (1926) 3019, on the other hand, of "macromolecular substances".
The distinctly opposed views of several investigators at the end of 1926, which was a critical year in many respects for the development of cellulose research, is interestingly apparent in the last part of the 59th volume of the "Berichte" (printed papers read at het Natural Science Convention held at Düsseldorf on 29th September 1926). Also compare *H. Staudinger,* Ber., 69, (1936) 1168.

before 1900, already proved the applicability of this principle to high-molecular protein-like substances. Moreover, in the fundamental work referred to, *M. Polanyi* [24] himself clearly stated that, as an alternative, the elementary cells of the cellulose lattice might be regarded as sections of much longer chains. A similar theory was also then current with regard to the diamond and to graphite.

A consistent interpretation of the X-ray data along these lines must be credited to *O. L. Sponsler* and *W. H. Dore* [25] in America, who thereby contributed in no small degree to the ultimate triumph of the molecular chain theory.

Meanwhile, particularly under the leadership of the English school of *Purdie*, *Irvine* and *Haworth*, the pure organic-chemical investigation into the structure of sugars had also made great strides since 1920. *J. C. Irvine* and *E. L. Hirst* [26] had proved that 2.3.6. trimethyl glucose is formed exclusively and in practically theoretical yield as the result of the hydrolysis of exhaustively methylated cellulose preparations. (They then drew up a ring formula with three glucosidically linked glucose radicals). Subsequently, in the year 1925, *W. N. Haworth* and his co-workers [27] were able to show that, in its normal form, glucose is to be regarded as a pyrane derivative and thus contains a six-membered, and not, as previously assumed, a five-membered, ring system. The now accepted structural formulæ of the two tautomeric forms of this *Haworth* "Pyranose", α and β-glucose, are given below.



By means of the atom diameters which had become known through the investigations of *W. H.* and *W. L. Bragg* and of the *Haworth* β-glucose formula, *Sponsler* and *Dore* (loc. cit.) built up a cellulose model which served to interpret the X-ray diagram of the ramie fibre. In it the glucose residues were continuously linked by ether-like oxygen bridges in the alternating position of 1.1 and 4.4. When *W. N. Haworth* [28] and *K. Freudenberg* with *E. Braun* [29] had succeeded in definitely establishing the constitution of cellobiose as being 1.4 β-glucosidoglucose, these investigators were able to

[24] *M. Polanyi*, Naturwiss., 9, (1921) 288.
[25] *O. L. Sponsler* and *W. H. Dore*, Colloid Symposium Monograph, 4, (1926) 174.
[26] *J. C. Irvine* and *E. L. Hirst*, J. Chem. Soc., 123, (1923) 518.
[27] *W. N. Haworth* and co-workers, Nature, 116, (1925) 430; J. Chem. Soc., (1926) 89.
[28] *W. N. Haworth*, Helv. chim. acta 11, (1928) 534.
[29] *K. Freudenberg* and *E. Braun*, Ann., 460, (1928) 288; 461, (1928) 130.

point out that, to vindicate the evolution of cellobiose from cellulose, *Sponsler* and *Dore's* chain formula would have to be modified so as to allow for identical 1.4 β-glucosidic bonds everywhere. In the same year *K. H. Meyer* and *H. Mark* [30] showed in a work since become famous that this chain formula could also be made to harmonise with the X-ray data [31].

The theory of molecular chains received more powerful support from the scientific work undertaken by *H. Staudinger* (published since 1925) on the polymerization first of formaldehyde (with *M. Lütky* [32]) and later of other substances as well [33]. These investigations left no doubt that long molecular chains, linear macromolecules, can be built up in this process and that, if the degree of polymerization is high enough, products could also be obtained whose behaviour resembled that of the natural high-molecular substances and which likewise possessed "colloidal" properties. Taking polyoxymethylene as an example, *H. Staudinger, G. Mie* and *J. Hengstenberg* [34] moreover pointed out shortly after that, here again, no conclusions as to molecular size (definitely established by other means) could actually be drawn from the size of the elementary cell ascertained by X-radiography.

Other decisive chemical arguments in favour of the chain theory were:

1°. The isolation and identification of some oligosaccharides from products of cellulose hydrolysis by *R. Willstätter* and *L. Zechmeister* [35], *L. Zechmeister* and *G. Toth* [36]. These are sugars consisting of three, four and six glucosidically interconnected glucose residues. The interpretation of the constitution of these sugars by *W. N. Haworth* and co-workers[37], *K. Freudenberg* [38] and co-workers confirmed that they are to be regarded as some of the larger fragments of hydrolysed cellulose chains.

2°. The proof supplied by *K. Freudenberg* and co-workers [39] that the optical rotation of the oligosaccharides moves steadily upwards from the bioses onwards to that of the cellulose, which at the same time proves that only 1,4, β-bonds exist.

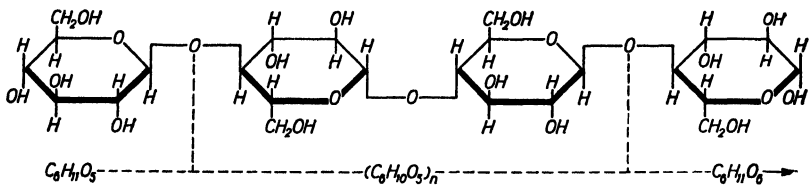
3°. The work of *W. Kuhn* [40] and *K. Freudenberg* and his associates [41] on the kinetics of cellulose hydrolysis in sulphuric acid of 50 per cent.

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30 *K. H. Meyer* and *H. Mark*, Ber., 61, (1928) 593.
31 *H. Mark*, Naturwiss., 16, (1928) 892.
32 *H. Staudinger* and *M. Lütky*, Helv. chim. acta, 8, (1925) 41.
33 *H. Staudinger*, Ber., 59 (1926) 3019.
34 *H. Staudinger, G. Mie* and *J. Hengstenberg*, Z. physik. Chem., 126, (1927) 432.
35 *R. Willstatter* and *L. Zechmeister*, Ber., 62 (1929) 722.
36 *L. Zechmeister* and *G. Toth*, Ber., 64, (1931) 354.
37 *W. N. Haworth* and co-workers, J. Chem. Soc. (1931) 824.
38 *K. Freudenberg* and co-workers, Ann., 494 (1932) 41, 63.
39 *K. Freudenberg* and co-workers, Ann., 494, (1932) 41, 63; Ber., 66, (1933) 177.
40 *W. Kuhn*, Ber., 63, (1930) 1503; Z. physik. Chem., A 159 (1932) 368.
41 *K. Freudenberg* and co-workers: Ber., 63, (1930) 1510; Ber. 68, (1935) 2082; Trans. Faraday Soc., 32, (1936) 74.

4°. The conversion of cellulose to polymerically similar products. *H. Staudinger* and co-workers [42] were able to show in a number of investigations that, by the substitution of hydroxyl groups, cellulose preparations of various degrees of polymerization can be converted to derivatives and may occasionally be changed back into cellulose without any alteration in the size of the particles (molecular size).

The following formula represents what may to-day be regarded as the established constitution of cellulose chain molecules:



At both ends this formula includes a pyranose residue different in composition from the fundamental formula $C_6H_{10}O_5$. Therefore, the analysis of a cellulose preparation will only agree with this formula within the accuracy of measurement if n is large enough. The two terminal members of a chain are differentiated from all others by the possession of four instead of three hydroxyl groups; that one of these groups to the extreme right of the figure is moreover distinguished by its aldehydic character and must have reducing properties. The number n is indefinite, apt to be very large in the case of natural cellulose preparations and to assume any lower value in that of the degradation products. According to *H. Staudinger's* nomenclature, the designation "cellulose" embraces the higher members of a whole range of "polymeric homologues", of which glucose represents the first and cellobiose the second member [43].

Terminal groups and molecular sizes will be dealt with elsewhere in this book. Suffice to say at this juncture that the formula given here as yet imperfectly represents the constitution of these substances, as it does not disclose the finer details of the configuration of the ring systems and the shape of the chains. We shall enter more closely into these matters in § 2. It may now be accepted as certain that glucosidic chains of considerable length form the molecular units of all cellulose preparations. They are classed as linear macromolecules (syn. chain molecules, thread molecules, main valence chains). They are the fundamental elements essential to every picture of the structure and physico-mechanical behaviour of the fibres.

[42] *H. Staudinger*, Ber., 59, (1926) 3019.
H. Staudinger and *O. Schweitzer*, Ber., 63 (1930) 3132;
— and *H. Eilers*, Ber., 68, (1935) 164;
— and *G. Daumiller*, Ann., 529, (1937) 219;
— and *E. Husemann*, Ber., 70 (1937) 1451.

[43] See *H. Staudinger's* recently published book: "Organische Kolloidchemie", Braunschweig 1940.

§ 2. THE SPATIAL CONFIGURATION OF THE CELLULOSE MOLECULE

In order to appreciate the rôle of the chain molecule as a unit of structure in cellulose fibres, it is necessary for us to examine a little more closely its spatial configuration. In attempts to explain the X-ray diagrams of cellulose preparations (cf. § 3), successive investigators have suggested spatial models of the cellulose molecule characterised by an evergrowing mass of detail. We shall here only discuss the most advanced suggestions, without entering into the details of this development [44], starting with the configuration of glucose.

Haworth's pyranose formula of glucose was given on page 6 in the form commonly used in organic chemistry. It consists of a six-membered ring system of 5 C atoms and a lactonic O atom and may be compared with the well-known six-membered carbon ring in cyclohexane, C_6H_{12}. The valence angle at the oxygen atom may at first approximation be assumed to be almost equal to the tetrahedron angle (109°28'), the distance of the atomic centres C-C in aliphatic compounds being 1.53-1.55 å and the distance C-O being 1.42-1.44 å, a value not very different from the former [45].

As a result of the investigations of *Sachse* [46], *E. Mohr* [47], *J. Böeseken* [48] and *H. G. Derx* [49] the spatial construction of the cyclohexane ring is known and it follows from geometrical deductions that it may exist in two configurations free from tension, i.e., the armchair form (position de chaise, Fig. 1A) and the bed form (position de lit; Fig. 1B).

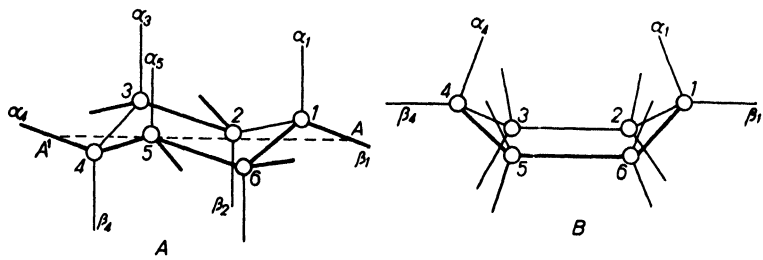


Fig. 1. Carbon frame of the cyclohexane ring; A — armchair form, B — bed form. The valencies pointing upward are marked α and those in a downward direction β.

The former is rigid but, owing to the "free rotation" around the C-C bonds, the latter is liable to assume various configurations without causing

[44] A brief summary will be found in *K. H. Meyer*, Ber., 70, (1937) 266.
[45] The particulars in this section respecting atomic distances, valence angles and spheres of activity in organic molecules have been taken from *H. A. Stuart*, "Molekülstruktur", Berlin 1934, p. 79; *L. Pauling* and *M. L. Huggins*, Z. Kristallogr., 87, (1934) 205; *P. G. Ackermann* and *J. E. Mayer*, J. Chem. Phys., 4, (1936) 377; *F. Laves*, "Funfundzwanzig Jahre Laue-Diagram", Naturwiss., 25, (1937) 721.
[46] *Sachse*, Z. physik. Chem., 10, (1892) 203.
[47] *E. Mohr*, J. Prakt. Chem., 98, (1918) 315.
[48] *J. Böeseken*, Chem. Weekblad, 33, (1936) 207.
[49] *H. G. Derx*, Rec. trav. chim., 40, (1921) 519; ibid. 41, (1922) 312.

tension in the ring system, that shown in Fig. 1B being the configuration in which one of the two cis pairs of hydrogen at the C atoms 1 and 4 are at the maximum distance from each other. (The centres of the H atoms themselves are not reproduced). This position at the same time represents the maximum longitudinal extension of the cyclohexane molecule in one direction.

The following established facts will be of assistance to us as we proceed:

1°. In the armchair form (Fig. 1A) the upward valencies α_1, α_3, α_5 and the downward valencies β_2, β_4, β_6 run parallel to each other and are, moreover, perpendicular to the axis of gravity AA' of the ring system represented in Fig. 1A by a broken line. The trans valencies β_1, α_4 at C atoms 1 and 4 are also parallel; with the axis of gravity they form an angle of 19°28'.

2°. In the bed form (Fig. 1B) the cis valencies β_1, β_4 are parallel, but the trans valencies β_1, α_4 here form an angle of 70°32'.

According to *Haworth's* structure, we then get for the nuclear frame of glucose the four configurations represented in Fig. 2. In β-glucose the hydroxyl groups at C atoms 1 and 4 are in the trans position, while in α-glucose they are in the cis position. A consideration of spatial conditions, which will not be gone into at any length here, makes it plain that chains extending in one direction can only be built up by continuous 1—4 glucosidic linkage from the frame of β-glucose in the armchair form (Fig. 2, top left).

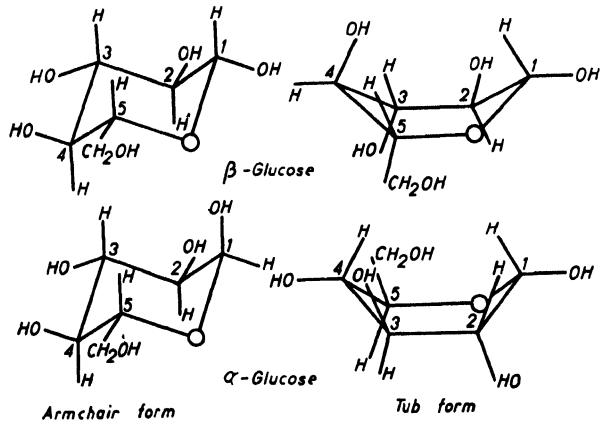


Fig. 2. Spatial configurations of the nuclear frame of α- and β-glucose in armchair and bed forms.

But then every second glucose residue must be turned in relation to the previous one through 180° around the longitudinal axis so that the angle of the valence at the glucosidic oxygen bridges may be the proper one.

The bed form (Fig. 2 below right) is the most likely configuration for the molecule of starch, consisting of 1—4 α-glucose residues connected

glucosidically. The molecule then easily assumes a spiral shape, with five to six glucose residues per coil. *K. Freudenberg* and *H. Boppel*[50] recently advanced arguments in favour of this configuration for starch. Oligosaccharides, which can be synthesized from the two other forms represented in Fig. 2, have so strange a shape as to make the occurrence in organized natural products seem improbable (though these forms might occur in the dissolved state).

Another noteworthy peculiarity of the β-glucose configuration is revealed in Fig. 2 and also comes to light in Fig. 3, which represents the framework of a cellobiose residue (that ever-recurring unit of structure in the cellulose chain); it is that all the hydroxyl groups are collected on the sides of the ring system, while only hydrogen-bearing valencies appear above and below.

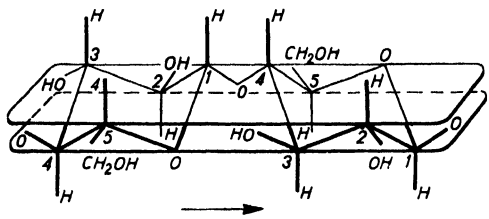


Fig. 3. Nuclear frame of a cellobiose residue. The centres of gravity of the atoms of the ring are distributed over two parallel planes. The hydrophobic H atoms are above and below these planes and laterally there are the hydrophilic OH groups.

Fig. 3 shows that the centres of gravity of the atoms of the ring can be distributed over two parallel planes, above and below these planes are the hydrogen atoms and laterally we have the hydroxyl groups. The cellulose chain exhibits two hydrophobic and two hydrophilic boundary surfaces. As is to be inferred from Fig. 3 and will be shown later, it is shaped like a small band twice as broad as it is thick. The middle part of the broad surfaces is of a hydrophobic character.

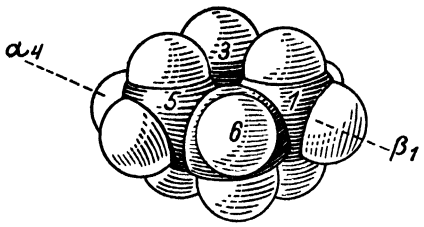
It will therefore be clear that, if several aligned chains meet, there will be a mutual orientation of the planes of the bands, in addition to a parallel orientation of the axes of the chains. And this tendency towards higher orientation does actually exist (cf. p. 249). Fairly powerful bonds ("hydrogen bonds"; see p. 14), will then be formed between the hydroxyl groups.

This may also provide a clue to the apparently incomprehensible contradiction between the absolute water-insolubility of cellulose and the far readier solubility of starch[51]. In the case of starch (see lower right-hand part of Fig. 2) the hydroxyl groups are distributed in various spatial directions[52]. The less compact configuration of the coiled chains of starch will also probably facilitate the ready flow of water from all sides into the molecular aggregates.

[50] *K. Freudenberg* and *H. Boppel*, Ber., 73, (1940) 609.

[51] According to the latest investigations (vide *K. H. Meyer* and *co-workers*, Helv. chim. acta, 13, (1940) 845 ff.) only the "amylo-amylose" component is comparable with cellulose. The erythro-amylose component contains branched chains.

[52] Reference should also be made to the different solubilities and adsorbabilities of the two stereo-isomeric hydrobenzoins (*P. H. Hermans*, Z. phys. Chem., 113 (1924) 385 and similar examples).



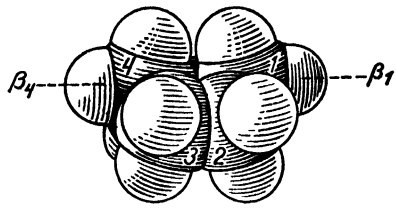


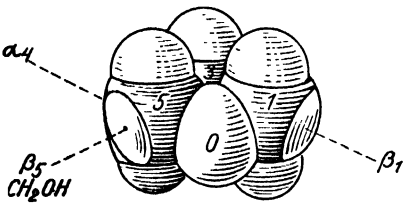
Fig. 4. A. Fig. 4. B.

Fig. 4. Stuart's models of cyclohexane.

Fig. 4. A. Armchair form. Fig. 4. B. Bed form.

To complete the picture we wish to make of the cellulose chain, we must now fill in the nuclear frame with the approximately known actual spheres of activity of the atoms. We shall then get Fig 4A and B for the two cyclohexane configurations of Fig. 1. These resemble the actual shape of the molecules far more closely than did the once familiar ball models [53].

Fig. 5 represents the same model as that of Fig. 4A after the C atom 6 in the ring has been displaced by oxygen and those H atoms which do not occur in β-glucose have been abstracted. The same object, turned slightly so that the bridge valencies α_4, β_1 are parallel to the plane of the drawing paper is shown in Fig. 6. Both figures 5 and 6 clearly show the hydrophobic upper and lower faces of the ring engaged by hydrogen. It may also be seen that the actual glucose residue may be represented as a shallow box with inclined end faces.



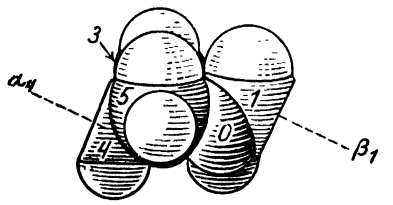


Fig. 5. Model of the β-glucose ring (occupied by H atoms only).

Fig. 6. Model of Fig. 5 turned slightly.

By further developing the model of Fig. 6 by attaching two hydroxyls at the still disengaged positions 2 and 3, and a CH_2OH group in position 5, we get the elementary unit $C_6H_{10}O_5$ of the cellulose chain. Fig. 7 shows its top view. The cellulose model will now be formed if these basic units are linked together in the 1.4 position in accordance with the diagram of Fig. 3, with every other link turned 180° around the 1.4 axis with respect to the preceding one and so arranged that a straight chain extending in one direction results.

[53] These illustrations were made with the help of wooden models after *H. A. Stuart*, Z. physik. Chem., B. 27, (1934) 350; Z. phys. Chem. Unterricht, 48, (1935) 19.

The stereochemical aspects of this interlinking were recently discussed comprehensively by *P. H. Hermans, J. de Booys* and *Chr. J. Maan*[54] on the basis of an earlier exact geometrical analysis of the six-ring model by *P. H. Hermans* and *J. Berk*[55], on the one hand, and the interatomic bond distances and atomic radii known from literature, on the other. These authors assume a zig-zag arrangement of the successive glucose residues on the lines of Fig. 8.

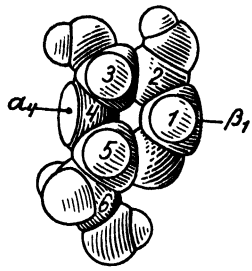


Fig. 7. Model of Fig. 6 seen from above, with appended CH_2OH group and 2 and 3 hydroxyl.

There can be no question of a chain with all ring planes parallel; for in that case not only would the valency angle at the bridge oxygen become improbably large, but in addition the length of the cellobiose group would far exceed 10.3 å, the value required by X-ray data (cf. § 3). As shown diagrammatically in Fig. 8, to attain the proper longitudinal extension the valency angle at the oxygen bridge must be approximately 100°.

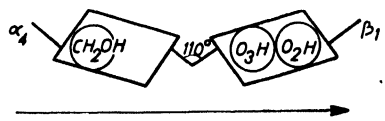


Fig. 8. Angled linkage of the glucose residues shown diagrammatically (vertical zig zag only).

An alternative to the purely vertical zig-zag arrangement which the foregoing authors favour as the more likely solution, is a spatial configuration with a combined vertical and horizontal zig-zag. This permits an almost flat arrangement in which the ring planes form an angle of no more than 10°30' with the horizontal plane and produces a fibre period of the correct length, viz., 10.3 å. Fig. 9A shows a top view of the *Stuart* model representing this configuration; Fig. 9B is a diagram of the positions of the atomic centres.

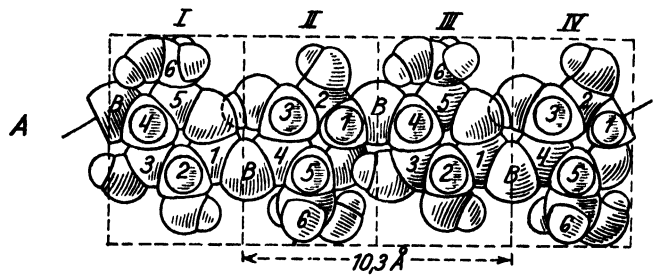


Fig. 9. A. Stuart's model of the cellulose chain with vertical and horizontal zig-zag, seen from above. (glucosidic oxygen numbered *B*).

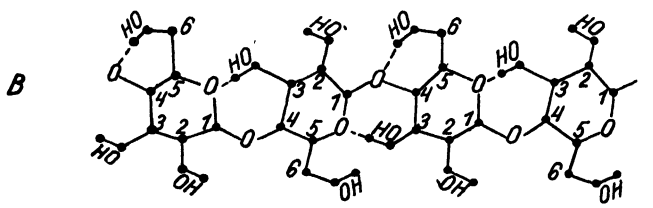


Fig. 9. B. Repetition of A with probable intramolecular hydrogen bonds indicated by broken lines.

[54] *P. H. Hermans, J. de Booys* and *Chr. Maan*, Kolloid. Z., 102, (1943) 169.
[55] *P. H. Hermans*, Thesis, Delft 1924, p. 34.

Further mathematical analysis of the model shows that various hydrogen bonds (according to *J. D. Bernal* and *H. D. Megaw* [56] and *H. Sherman* [57]) are possible and, therefore, most probably actually exist. It is known that bonds of this kind are liable to be formed between a hydroxyl group and an oxygen atom, when the oxygen to oxygen spacing will be 2.5-2.6 å. This distance can be reached between the O atom of the OH-group in the 6 position (being capable of rotation) and the bridge oxygen; also between the OH group in the 3 position and the ring oxygen of the neighbouring glucose group. These bonds are represented by dotted lines in Fig. 9B. As will be seen, they give rise to the formation of additional ring systems. The latter would impede the mutual rotation of adjacent glucose groups around the glucosidic C_1-O-C_4 bonds, thus to some extent stiffening the straight configuration of the chain. In cellulose solutions these secondary valence bonds, engaged, maybe, in other functions (e.g., binding the solvent), can be ruled out. If they are ignored, the question arises as to whether there are other factors hampering rotation.

Experiments with *Stuart* models have shown that there is by no means complete steric hindrance to rotation, for which there remains a certain scope even after the substitution of the OH group by the far larger NO_2 groups (cf. Chapt. III § 6) [58]. If it is given free play, the chain will not, of course, maintain its straight configuration, but will tend to show kinks and convolutions.

There is another, more cogent, reason for assuming the not inconsiderable flexibility of the cellulose chain. Since isomers corresponding to the armchair and bed forms of the cyclohexane ring have never yet been observed in organic chemistry, it may be assumed that the transition between the two configurations is effected with comparative ease and may occur without passing a potential barrier of appreciable height. Supposing glucose rings to be subject to the same transformation of one configuration into the other, the inner "suppleness" of the bed configuration might be expected to impart considerable flexibility to the cellulose chains, similar to that of paraffinic or olefinic chains. As we shall see later, to account for all the facts observed it will be necessary to take the occasional occurrence of these kinked shapes into consideration.

As to the lateral dimensions of the cellulose molecule in its straight configuration, stereochemical analysis, allowing for the value of the atomic radii, shows the width to be 9 å and the thickness 4.7 å. The dimensions of

[56] *J. D. Bernal* and *H. D. Megaw*, Proc. Roy. Soc. London, 151, (1935) 384.
[57] *J. Sherman*, J. Phys. Chem., 41 (1937) 117.
[58] As far back as 1939 the author, with the kind assistance of Professor *K. Freudenberg*, of Heidelberg, studied the possibility of rotation around the glucosidic bonds. Meanwhile *E. Jenckel*, Kolloid Z., 100, (1942) 163, has published analogous investigations with reference to the intramolecular mobility of polymers of vinylic and acrylic derivation. With the aid of models he was able to elucidate certain differences in the "solidification temperatures" of these substances. Conversely, comparing these results with the solidification temperatures of cellulose and its derivatives (likewise measured by *Jenckel*), appreciable flexibility of the cellulose chain is to be inferred.

the chain are represented in the form of a diagram in Fig. 10, where shading shows the outer hydrophilic zones of the molecule.

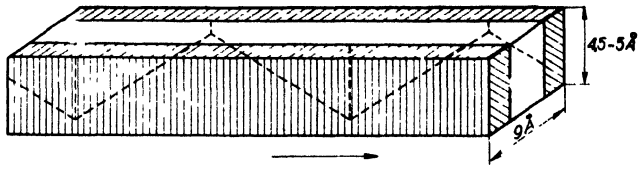


Fig. 10. Scheme of cellulose chain, with hydrophilic part shaded, broken lines connecting the centres of gravity of the glucosidic oxygen atoms (spatial zig zag).

Finally, it should be borne in mind that the cellulose chain has a polar axis; the picture obtained by rotating the molecule through 180° around an axis perpendicular to the chain axis differs from the original one. This is obvious from Figs. 3 and 9, showing that all the oxygen atoms in the rings point in one direction. This direction is marked by an arrow in Figures 3, 8 and 10, pointing towards C atom 1 and, therefore, towards the reducing terminal group.

The straightened chain has the symmetry of a digonal helix; each link can be shifted to the position of the next one by a rotation of 180° around the chain axis.

§ 3. THE CRYSTALLINE STRUCTURE OF CELLULOSE

Cellulose is known in at least four different crystalline modifications, the most important of which we shall now discuss in greater detail.

§ 3.1 *Cellulose I (Native Modification)*

The X-ray spectrography of native cellulose has shown that its micro-crystalline components are invariably of the same structure. Thus an identical lattice was found in the fibres of ramie, cotton and wood cellulose, in the cell walls of the marine alga Valonia and in the cellulose films generated by acetobacter xylinum and in tunicin (animal cellulose). This is designated as the "native" or "Cellulose I" lattice [59].

As to the position of the individual atoms in this lattice, with molecules as complicated as those now under consideration the lattice structure cannot be derived by direct computation from the X-ray data alone. One can but select the most probable molecular configuration on the grounds of other evidence, see whether this fits in with the elementary cell disclosed by the X-ray pattern and then ascertain whether it is or is not in conformity with the positions and intensities of the various X-ray diffraction spots. This inevitably involves difficult and tedious investigations.

Sponsler and *Dore*, in their classical work referred to in § 1, and later investigators dealing with this problem have all gone to work in this way. The best-known papers on the subject are listed at the end of this chapter, while

[59] *T. Kubo* (Z. physik. Chem., A 187, (1940) 297) has recently advanced the view that certain small variations occur in the lattice structure of cellulose from various plants.

a survey of its history is provided by *K. H. Meyer* and *L. Misch* [60] and also by *H. Kiessig* [61].

Informative details of the structure of the crystalline lattice can only be obtained in investigations of this kind if well-orientated samples are used. Native cellulose has usually been represented by ramie fibre, being easy to obtain and with the further advantage that its crystallites are almost completely orientated with their crystallographic b-axis parallel to the fibre axis. Samples possessing what is known as "higher orientation" are even better, for in them the other crystallographic axes of the crystallites are likewise orientated uniformly, which is not the case in vegetable fibres. Samples of this kind were obtained from the cell wall of the Valonia species and also, after adequate previous deformation, from the films of bacterial cellulose. The latter expedient may be utilised for accurate X-ray examination of the lattice structure of regenerated cellulose. (For further details vide Part II, Chapter V, § 1.3)

By gradual refinement of the basic stereochemical molecular model, coupled with improved X-ray technique, it has been possible to build up a picture of the lattice structure which in broad outline, it is believed, closely approximates the truth. The latest detailed revision of the structural analysis of native cellulose was undertaken by *K. H. Meyer* and *L. Misch* [62]. Though some progress may have been made, this picture still fails to harmonise completely with all the X-ray data, as recently pointed out by *H. Kiessig* [63]. Ignoring the refinements which have obviously yet to be applied, the general picture as we have it before us to-day, may be described somewhat as follows.

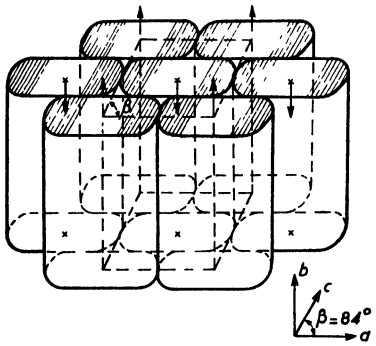


Fig. 11. Diagram of latticed molecules of native cellulose with indication of crystallographic elementary cell by broken lines. Regions containing the hydroxyl groups shaded.

In accordance with the fundamental assumption in the original pioneering work of *Sponsler* and *Dore*, the molecular chains in the crystallite are arranged parallel to one another as shown in Fig. 11. (The chains must be imagined as prolonged upwards and downwards by multiple of the length given). The direction of the chain coincides with the longest *b*-axis of the crystallographic elementary cell, which cell is shown in the figure. Its *b*-axis measures 10.3 å and exactly corresponds to the length of a complete cellobiose group. In well-orientated plant fibres, like ramie fibre, the crystallites are arranged with this axis in the fibre axis.

[60] *K. H. Meyer* and *L. Misch*, Helv. chim. acta, 20, (1937) 232.
[61] *H. Kiessig*, Z. physik. Chem., B. 43, (1939) 79.
[62] *K. H. Meyer* and *L. Misch*, Helv. chim. acta, 20, (1937) 232.
[63] *H. Kiessig*, Z. physik. Chem., B. 43, (1939) 79.

The volume of the cell corresponds to the space occupied by two cellobiose groups. Looking down, one sees the somewhat oblique angled base of the monoclinic cell. With the *a*-axis, the *c*-axis encloses an angle of 84°. The *c*-axis represents twice the "thickness", while the *a*-axis represents the "breadth" of a chain. The top cross-section is shaded to show the space filled mainly by the hydroxyl groups. The lattice of cellulose is a typical linear primary valence lattice. The particularly stable primary valency bonds stretch in only one direction, while perpendicularly thereto the cohesion is maintained by far weaker forces. Similarly, *J. Hengstenberg* and *H. Mark*[64] found far larger linear thermal expansion coefficients perpendicularly to the c-axis than parallel with it and *A. Frey-Wyssling* and *K. Wuhrmann*[65] discovered an analogous difference in the thermal dependence of the refractive indices for light polarised perpendicularly and parallel to the fibre axis, from which it follows either that there are no cross links of primary valence character at all between the chains, or, if there are, then only at very considerable intervals. (The occurrence of such occasional truly chemical cross links in native cellulose is assumed by some authors — vide page 85 — but they are not to be found in regenerated cellulose.)

The lateral lattice forces, though considerably smaller than the primary valence bonds in the fibre direction, are nevertheless fairly stable. As the spatial analysis implies, hydrogen bonds (cf. page 14), which are relatively stable, may be formed between the chains, which is probably one of the reasons why cellulose does not dissolve easily. The cellulose chain, plentifully supplied with hydroxyl groups, has, it is true, great affinity to water and binds it with considerable heat effect, but the combining energy of parallel chains imparted by the hydrogen bonds is even greater. The cellulose-cellulose bond is stronger than the cellulose-water bond.

According to *Meyer, Mark,* and *Andress* the chains in each alternate layer of the molecules (these layers following each other in the plane of the *c*-axis) shift by about 7.5 å in the direction of the *b*-axis with respect to the chain in the first layer, while *Sponsler, Meyer,* and *Misch* maintain that the polarity of the chain then also changes, in the sense shown by the arrows in Figure 11, which correspond to those shown in Figs. 3, 8 and 10. These conditions are also represented in diagram by Fig. 12, where the approximate position of the centres of the C and O atoms in the elementary cell is given for two sections of

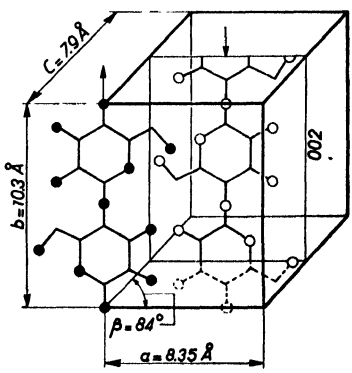


Fig. 12. Diagram of the positions of the atoms in the elementary cell of native cellulose after *Meyer* and *Misch*.

[64] *J. Hengstenberg* and *H. Mark*, Z. Krist., 69, (1928) 271.
[65] *A. Frey-Wyssling* and *K. Wuhrmann*, Helv. chim. acta, 22, (1939) 981.

the chain. The symmetry of the lattice requires that it should be traversed in the *b* direction by digonal helical axes.

We have already seen in § 2 what configuration the cellulose group must have in accordance with its length to fit into the elementary cell, (Fig. 12 takes no account of the somewhat inclined position of the ring systems with respect to each other.)

Comparing the lateral dimensions of the chains derived from stereochemical evidence -- viz., 4.7 and 9 å — with those of the cell (Fig. 12), the former would at first seem to be too large; yet, with the packing possibilities provided by the *Stuart* model, the chains could exactly fit into the elementary cells. For, in accordance with the principle of the densest packing of spheres, the globular spheres of action of the outer atoms may be in close proximity and, therefore, the chains may be rather more closely packed than the external lateral dimensions referred to in § 2 would seem to admit.

This, however, is only possible if the successive chains in the 101 plane change their polarity and shift by 21 to 28% of the lattice spacing with respect to each other in the direction of the fibre axis. Thus we have gratifying substantiation of conclusions drawn from the X-ray results, and in this way we also have confirmation of the fact that the chains lying side by side in the 002 plane must have identical polarity.

As was stated above, the reciprocal position of the hydroxyl groups in parallel chains makes it clear that "hydrogen bonds" may well occur between the chains. These ensure strong lateral cohesion.

§ 3.2. *Cellulose II (Hydrate Cellulose)*

After mercerization, the translation lattice of native cellulose is found to have undergone some slight change (see also § 4) and a different crystalline modification appears, called hydrate cellulose or Cellulose II, also occurring in the cellulose recovered from solutions. We shall see later (§ 4) that this modification may likewise occur with water of hydration enclosed in the lattice. In its dry state, however, "Hydrate cellulose" has the same chemical composition as native cellulose, so that this name for it is misleading and should be dropped in favour of "Cellulose II".

The representation of the lattice structure of Cellulose II is usually based on the elementary cell found by *K. R. Andress, K. H. Meyer,* and *H. Mark,* according to which the ring faces of the glucose groups turn approximately 35° around the *b* axis during mercerization (see p. 25). *E. Sauter*[66] considers the choice of this elementary cell to be inappropriate and that proposed by *O. L. Sponsler* and *W. H. Dore*[67], likewise regarded as adequate for Cellulose II by *A. Burgeni* and *O. Kratky*[68], to be preferred. In the transition from Cellulose I to Cellulose II all that takes place, then, is slight widening

[66] *E. Sauter,* Z. physik. Chem., B. 43, (1939) 294.
[67] *O. L. Sponsler* and *W. H. Dore,* J. Amer. Chem. Soc., 50, (1928) 1940.
[68] *A. Burgeni* and *O. Kratky,* Z. physik. Chem., B. 4, (1929) 401.

of the lattice, in that there is an expansion of 0.7 å in the *a* axis and a contraction of 0.3 å in the *c* axis, with no change in the orientation of the chain. This is represented diagrammatically in Fig. 13.

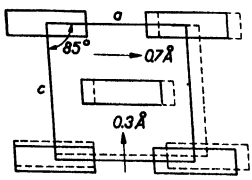


Fig. 13. Transition from the native lattice to that of hydrate cellulose (after *E. Sauter*).

This idea seems, however, to be inconsistent with density data.

Mercerization with strong caustic soda at first causes considerable widening of the lattice owing to the penetration of NaOH molecules between the chains, but after the caustic soda has been washed out, the lattice contracts again to a new state of equilibrium and the original density of the native lattice is not regained. The identity period in the fibre axis remains the same for both modifications.

§ 3.3. Cellulose III and IV

A third lattice modification, termed "Cellulose III" was obtained by the decomposition of an addition compound of cellulose with ammonia and is described by *K. Hess* and *J. Gundermann* [69]. We shall not discuss it here.

By thermal treatment (heating in polar liquids such as formamide, glycol, glycerol), Cellulose II can be changed to a fourth modification, viz., Cellulose IV, the lattice of which has been described by *K. Hess, H. Kiessig* and *J. Gundermann* [70], who suggest "High-temperature cellulose (HT Cellulose)" as a second name for it. The Cellulose IV lattice resembles that of Cellulose I so closely, that its discoverers at first thought they were dealing with the native modification (see Part I, Chapter V, § 4). The *a* and *c* axes of the elementary cell stand vertically one upon the other and its symmetry is accordingly rhombic.

Other comparable details of the elementary cells of Cellulose I, II and IV are dealt with in Part II (see page 246 and also Fig. 14).

§ 3.4 Some Open Questions

The foregoing fairly detailed picture of the structure of cellulose modifications I and II, which are the most important, may be regarded as a useful approximation, but it leaves many open questions.

With regard to the alternating polarity of the chains, *Meyer* and *Misch* argued that the lattice structure deduced from the X-ray diagrams of cellulose regenerated from solutions is a replica of that of mercerized native cellulose. Since the process of dissolution will probably completely disintegrate the original lattice and separate the molecules, it can hardly be assumed that all the polar axes will be directed in an identical sense

[69] *K. Hess* and *J. Gundermann*, Ber., 70, (1937) 1788.
[70] *K. Hess, H. Kiessig*, and *J. Gundermann*, Z. physik. Chem. B. 49 (1941). 64.

upon re-aggregation of the chain molecules to form a new lattice order. These authors therefore assumed alternating polarity in the lattice of native cellulose as well. Yet, reasoning along these lines, it may be asked why alternating polarity, obeying the rules of chance, should not also occur in the direction of the *a* axis in regenerated cellulose. But, as stated before, if it does, the lattice will not fall into proper order. This may to some extent account for the apparent difficulty with which these chain molecules recrystallize, though they certainly can be induced to do so as we shall see later. It may also be responsible for certain lattice distortions or lattice faults.

It should be mentioned that *G. V. Schulz* and *E. Husemann* [71] have recently directed attention to the fact that a "super period" in the direction of the *c* axis probably exists in native cellulose, corresponding to a spacing of 2600 å, which X-rays would not detect, basing this supposition on their discovery of alien groups at regular intervals of about 510 glucose residues in the cellulose molecule (cf. p. 84 and 85).

§ 3.5 *Density of crystalline cellulose*

The density of crystallized cellulose I and II can be calculated from the known volume of the elementary cell and the known weight of two cellobiose residues as being 1.592 and 1.583 respectively, the difference between the two being no more than 0.6% (whereas by *Sauter's* computation it would be about eight times greater). It should at once be added that the densities of all known cellulose preparations recorded by direct experiment are well below these values. This very fact, to which we shall revert later (Part II, Ch. III, § 2), makes it evident that a regular lattice order and the very dense packing of the kind just described are never homogeneously represented in cellulose preparations, but may, at best, be realized locally in submicroscopic ranges. Next to these, other regions of less perfect arrangement must exist.

§ 3.6. *Size and Nature of the Crystallites.*

A considerable volume of research, both experimental and theoretical, has been devoted to the spatial extension, the dimensions and the nature of the "crystalline" portion of cellulose and to their relevance or otherwise to the non-crystalline or imperfectly crystalline portions. In this book we shall have occasion to revert frequently to these questions so fundamentally important, not only to science, but also to the practical work connected with fibres. The X-ray spectrographical method, alone, cannot supply the complete answer; valuable though its contribution is, it calls for complementary knowledge acquired by other means.

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[71] *G. V. Schulz* and *E. Husemann*, Z. physik. Chem. B. 52 (1942) 23.

Until recently, no means had been found of obtaining quantitative data by X-ray methods on the still more pressing question of the percentage of "crystalline" substance in the fibre. At best, only very rough approximations could be suggested, to which nothing was added until a short time ago. *O. Kratky, K. Kainz,* and *R. Treer*[72], however on the basis of special investigations which we shall not now describe, have estimated the "crystallized" portion of ramie fibre at one third, at the most, of the fibre aggregate. Pursuing a different method, *H. Mark*[73] found 40—70% of "crystalline" substance for filaments regenerated from viscose, dependent upon its preliminary treatment. In Parts II and III we shall see that the figures are more probably 70% and 40%, or thereabouts, in native and regenerated fibres respectively.

It had, however, long been obvious that, not only the majority of synthetic fibres, but also the native product must contain a considerable amount of non-crystalline cellulose. The lack of a suitable, comprehensive method of experiment is patent all through the history of fibre research. The prominence given to the "crystalline" portion by X-ray spectrography fostered the tendency to ascribe or relate to it many of the properties and phenomena of fibres, and it was not till later that investigators began gradually to recognize the essential significance of the "amorphous" portions. From the early days of X-ray spectrography attempts were made to wrest from it knowledge of the dimensions of the "crystallites". It follows from the diffraction theory that the breadth of the interferences of a crystalline substance is related to the size of the crystals. According to *M. v. Laue*[74], beyond a given size of crystal this breadth diminishes in quantitatively expressible terms; the black spots on the film broaden[75]. Exact calculations applied on this principle by *J. Hengstenberg* and *H. Mark*[76] to ramie showed that the interferences corresponding to the identity period in the fibre axis appear here in sharp outline, which means that the dimensions of the crystallite in this direction are at least 600 å; 50-60 å was the dimension derived from the broadening of the lines of the corresponding interferences perpendicular to the fibre axis. Hence the crystalline regions would be rod-shaped and the number of chain molecules contained therein would, in the case of ramie, be 40 to 50.

The filaments of viscose rayon were subjected by *Hengstenberg* and *Mark* to similar examination, which produced appreciably smaller values, viz., roughly 300 å in the fibre axis and about 40 å across. *Carpenter*[77], applying the same method to sulphite cellulose, found more than 600 å for the longitudinal axis and between 13 and 17 å for the crystal width.

[72] *O. Kratky, K. Kainz,* and *R. Treer,* Holz als Roh- und Werkstoff, 2, (1939) 409.
[73] *H. Mark,* J. Phys. Chem., 44, (1940) 764.
[74] *M. v. Laue,* Z. Kristallogr., 64, (1926) 115.
[75] Also see *R. Brill* and *H. Pelzer,* Z. Kristallogr., 72, (1929) 398; 74, (1930) 147. Z Kristallogr., 68, (1928) 387; 75, (1930) 217.
[76] *J. Hengstenberg* and *H. Mark,* Z. Kristallogr., 69, (1928) 271.
[77] *Ch. Carpenter,* Cellulosechemie, 16, (1934) 64.

The results obtained by *Hengstenberg* and *Mark* were given wide publicity in the older literature and were often the premise for further postulates on fibre constitution. It would be dangerous, however, to draw conclusions from these investigations not warranted by the actual facts. The underlying theory presupposes a perfectly formed lattice within the particles, but any aberrations from the ideal lattice structure — as may certainly be expected in a substance such as cellulose (and particularly in synthetic fibres) — may cause indistinctness of the interference lines. It should also be borne in mind that, at best, such experiments may tell us something about the average order of magnitude of the crystallites, but nothing about their geometrical distribution, and they certainly provide no proof whatever of the existence of individual crystalline particles.

A newer and more promising means of obtaining useful information respecting the dimensions and geometrical distribution of the crystalline regions is provided by the diffuse blackening which appears under very small diffraction angles (of the order of magnitude of 1°) and, therefore, occurs close to the centre of the X-ray diagram. We shall be reverting to this in § 5. (A separate list of documentary references on the subject of particle size determinations by X-ray or electron interference is appended at the end of this Chapter).

At this point it must be emphasized that the results of X-ray experiments do not warrant any definite conclusions about the length of the chains. The elongated crystalline regions were, it is true, at first regarded as individual rod-shaped crystallites and their length was supposed to be the chain length of the component molecules, but, according to current views, there is absolutely no foundation for that assumption. The terminal groups bordering the chains are just as liable to lie within as outside the crystalline regions (cf. § 5).

As may be seen from the few examples given, there are likewise no generally characteristic crystallite dimensions for cellulose preparations. Rather should we regard the crystalline regions as islands of highly ordered arrangement in a mass consisting of chain molecules. The number, size and regularity of structure of these islands differ from case to case. With many natural objects they may be particularly highly developed and govern the general picture of the fibre structure, but, even so, they are still of submicroscopic dimensions and alternate with regions of less perfect arrangement.

Still more problematic is the crystalline structure of regenerated cellulose fibres. Though there is little doubt that a more detailed knowledge of the nature of the crystalline fraction, its proportion, the size and shape of the lattice ordered regions and similar details would also be of practical value, there is as yet very little reliable information in this respect. Only quite latterly some new lines of attack on these problems have been explored.

According to recent findings (cf. p. 316) states of two dimensional instead of three dimensional lattice order seem to play a part in regenerated fibres. *V. A. Kargin, Karpov* and *Pinsker*[78] were able to show that the width of the interference lines on the electron diagram of thin films of cellulose nitrate is nearly that shown on the X-ray diagram of the same preparations. It was discovered at the same time that the majority of the identity periods derived from the electron diagram agree with those computed from the X-ray data. On the basis of X-ray and electron diffraction experiments the japanese author *Kakinoki*[79] suggested that nitrocellulose does not form a true crystalline lattice at all, in which *V. A. Kargin* and *D. I. Leypunskaja*[80] later agreed with regard to hydrate cellulose, stating that in these preparations there is an approximate, but no true crystal lattice order of the molecules. *K. H. Meyer* and *A. J. A. van der Wyk*[81] have recently expressed similar views (in all likelihood independently), justly pointing out that in this matter there can be no sharply defined differentiation between "crystalline" and "amorphous" regions. The distinctness of the X-ray interference lines would then be merely an expression of the average order in the diffracting substance. In this connection we may also refer to the work of *W. O. Baker* et al[82] on the crystallinity of cellulose esters. Unlike cellulose, its triesters, like the triacetate and the tributyrate, can be melted. When the melts are allowed to solidify a few degrees below this melting point, they show an X-ray diffraction pattern exhibiting a number of sharp lines, corresponding to lattice order and to a fair amount of crystallisation. If, on the other hand, the melts are "quenched" (rapidly cooled to a low temperature), a diffuse pattern, similar to that given by liquids, is obtained. Upon "annealing" (heating to higher temperatures below the melting point), the "crystalline" X-ray pattern is gradually restored, indicating an increase of "local order". All transitional states between the "amorphous" ones in the quenched condition and the state of maximum crystallinity, which may be reached by the given substance, seem to be realizable in these instances.

Similar phenomena have been observed in other high polymers too. Discussing ordinary cellulose, allowance should be made for the very same structural characteristics. For practical reasons, however, we shall frequently use the term "crystalline and amorphous regions". It should be noted, however, that a quantitative rather than a qualitative difference is referred to and that all transitional states between the two may occur. Methods aiming at a quantitative computation of the "crystalline-amorphous ratio" will be discussed later.

In this book we shall moreover henceforth always refer to a crystalline

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[78] *V. A. Kargin, Karpov* and *Pinsker*, Acta physicochim. URSS 7, (1937) 646.
[79] *Kakinoki*, Proc. Phys. Mat. Soc. Japan, 21, (1939) 66.
[80] *V. A. Kargin* and *D. I. Leipunskaja*, Acta physicochim. URSS, 12, (1940) 397.
[81] *K. H. Meyer* and *A. J. A. van der Wijk*, Z. Elektrochem., 47, (1941) 353.
[82] *W. O. Baker et al*, J. Amer. Chem. Soc., 64, (1942) 776; Ind. Eng. Chem., 37, (1945) 246.

portion if the corresponding typical X-ray interference lines are visible. We shall then know that we are dealing with regions in the preparations consisting of chain molecules in parallel alignment and also possessing lateral order.

The investigation of lattice structure and fibre structure by means of X-rays and electron rays is not, as is so often assumed, a matter purely of scientific interest, but must help to clear up many pressing problems relating to the constitution of artificial fibres, especially as this subject now promises to develop. Utilization of the inherent possibilities has by no means been exhausted; on the contrary, it has only just begun.

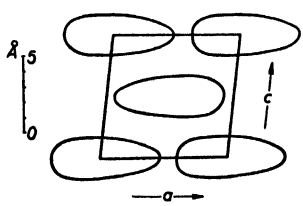
For this reason we feel justified in referring to the relevant problems of structure analysis in this book and in taking them into account when drawing up our list of documentary references (see separate lists at the end of this Chapter).

§ 4. CRYSTAL STRUCTURE OF SOME ADDITION COMPOUNDS OF CELLULOSE

(Alkali Cellulose and the two Cellulose Hydrates)

Many cases are known of alien molecules penetrating into the lattice of cellulose to form an addition compound likewise of crystalline order, when, of course, a new X-ray diagram is exhibited. It would be outside the province of this book to enter into a detailed discussion of such compounds [83]. We shall only briefly mention some of the few cases to which reference will have to be made later.

A series of these compounds — called alkali celluloses — is found when concentrated caustic soda is allowed to act on cellulose preparations. Various stoichiometric quantities of sodium hydroxide and water infiltrate between the cellulose chains, and the cellulose lattice widens. The most important of these compounds, Sodium Cellulose I, is formed during the mercerization of cellulose, i.e., during the action of sodium hydroxide of 16—20% at ordinary temperature. According to *H. Sobue, H. Kiessig,* and *K. Hess* [84] and also according to *I. Sakurada* and *S. Okamura* [85], 1 NaOH and approximately 3 H_2O per glucose group penetrate into the lattice.



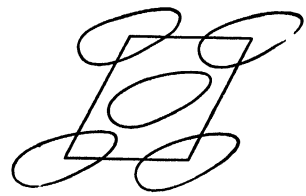


Diagram of lattice types after *K. H. Meyer.*

Fig. 14a, Cellulose I. (native).
a = 8.35 å, c = 7.9 å
β = 84°

Fig. 14b, Cellulose II (hydrate cellulose)
a = 8.14 å, c = 9.14 å
β = 62°

[83] For which see *K. Hess* and *K. Trogus,* Ergebn. d. Tech. Röntgenkunde, 4, (1934) 21
[84] *H. Sobue, H. Kiessig* and *K. Hess,* Z. physik. Chem., B. 43 (1939) 312.
[85] *I. Sakurada* and *S. Okamura,* Kolloid-Z., 81, (1937) 199.

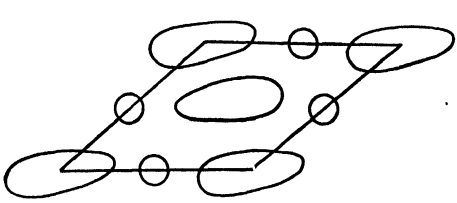


Fig. 14c, Alkali cellulose I.
a = 12.8 å, c = 13.2 å
β = 40°

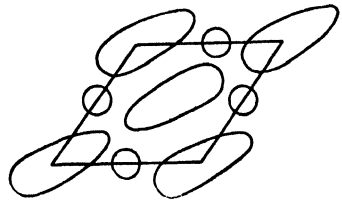


Fig. 14 d, Cellulose hydrate.
a = 10.0 å, c = 9.8 å
β = 52°

Figure 14, taken from a paper by *K. H. Meyer, L. Misch* and *N. P. Badenhuizen*[86], represents diagrammatically the lattice transformation with the aid of cross sections through the elementary cell perpendicular to the fibre axis. For comparison the cross sections for the lattice of cellulose I and that of cellulose II are represented at a and b, while c gives the lattice of sodium cellulose I which is formed from both modifications during mercerization. The small circles represent the position of the invading sodium hydroxide molecules.

When this compound is washed out in the cold, it decomposes while eliminating the sodium hydroxide, and a hydrate of cellulose is formed, described by *I. Sakurada* and *K. Hutino*[87], who gave it the name of Water Cellulose. Its lattice is represented at d in Fig. 14. Although the cellulose chains lie nearer to each other, some water has nevertheless remained in the lattice. The lattice of this hydrate is also found with cellulose freshly regenerated from solutions (such as viscose); apparently this is the lattice order into which dispersed cellulose separated out of aqueous media preferably falls. None the less, this hydrate is very unstable, losing water steadily when left for a long period at rest, and rapidly both when heated and dried.

Later experiments by *P. H. Hermans* and *A. Weidinger*[88] have shown that it is not, as previously supposed, then transformed into cellulose II, but it becomes a hydrate of low water content. According to these authors[89], the most probable composition of the hydrate of high water content is $C_6H_{10}O_5 \cdot 1\,^1/_3\ H_2O$ or $C_6H_{10}O_5\ 1\frac{1}{2}\ H_2O$ and that of the hydrate of low water content $C_6H_{10}O_5 \cdot {}^1/_3\ H_2O$ or $C_6H_{10}O_5 \cdot \frac{1}{2}\ H_2O$. Following their suggestion we shall designate these hydrates of cellulose II henceforth as "Cellulose hydrate II" and "Cellulose hydrate I". Only when it is thoroughly dried does cellulose hydrate I lose its water and the lattice of cellulose II is formed. It needs only humid air for cellulose II again to attract water into its lattice and it then changes into cellulose hydrate I. On swelling in water, the lattice remains unchanged. The hydrate richer in water is formed only

[86] *K. H. Meyer, L. Misch* and *N. P. Badenhuizen*, Helv. chim. acta, 22, (1939) 59.
[87] *I. Sakurada* and *K. Hutino*, Kolloid-Z., 77, (1936) 347.
[88] *P. H. Hermans* and *A. Weidinger*, J. Colloid Sci., 1, (1946) 185.
[89] For this compare also *P. H. Hermans*, Contribution to the Physics of Cellulose Fibers, Elsevier, Amsterdam—New-York, 1946.

in the manner described. In contrast, the lattice of cellulose I absorbs no water at all.

If we compare the lattice of cellulose II with that of its two hydrates, we shall see that the latter can be produced from the former by a widening perpendicular to the crystallographical plane 101 (which, in Fig. 14b lies in the diagonal from the left below to the right above). These are the planes of the lattice most densely occupied by hydroxyl groups, which are, as it were, forced somewhat asunder by the invading water. The spacing (101) thereby shifts from 7.32 to 7.73 or 9.98 å, which is exhibited in a corresponding shift of the interference proper to this plane in the X-ray diagram. The concomitant increased volume of the elementary cell is practically proportional to this shift and amounts to 5.7% for cellulose hydrate I and to 22.6% for cellulose hydrate II. The angle β between the *a* and *c* axes changes from 62° to 59°, or 52°.

The existence of the cellulose hydrates plays an important part in the phenomenon of sorption of water vapour by cellulose, to which we shall be reverting in greater detail in the second part of this book, Chapter II, § 1.

§ 5. THE MICELLAR THEORY AND ITS MODIFICATIONS

§ 5.1. *Historical Development*

In the last half of the previous century, the botanist *C. v. Nägeli* developed, in a series of brilliant articles, a well-founded theory dealing with the intrinsic nature of birefringent structures occurring in living organic matter, such as cell membranes and starch grains. He maintained that these substances are built up of submicroscopic, anisodiametrical, crystalline particles which he called micellæ (singular: micella), applying the same theory to solutions of those substances. According to the theory, the micellæ are retained as units in these solutions, which were accordingly, "Micellar Solutions". When, much later, the existence of crystalline particles in these objects appeared to have been unquestionably proved, first by *Ambronn's* [90] classical optical experiments and afterwards by the introduction of X-ray tests, *Nägeli's* ideas were infused with new life [91] and were adopted by chemists, especially after the publicity given to them by *Meyer* and *Mark* [92]. The micellae were assumed to be particles of a crystalline nature of supermolecular dimensions and colloid chemists had a tendency to regard all solutions exhibiting characteristic colloidal behaviour as dispersions of such supermolecular particles. When, therefore, the crystalline character of the particles of many colloidal solutions (hydrophobic sols in particular) was also established by the X-ray method, everything seemed to point to the truth of the micellar theory.

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[90] *H. Ambronn*, Ber. Sächs. Ges. Wiss., 63, (1911) 249; Kolloid-Z., 18, (1916) 90, 273; 20, (1917) 173.

[91] *P. Karrer*, Cellulosechemie 2, (1921) 125.

[92] *K. H. Meyer* and *H. Mark*, Ber., 61, (1928) 593; "Der Aufbau der hochpolymeren Naturstoffe", Leipzig (1930).

Thus the assumption gained ground that the submicroscopic "crystalline" particles in cellulose fibres are presumably the ready-made colloidal particles of cellulose solutions, for crystallites of the same nature are found in the fibres regenerated from such solutions by reprecipitation, and this was in accordance with the theory. This conclusion was drawn despite the fact that the cellulose solutions did not give a "crystalline" X-ray diagram. On this hypothesis the micellae play the part of special individual units of the fibres, which govern their behaviour both in the solid state and in solutions and therefore represents true intermediate entities. This view has been clearly expressed by *R. O. Herzog* [93], *P. Karrer* [94], and *K. Hess* [95].

K. H. Meyers [96] well-known diagram of the micellar structure of cellulose fibres, which found its way to all text books, also dates from this time. It shows individual, well-defined rod-shaped crystallites, like bricks packed together in a wall; they form a "disperse phase" surrounded by intermicellar volumes. According to this picture the fibres would consist almost entirely of crystalline particles.

Just as an incorrect interpretation of X-ray results first led to the erroneous assumption of a quite small molecule in cellulose, so here an exaggeration of the part ascribed to the crystalline portion of the fibres has given rise to a welter of often inappropriate representations and to misconceptions which impeded progress for a considerable time and which even now have not been entirely swept away [97].

The determinations by *R. O. Herzog* and *D. Krüger* [98] of the "particle size" in cellulose solutions by diffusion measurements at first lent strong support to the micellar theory in its extreme form. Their results were in excellent agreement with the particle sizes deduced from the X-ray diagrams (see § 3), but later on they proved to be incorrect [99].

Special "micellar forces" were supposed to keep "micellae" together in a stable system, said by *Meyer* and *Mark* to be exceedingly strong of cohesion for which the many OH groups were responsible. But as the same forces were supposed to operate in the core of the micella as lattice forces, it was not clear what the difference was between the intramicellar cohesion of the chain molecules and the micellar forces.

Meyer and *Mark* [100] themselves felt and admitted the inadequacy of the conception of sharply defined individual crystallites as units in the fibre. They pointed out that a portion of the cellulose must consist of amorphous sub-

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[93] *R. O. Herzog*, Ber., 58, (1925) 1257.
[94] *P. Karrer*, "Lehrbuch der organ. Chemie", Leipzig (1928) p. 354.
[95] *K. Hess*, "Die Chemie der Zellulose", Leipzig (1928) p. 265.
[96] *K. H. Meyer*, Biochem. Z., 208, (1929) 1.
[97] As a touchstone of the views held around the year 1928 see the articles by *H. Mark*, Naturwiss., 16, (1928) 892 and by *K. H. Meyer*, Z. angew. Chemie 41, (1928) 935.
[98] *R. O. Herzog* and *D. Krüger*, Kolloid-Z., 39, (1926) 250; Naturwiss., 14, (1927) 599.
[99] *R. O. Herzog* and *H. Kudar*, Z. physik. Chem., A. 167, (1933) 393.
[100] *K. H. Meyer* and *H. Mark*, Ber., 61, (1928) 593.

stance, in which, however, the same principle of molecular structure prevailed. On this hypothesis the chains should be longer than the crystallites and should gradually pass over into the rind substance. Their actual words, translated, were: "We even think it likely that at the edges of the crystallites the well-orientated chains at the core gradually fall into disorder and pass into the amorphous 'rind substance'." Here, in the classical treatise by *Meyer* and *Mark* we find the path indicated along which later research was to travel in the attempt to explain the cohesion of the "micellae" and, in particular, the fact that that cohesion persists during swelling. X-ray investigations by *J. R. Katz* [101] showed that, when cellulose swells in water, the liquid merely enters between the "micellae" but does not penetrate into them; for the lattice structure undergoes no change whatever owing to the swelling. Therefore, the "micellae" are driven apart — as, indeed, the considerable increase in volume would seem to indicate — and it may well be asked why then the firm cohesion should nevertheless be maintained; for a cotton hair soaked in water is just as firm as a dry one. This difficulty is even greater in the case of other substances far more liable to swell, whose volume increases by a multiple of it on swelling and to which the micellar theory should also be applicable. It meets us again in products made from regenerated cellulose, products that are swelled to a considerable degree, yet are relatively firm. We shall deal with this question in greater detail in the third part of this book.

The assumption of an intermicellar "intermediate substance" capable of swelling, acting as an interlinking substance ("Kittstoff"), led to contradictions and had to be relinquished. For instance, the fact that artificial fibres, made from highly refined cellulose, behave in an analogous manner clearly disproves the "Kittstoff" hypothesis. Within the framework of this book we may, we think, be exonerated from discussing the "Kittstoff" hypothesis, except to mention the fact that this theory, though in a somewhat modified form and on the basis of extensive experimental material, has recently been brought very much to the fore again by the American *W. K. Farr* [102] and her co-workers [103]. These articles created some sensation and particularly the statement made by these authors to the effect that a microscopically determinable number of cellulose particles exactly corresponding to the quantity of dissolved cellulose was to be found in cuprammonium solutions of cellulose. Since the publication of the investigations by *M. Harris* and his co-workers [104], however, this observation

[101] *J. R. Katz*, Ergebn. der exakt. Naturwiss., 3, (1923) 365; compare article by *Katz* in book by *K. Hess*, "Chemie der Zellulose", Leipzig (1928).

[102] W. *K. Farr* and *S. H. Eckerson*, Contrib. Boyce Thompson Inst., 6, (1934) 189, 309; *W. K. Farr:* J. Appl. Physics 8, (1937) 228; J. Phys. Chem., 41, (1937) 987; J. Phys. Chem., 42, (1938) 113; Contrib. Boyce Thompson Inst., 10, (1938) 7.

[103] *W. A. Sisson*, Contrib. Boyce Thompson Inst., 10, (1938) 113.
J. Compton, Contrib. Boyce Thompson Inst., 10, (1938) 57; J. Amer. Chem. Soc., 60, (1938) 1807.

[104] *M. Harris, C. W. Hock, A. R. Martin* and *R. L. Whistler*, J. of Research Nat. Bur. of Standards 24, (1940) 13, 555, 743.

has been subjected to scrutiny and declared to be an error[105]. The other experimental observations made by *Farr* and her associates will be having further attention in the first Chapter of Part II. They in no way call for a revision of the views set forth here.

§ 5.2. *The Modern Outlook*

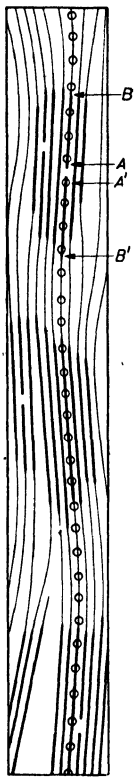


Fig. 15 A. Diagram of the micellar structure after *O. Kratky* and *H. Mark* (1937). The parallel parts of the chain constitute the "crystalline" regions, the "Micellae". That part of the chain marked by circles illustrates how, in a mechanical sense, it behaves like a single chain if the terminals lie within a "micella".

As the work of a long list of research workers[106] progressed, the theory of micellar structure which we anticipated at the end of § 3 began to emerge, viz., that the "micellae" are to be considered as statistically, distributed regions of a latticed order in a mass of substance consisting of approximately parallel chain molecules, as represented graphically in Fig. 15 A. The "crystalline" regions alternate with less well-ordered "amorphous" regions. There is, therefore, no connection between the linear extension of the "micellae" and the lenght of the chains. There are no individual crystallites within confined limits and no "boundary layers" as in the case of polycrystalline metals; on the contrary, the primary valence chains bring about a coalescence of the whole structure. Rather should the intermicellar empty spaces be regarded as "flaws", or points of distortion in a larger system. The chains arrange themselves "as well as they can", as *W. T. Astbury*[107] puts it, without, however, forming definite

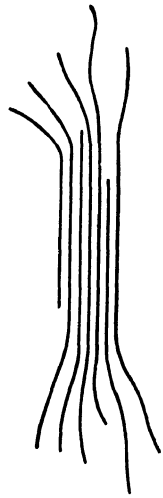


Fig. 15 B Diagram of a "Fringe micella"

[105] Also see *A. Frey-Wyssling*, Naturwiss., 28, (1940) 385.

[106] *H. Staudinger* and *R. Signer*, Z. Kristallogr., 70, (1929) 193; Z. angew. Chem., 42, (1929) 71.
O. Gerngross and *C. Herrmann*, Z. physik. Chem., B. 10, (1930) 371.
O. Gerngross and *R. Lademann*, Kolloid-Z., 60, (1932) 276.
F. D. Miles, Trans. Faraday Soc., 29, (1933) 110.
S. M. Neale, Trans. Faraday Soc., 29, (1933) 288.
F. T. Peirce, Trans. Faraday Soc., 29, (1933) 50.
W. T. Astbury, Trans. Faraday Soc., 29, (1933) 193, 204. (General Discussion on the Colloid Aspects of Textile Materials).
A. Frey-Wyssling, Protoplasma, 25, (1936) 261; 26, (1936) 45.
O. Kratky, Kolloid-Z., 70, (1935) 14; Kolloid-Z., 84, (1938) 149.
O. Kratky and *H. Mark*, Z. physik. Chem., B. 36 (1937) 129.
H. Mark, Confer. on 8.4. 1939 at the Amer. Chem. Society meeting in Baltimore.
E. Sauter, Z. physik. Chem., B. 36, (1937) 129.
W. Schramek, Papierfabrikant 36, (1938) 266.
P. H. Hermans and *A. J. de Leeuw*, Kolloid-Z., 81, (1937) 300.
P. H. Hermans, Kolloid-Z., 83, (1938) 71.

[107] *W. T. Astbury*, Trans. Faraday Soc., 29, (1933) 193, 204; (General Discussion on the Colloid Aspects of Textile Materials).

particles bounded on all sides[108]. This view requires no further assumptions to account for the persistence of cohesion during the process of swelling in water. The water penetrates between the molecular chains into the fine, and even finest "amorphous" regions, but does not reach the core of the crystalline regions. Now if the molecular chains are aligned in the direction of the fibre, the fibre will swell transversely only, but not longitudinally, in accordance with the observed behaviour of well-orientated cellulose fibres.

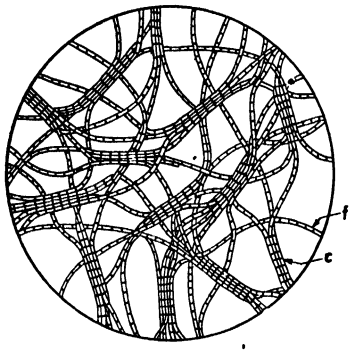


Fig. 16. Micellar structure of gelatine gel after *O. Gerngross* and *C. Herrmann*

K. H. Meyer and *W. Lotmar*[109] have shown by experiment that, under suitable conditions (for very brief deformations), the modulus of elasticity of native cellulose fibres closely approximates to the value predicted by the theoretical assumption of endlessly long chains. Our picture enables us to understand this fact as well, since the cohesion in the direction of the fibre is brought about everywhere by primary valence chains.

P. A. Thiessen[110] has an illuminating definition for the cellulose "micella". viz., "The cellulose micella is an ultramicroscopic mixed crystal of cellulose chains of different lengths. The ends of the long chains extend from the end of the micella to beyond the shorter ones". This definition leads to the concept of "fringe micellae" (Fig. 15 B) which has been discussed by various authors for the dispersed particles in cellulose solutions, or for the structure of regenerated cellulose gels, to which we shall revert later. Closely associated with this are the theories as to the structure of gels formerly propounded by *Gerngross* and *Herrmann*[111] for gelatine (Fig. 16) and by *Frey-Wyssling*[112] for gels in general (Fig. 17), but the part played by the "micellae" in the structure of cellulose gels was not dealt with

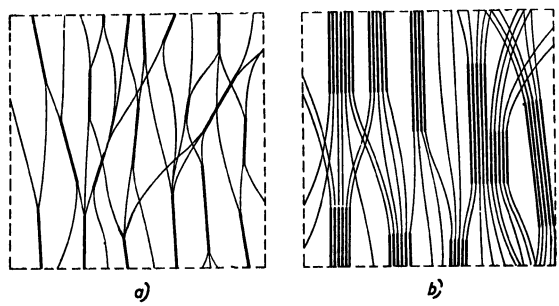


Fig. 17. Ordered regions in gel frame after *A. Frey-Wyssling*. a. Parallel thread molecules, b local formation of crystal lattice.

[108] Compare also *W. T. Astbury* and *H. J. Woods*, J. Text. Inst., 23, (1932) T 17. *A. Frey-Wyssling*, Protoplasma, 25, (1936) 261; 26, (1936) 45. *K. Freudenberg*, Papierfabrikant, 35 (1937) 1.
[109] *K. H. Meyer* and *W. Lotmar*, Helv. chim. acta, 19, (1936) 68.
[110] *P. A. Thiessen*, Z. angew. Chem., 51, (1938) 170.
[111] *O. Gerngross* and *C. Herrmann*, Z. physik. Chem., B. 10, (1930) 371.
[112] *A. Frey-Wyssling*, "Submikroskopische Morphologie des Protoplasmas und seiner Derivate", Berlin (1938) p. 79.

in detail till later. Fig. 18 reproduces a particularly graphic picture given by *E. Sauter*[113] of the micellar structure of native fibres. *Sauter* speaks of "ultracrystalline, fibrillar lattice distortions" between the crystalline regions: At their extremities, the crystallites pass over, in an irregular way, into loose bundles of molecular chains. The orientation of these chains in relation to the direction of the fibre is approximately the same as in the crystalline regions, with which the fibre period agrees, but perpendicularly to the fibre axis the lattice order is deranged. The theory predicts that the X-ray pattern should show a continuous amorphous underground shadow right along the layer lines, and this, *Sauter* stresses, actually is seen in many cases. This picture clearly represents the firm coalescence between the crystalline regions, as also the intermicellar swelling capacity by water absorption in the amorphous regions, with pronounced retention of stability and almost exclusively lateral swelling. *Sauter* also points to the exceptional flexibility and bending resistance of native cellulose fibres, which make them so suitable as raw material for textiles. Since the cellulose crystallite, like a sugar crystal, must be regarded as a brittle and relatively hard structure, the properties just mentioned can only be reconciled to the crystalline nature of the fibres if characteristic, flexible, yet strong interlinking regions hold the crystallites together.



Fig. 18. Diagram of the submicroscopic structure of a cellulose fibre after *E. Sauter*. Rigid crystalline fibrillar regions and ultracrystalline fibrillar lattice fragments, resulting in flexibility with the retention of great strength.

The representation of the micellar fibre structure in this sense has, as we shall see repeatedly further on, become remarkably fruitful. It is able to explain, without begging questions, the ready cleavage of native fibres into fibrils, the appearance of dislocation marks in bast fibres[114] and many typical phenomena observed in the chemical treatment of fibres. We shall revert to this matter later (Part II, Chap. VII).

Sauter's picture of fibre structure brings the lattice distortions in the micellar frame into special prominence. As these exist as typical structures, it would be pointless to infer the dimensions of the crystallites from the indistinctness of the X-ray interferences, as already emphasized in § 3, and, indeed, the results there given of the relevant determinations made by *Hengstenberg* and *Mark, Carpenter,* etc. are no longer considered authoritative.

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[113] *E. Sauter,* Z. physik. Chem., B. 35, (1937) 83.
[114] Cf. *G. Van Iterson,* Chem. Weekbl., 30, (1933) 2.
A. Frey-Wyssling, Z.f. Wiss. Mikroskopie, 56, (1939) 309.

In recent times *O. Kratky* [115] et al and *R. Hosemann* [116] have taken a new method in hand, offering other means of obtaining information from the X-ray diagram respecting the lateral dimensions of the crystalline regions [117]. If the latter were all of the same width and followed each other laterally at equal distances (as represented in Fig. 19), the new periodicity thus given would likewise cause certain X-ray interferences to appear. But since in this case the period comprises far greater distances than the period in the lattice (distance between the individual chain molecules), by *Bragg's* law the diffraction angle will be much smaller than that for the crystal lattice interferences. The corresponding lines must, therefore, be sought for quite near the central point of the diagram. As the sizes and distances of the crystalline regions, however, are not in reality the same, but vary, the periodicity fades and diffraction accordingly is not a clearly defined angle, but within a fairly wide angular range. It is possible to infer the statistical distribution of the dimensions of the coarser scattered "lattice" by measuring the course of the shadow.

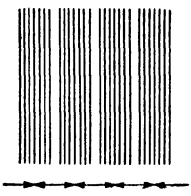


Fig. 19. Consecutive crystalline regions of the same thickness at equal distances (diagrammatically). New periodicity corresponding to distance between the crosses.

On the basis of the elaborated theoretical principles originally laid down by *A. Guinier* for this "low angle scattering", *R. Hosemann* [118] has recently introduced some refinements into this experimental test. He was able to reach certain conclusions as to the thickness and length of the "micellae", according to which there is no predominant crystallite thickness in cellulose preparations. The very thin "micellae", consisting of only one primary valence chain, are very numerous. The thicker they are, the more seldom do they occur. He was unable to give an upper limit for the thickness in ramie fibres and in a fibrous triacetyl cellulose, but it would certainly be below 400 å. He did, however, find a frequency maximum for a given length (this being approximately 300 å in ramie and 200 å in cellulose triacetate). The frequency of the greater lengths diminishes gradually and that of the smaller more quickly.

Hosemann's conclusions have, to be sure, been criticized in several quarters [119] since their publication and the subject has been thoroughly gone into by *O. Kratky, A. Sekora* and *R. Treer* [120]. These investigators contend that, if the

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[115] *O. Kratky* and *F. Schossberger*, Z. physik. Chem., B. 39, (1938) 145.
O. Kratky, Naturwiss., 26, (1938) 94;
O. Kratky, A. Sekora and *R. Treer*, Z. Elektrochem., 48, (1942) 587.

[116] *R. Hosemann*, Z. physik. Chem., A. 183, (1938) 185; Z. angew. Chem., 53, (1940) 322; Z. Elektrochem., 46, (1940) 80; Naturwiss., 28, (1940) 665; Z. Elektrochem., 46, (1940) 535.

[117] Also compare *R. Fricke*, Z. Physik., 113, (1939) 751; 114, (1939) 133; Z. angew. Chem., 53 (1940) 332; Naturwiss., 28 (1940) 665.

[118] *R. Hosemann*, Z. angew. Chem., 53 (1940) 332; Z. Elektrochem., 46, (1940) 80, 535; Naturwiss., 28 (1940) 665.

[119] *K. H. Meyer* and *A. J. A. v. d. Wijk*, Z. Elektrochem., 47 (1941) 353; Naturwiss., 30, (1943) 542.

[120] *O. Kratky, A. Sekora* and *R. Treer*, Z. Elektrochem., 48, (1942) 587.

low angle scattering method is applied in the right way, it produces values for the mean width dimension of the crystallites closely approximating those obtained by the classical method devised by *Hengstenberg* and *Mark*. It is to be hoped that these investigations will be followed up and also applied systematically to artificial fibres.

In any event, there is every reason to believe that the crystalline regions are not individual structural corpuscles in the fibre, but rather statistically distributed, particularly well-arranged agglomerations within a larger system of approximately parallel molecular chains. Taking the view of *Kargin* and *Kakinoki*, already referred to, into account, however, it is quite likely that there never can be any question of quite undisturbed lattice development, particularly where regenerated fibres are concerned (see p. 20, 23).

As stated in § 3, methods by which we can determine the percentage of crystalline substance are still in the earliest stages of development, but the first results point to the presence of considerable amounts of non-crystalline substance in the fibres, which bears out the assumptions.

The conception of cellulose fibre as built up of crystalline and amorphous component parts involves in many respects a certain duality in its behaviour and properties, which is also apparent in some theoretical reflections. We shall come across this duality in several subsequent chapters.

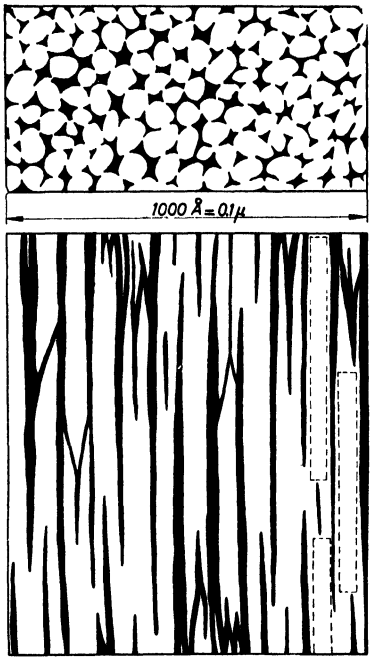


Fig. 20. Diagram of micellar texture of cellulose fibres after *A. Frey-Wyssling*. (The black spaces in the diagram represent the voids).

No summary of modern views on the micellar structure of fibres would be complete without mention of the instructive concepts developed by *A. Frey-Wyssling*[121] in a series of exhaustive and important studies. While *Sauter* stressed in particular the ultrafibrillar splitting up of the micellar structure, *Frey-Wyssling* is primarily concerned with the strongly developed system of hollow spaces consisting of the finest capillaries, present in all native fibres. He studied this capillary system by the introduction of colloidal particles of noble metal into the fibres and the determination of the size and distribution of the metal particles by X-ray spectrography and optical experimental test. Fig. 20 reproduces in diagram a longitudinal and a cross section through

[121] *A. Frey-Wyssling*, Protoplasma, 25 (1935) 261, 26, (1936) 45; 27, (1937) 372, 563; Submikroskopische Morphologie des Protoplasmas und seiner Derivate, Berlin (1938) p. 79.

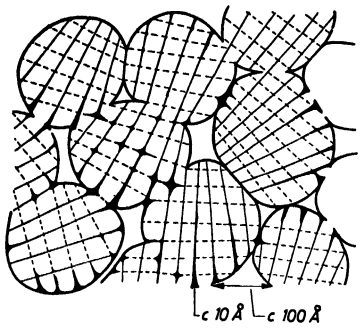


Fig. 21. Perfected cross-section of Fig. 20. Lattice faults and distortions in the orientation of adjacent fibrils (after *A. Frey-Wyssling*).

the micellar system of ramie fibres. Fig. 21 represents a refinement of the cross-sectional picture and illustrates the coalescence of individual fibrils, the lattice distortions and also the possibility of certain variations in the relative orientation of the adjacent crystalline regions.

It need hardly be said that pictures as those represented in Figs. 16, 17, 18 and 20 include several hypothetical elements; nevertheless, together they do contrive to present to us the essential features of fibre structure. The order of magnitude of the single microfibrils depicted in Fig. 19 is in the region of 50—100 å and that of the fine capillary system is correspondingly smaller. *Frey-Wyssling* decided on the basis of his experiments with the deposition of metal particles that ramie fibres furthermore contain some large capillaries of the order of 100 å interior width, spaced at 100—1000 å.

The "porosity" of the fibres will be dealt with anew in Part II, Chapter III, § 2. All we need say here is that the existence, at any rate, of the larger capillaries just referred to would seem to be established by the work of *Frey-Wyssling*, but the inferences made in regard to the smaller cavities can by no means be accepted at their face value.

Still more recently attempts have been made to extend our knowledge of the structure of fibre by using the electron microscope as devised by Boris and Ruska (the resolving power of which attains about 30—40 å). The first experiments made by *H. Ruska*[122] disclosed, unexpectedly enough, a vesicular pore system both in native and in artificial fibres, which is entirely at variance with the supposed pronounced density of the latter, in particular. Then, immediately after, *Ruska* and *M. Kretschmer*[123] obtained very interesting photographs of preparations of staple fibres, partly broken down previously by acid treatment, showing a distinctly fibrillar structure and strongly reminiscent of the micellar structure hypotheses developed along indirect lines beforehand. Experiments conducted by *D. Beischer*[124] with an electron microscope also clearly showed fibrillar fringes to wedge-like sections with fibrils of 50—100 å thickness. Shortly after this, *H. Mahl*[125] was able to show that the vesicular structures first obtained by *Ruska* must have been due to decomposition of the fibrous substance owing to excessive heating during

[122] *H. Ruska*, Kolloid-Z., 92, (1940) 276.
[123] *H. Ruska* and *M. Kretschmer*, Kolloid-Z., 93, (1940) 163.
[124] *D. Beischer*, Z. Elektrochem., 46, (1940) 555.
[125] *H. Mahl*, Kunstseide und Zellwolle, 23, (1941) 77; Z. angew. Photographie, 11, (1941) 58.

the exposure [126]. Very soon after this, again, it was discovered that microtome sections of fibres cannot be made thin enough for the electron microscope. However, preparations enabling the investigator to gain some insight into the structure of fibres can be obtained, either by mechanical means (i.e. in a ball mill of special design), or by swelling and flattening out the swollen fibres, or else by partial chemical decomposition. In further work *E. Kuhn* [127] *E. Franz* [128], *E. Franz L. Wallner* and *E. Schiebold* [129], *W. Wergin* [130], *L. Wallner* [131], *O. Eisenhuth* and *E. Kuhn* [132], *E. Husemann* [133], *R. B. Barnes* and co-workers [134] obtained results which are in agreement with the theories on structure developed along different lines (cf. Part II, Chap. I).

§ 5.3 Standardisation of Terminology.

Before concluding this chapter on the micellar theory and its variations, we feel a word should be said about the dangerous use of inadequate or ambiguous terminology and an attempt should be made to clear up the doubtful points of nomenclature. It has frequently been stated in the most authoritative quarters [135] that loose terminology has already been responsible for many misunderstandings and fruitless polemics, particularly in German literature. These impediments constitute a most undesirable hindrance to progress, especially now when so much enlightenment prevails.

First of all, it should be borne in mind that the micellar theory in *Nägeli's* original sense, i.e., the "micella" as a well-defined crystalline particle and as the individual elementary unit in a series of native structures, no longer holds. As explained with praiseworthy clarity in his book entitled "Submikroskopische Morphologie des Protoplasmas" *A. Frey-Wyssling* insists that, in respect of the structure of gels, fibres and like object, reference can really only be made to a micellar system and not to individual "Micellae". He develops a "micellarology" to which we shall adhere further on in this book, as it suits our purposes admirably and provides us with unequivocal terminology for many cases which would otherwise be difficult to deal with in clear language.

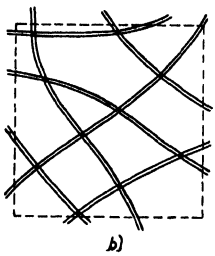
The micellar system, as represented in Figs. 16 and 20 for intance, is a disperse system consisting of two components, the network structure and the hollow spaces, which interpenetrate. There can no longer be any question as to

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126 See also *H. Jentgen*, Kunstseide und Zellwolle 23, (1941) 76; and particularly *A. Haman*, Kolloid-Z., 100, (1942) 248.
127 *E. Kuhn*, Melliands Textilber., 23, (1941) 249.
128 *E. Franz*, Cellulosechemie, 2, (1941) 42.
129 *E. Franz, L. Wallner* and *E. Schiebold*, Kolloid-Z., 97, (1941) 36.
130 *W. Wergin*, Kolloid-Z., 98, (1941) 131.
131 *L. Wallner*, Cellulosechemie, 20, (1942) 87.
132 *O. Eisenhuth* and *E. Kuhn*, Die Chemie, 55, (1942) 198; 3. Forschungstagung Weimar, (1942) p. 74.
133 *E. Husemann*, J. Makromol. Chem., 1, (1943) 16, 158.
134 *C. J. Burton, R. B. Barnes* and *T. G. Rochow*, Ind. Eng. Chem., 34, (1942) 1429; *R. B. Barnes* and *C. J. Burton*, ibid., 35, (1943) 120.
135 *Wo. Ostwald*, Kolloid-Z., 3, (1934) 67. *A. Frey-Wyssling*, Submikroskopische Morphologie des Protoplasmas und seiner Derivate, Berlin (1938) p. 79. *P. A. Thiesen*, Z. angew. Chem., 51, (1938) 170.

which is the disperse phase and which the dispersing agent, for each of the two phases is continuous in itself [136].

It should also be remembered when discussing the structure of gels that one of the components of the system consists of a network, or aggregate of individual chain molecules. These then cohere at certain places, which *Frey-Wyssling* calls "junction points" (a designation which in no way anticipates the nature of these places). Fig. 22 illustrates a case in point. Here, in the sense of the phase theory, we are no longer concerned with a two-phase, but with a one-phase system. Even this *Frey-Wyssling* classifies as one of the micellar systems. It is microscopically and optically void and, even physically, it is to be regarded as homogeneous. Fig. 17a reproduces a transitional form between the one-phase and two-phase systems. The more parallel the position of these chains within the frame, the more likely is it that crystalline regions will be formed (Fig. 17b).



b)

Fig. 22. Gel formed as a lattice or aggregate of individual chain molecules (after *A. Frey-Wyssling*).

There are, therefore, one-phase and two-phase micellar systems together with all the possible transitions and combinations. Their physical (e.g., optical) properties differ, of course, from case to case. For instance, if the beams of the frame are thick enough, the two-phase system need no longer be optically empty. With greater concentration of the solid components, systems are formed of the cellulose-fibre, cell-wall, chitin shields etc. order. The gels as we find them in, say, regenerated cellulose which, though very rich in water, display good mechanical cohesion, should be regarded as systems in the sense of Fig. 17a or Fig. 17b.

Now, however, the micella concept has, historically, at the same time been incorporated in the classical dispersion doctrine. The designation "micella" has meanwhile been generally adopted by colloid chemistry for the kinetically independent particles in colloidal solutions, notably in German as a rule in the form of the variant "die Mizelle" (plural: die Mizellen) instead of "das Micell" (plural: die Micelle). This colloid-chemical term "die Mizelle" is more comprehensive than *Nägeli's* "das Micell" inasmuch as it is used to denote all sorts and varieties of colloidal particles, whether they be of a crystalline nature or not. This application of the word "Mizelle" has been recommended by such well-known researchers as *J. Duclaux* [137], *R. Zsigmondy* [138] and *S. P. L. Sörensen* [139]. It has frequently been suggested that the word "Micell" should be used for crystalline particles and "Mizelle" for particles not exhibiting a lattice pattern. As a result, there is a regrettable confusion in the

[136] One phase is represented by the cellulose substance and the other by the gas or liquid in the void system. The latter may also be filled with a solid substance, such as lignified wood fibre.
[137] *J. Duclaux*, Les colloides, Paris 1929.
[138] *R. Zsigmondy*, "Kolloidchemie", 5 Ed., Leipzig 1925.
[139] *S. P. L. Sörensen*, Kolloid-Z., 53, (1930) 123.

terminology and when the word "Micellen" is used, there is often uncertainty as to whether a particle in *Nägeli's* understanding of it is meant, or some indeterminate colloidal particle.

If, when studying the colloidal solution of a cellulose fibre, one were to ask what kinetically independent particles it contains, it would be necessary to allow for three possibilities, viz.,

1. The dispersion has advanced as far as the individual chain molecules and these are present as independently moving particles in the solution.
2. The solution contains (like many solutions of low molecular weight) groups (complexes, associations) of mutually cohering chain molecules, though there is no lattice order. All according to their internal equilibrium, moreover, the size of these complexes depends upon prevailing conditions such as concentration and temperature (cf. p. 51 ff.).
3. During the dispersion of the fibres, parts of the original structure, including crystalline regions, have remained together. The solution contains particles, say, as understood by the "fringe miccellae" theory (Fig. 15b).

If we follow the suggestion made above, we should in case 2, as with associations of molecules in a concentrated soap solution, speak of "Mizellen", whereas in case 3, as with a gold sol, we should use the term "Micelle". But this is by no means attractive and, moreover, many languages would not lend themselves to such a differentiation.

Even to this day it is a matter of contention as to which of the three alternatives actually occurs in colloidal cellulose solutions. One group of investigators, whom *H. Staudinger* may be said to represent, takes the view that "free" chain molecules are at any rate dispersed in very dilute solutions ("Sol-Lösungen" in Staudinger's terminology). But they do admit the possibility of molecule associations, in which supermolecular complex particles may be formed, occurring in more concentrated solutions ("Gel-Lösungen", as *Staudinger* calls them). This would be equivalent to our second alternative; so, according to current colloid-chemical nomenclature, the solution contains "Mizellen".

Another group of investigators, among whom are *Th. Lieser* and *W. Schramek*, assumes the presence of "Micelle" in the original sense, i.e., supermolecular particles of lattice structure (at any rate in certain solvents). It is quite evident that the distinction between "molecular" and "micellar" solutions will not suffice to express the subtle differences between alternatives 2 and 3; indeed, in the absence of a decisive and clarified terminology, it leads only to misunderstandings and confusion, as the literature only too well testifies. Yet, even if we succeeded in formulating the problem with greater precision, we should not thereby have achieved unity (cf. Chapter II, § 4.). Probably the actual position is that one group of investigators tries to cover too much ground with the purely "macromolecular" view, whereas the second group, including the "pure colloid chemists" is conscious of an undue

deviation from molecular hypotheses and rightly demands more consideration for the classical colloid-chemical postulates. It should nevertheless be borne in mind that the well-known representative of colloid chemistry, *Wo. Ostwald*[140], said unequivocally that a dispersion of individual molecules sufficiently large in one dimension, must likewise lead to solutions with all the characteristic properties of colloids.

Since, later in this book, we shall have to define our attitude to a certain extent towards these debated questions, it has seemed proper to discuss them at some length at this juncture so that we may clearly realize the implications. Like *Frey-Wyssling*, we shall refrain from mentioning the micella hypothesis and shall eschew the expression "micellar solution". If we should have occasion to speak of dispersed particles of a crystalline nature in a solution, we shall call them lattice-ordered particles; if, on the other hand, the particles we are dealing with consist of several chain molecules in mutual mechanical cohesion though not in lattice order, we shall designate these as supermolecular particles.

The term micellar systems will be retained for non-liquid gel-like objects. These may or may not contain lattice order regions.

In Table I the distinctive features of the doctrine of dispersion and the micellar doctrine according to *A. Frey-Wyssling*[141] are set out conveniently for comparison.

TABLE I

	Doctrine of Dispersion	*Transitional Area*	*Micellar Doctrine*
Colloidal condition	Sols	"Gel solutions"	Gels
Dispersed substance	Individual, mutually independent particles possibly macromolecules (disperse phase)	Incipient interaction between particles.	Coherent framework structure.
Solvent	Dispersion agent	—	Imbibition liquid.
Swelling	Solution	Infinite swelling capacity	Limited swelling capacity.
Structure	Not structured	Signs of structure	Plainly structured.
Elasticity	Not elastic	Yield value very small.	Elastic; marked yield value.
Condition	Fluid.	Viscous	Almost or entirely solid.

[140] *Wo. Ostwald*, Kolloid-Z., 53, (1930) 42.
[141] *A. Frey-Wyssling*, , "Submikroskopische Morphologie des Protoplasmas und seiner Derivate", Berlin (1938) p. 79.

The disperse systems in the classical sense are transformed into micellar systems if such forces come into action between the dispersed particles as will ensure mechanical coherence extending throughout the systems (sol-gel transition). Between the two species there is a continuous series of transitionary states determined by the relaxation time (durability) of the bonds, this being a measure of the velocity with which a strain imposed upon the system relaxes. The system does not lose its fluid character in the usual sense until the relaxation time reaches a relatively high value. It should be noted that continuous transitions between "free molecules" and "associated molecules" may also — and indeed are expected to — occur in a dispersion of chain molecules (Cf. Chapter II, § 4, 6 and 8).

Finally, the following definitions according to Frey-Wyssling may be recapitulated:

Micellar doctrine	=	Doctrine of the gels, particularly of gel structure.
Micellar frame	=	Coherent structure of colloid substance.
Molecular frame	=	Network structure consisting of cohering single molecular chains.
Intermicellar substances	=	Substances in the interspaces of a micellar frame.
Intermicellar processes	=	Occurences in the interstices of the framework substance.
Intramicellar processes	=	Occurrences within the framework substance.

§ 5.4. *Some remarks on the structure of artificial fibres*

The essential features of the ideas developed in this chapter on micellar structure, mainly in reference to native fibres, are also applicable to artificial cellulose. As, however, the latter are always regenerated from a solution in the form of a gel, the swollen condition and the orientation of the micellar frame are of paramount importance in this instance. Examination of the finished products has shown that the micellar structures of native and artificial fibres are quite comparable, though the crystalline regions might, generally, be of smaller size and contain more lattice distortions than those in native fibres (cf. § 3). The percentage of the "crystalline" part may also be smaller generally speaking. Hence it is the "amorphous" portion of these fibres which calls for closer attention. From a scientific point of view, little systematic work has yet been devoted to these objects, but conditions may be more favourable at the present time and there are several ways open to us to make up the arrears.

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CHAPTER II

CELLULOSE SOLUTIONS AND GELS

§ 1. INTRODUCTION

The literature on solutions of cellulose and its derivatives is exceedingly voluminous, but both the theoretical views and the existing copious experimental material lack uniformity and, indeed, are often contradictory. Though certain aspects of this most intricate problem have been and are being attacked, we are only at the beginning and satisfactory clarification has by no means yet been achieved.

For instance, as pointed out on page 46, opinions still differ as to the state of dispersion in cellulose solutions and solutions of high-molecular substances in general and it is indeed no easy matter to solve this difficult and complicated problem. With the lack of properly authenticated physico-chemical evidence, any onesided application of this or that pet theory may only too easily lead to serious errors. The existing theoretical difficulties and the attempts so far made to overcome them are admirably described in a book by *H. Mark* [1], to which reference may be made for further information. The author points out that, at the beginning, the approach to this subject is limited, because it deals with systems characterized by pronounced reciprocal action between the solvent and the solute and also mutually between the dissolved particles. It is always difficult to account theoretically for the action of such forces and inferences as to size and state of the dispersed particles drawn from the results of physico-chemical experimental tests should therefore be accepted with the utmost reserve. This applies in particular to the relatively concentrated solutions used in actual practice, with which we are mainly concerned. For the structure of the gels formed during "coagulation" (i.e., the reaggregation of the dispersed particles to a new pattern) is probably intimately connected with the fundamental structure of the solution at the moment of coagulation. To understand the structure of gels it is necessary to know something about the structure of the solution. In the third part of this book, therefore, we shall have to occupy ourselves

[1] *H. Mark*, "General and Physical Chemistry necessary to a Study of High Polymers", New-York—Amsterdam 1940, "Algemeine Grundlagen der hochpolymeren Chemie", Leipzig 1940.

with these troublesome matters, troublesome, that is, at the present stage of research.

Naturally, it is not within the province of this book to deal with this subject exhaustively. In the following chapters we shall confine ourselves to the discussion of only a few selected generalities. In Section 6 we shall consider the close relationship between solution and swelling on the one hand and between the mechanism of swelling and micellar structure on the other. Section 7 will deal with the fundamental features of the structural growth of cellulose gels as an introduction to the more thorough examination of this subject in the third part of this book.

§ 2. REMARKS ON THE COLLOIDAL NATURE OF CELLULOSE SOLUTIONS

Cellulose solutions exhibit all the characteristics peculiar to the "colloidal" state, e.g., low osmotic pressure, slow rate of diffusion, tendency to flocculate, gel formation, and so forth, while considerable viscosity is another of their hall-marks. Many researchers, it was stated in the previous Chapter (§ 5), following *Nägeli's* lead, at first attributed the colloidal properties of cellulose solutions to the presence of larger, supermolecular particles, as was only natural at that time. It should, however, be emphasized that neither the colloidal character, nor the high viscosity in themselves warrant any such assumption.

At least thirty years ago *Wo. Ostwald* established the concept "colloid" as a definition of dimension and in 1930 this author once again clearly set forth the case (see documentary references to Chapter I), which we shall here invoke.

Thomas Graham's classical definition of colloids referred to the capacity for diffusion of the dissolved substance. The absolute coefficient of diffusion D of a dispersed spherical particle depends upon the radius of the particle r according to the equation

$$2\,rD = RT/2\pi\,N\eta = 0.425 \cdot 10^{-3}\ cm^2/sec.$$

Here the numerical value applies to water at 20°. (N = *Avogadro's* number; η = viscosity of solvent). If D is plotted against 2r, the result is a rectangular hyperbola (Fig. 23).

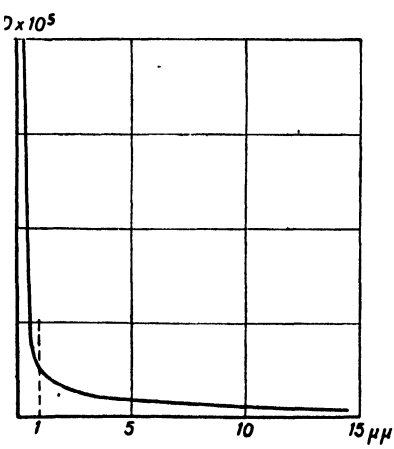


Fig. 23. Coefficient of diffusion as a function of the particle diameter.

It appears that the coefficient of diffusion is still small for particles of diameter 2r > 1μμ and then below that value increases very considerably indeed. Therefore, the lower limit of colloidal dimensions is reckoned from 1μμ. This is without reference to the nature and

constitution of the particles, so it is immaterial whether they consist of many or of few molecules [2].

As soon as a single molecule attains colloidal dimensions a molecularly disperse solution of such molecules will exhibit colloidal properties. The chain length of cellotrioses (1.5μμ) already enters the region of these critical dimensions and it is evident that the dispersions of the far higher members with which we are concerned display typical colloidal properties, since the molecule is the smallest possible particle. Hence these colloidal properties need by no means imply supermolecular particles.

Wo. Ostwald [3] affirms that substances made up of large molecules are colloidal substances, the colloidal character being a property of the substance, and he gives them the designation "eucolloids". *H. Staudinger* speaks of "molecular colloids" (Molekülkolloide) and reserves the term eucolloids for substances of a very high molecular weight which exhibit structural viscosity even in very dilute solutions [4].

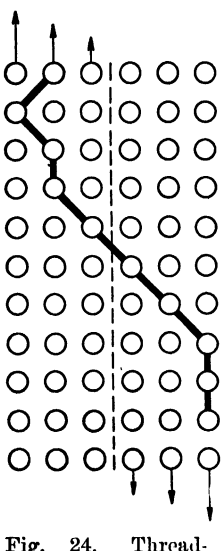


Fig. 24. Thread-like particles in a stationary field of flow.

The high viscosity of cellulose and its derivatives, even in solutions of very low concentration, does not in itself imply that the dissolved particles are polymolecular. From early times it has been presumed to stand in relation to the shape of the particles in the solution. *R. Eisenschitz* [5], *W. Kuhn* [6], *E. Guth* and *O. Gold* [7], *M. L. Huggins* [8] and others declare that the viscosity of sols containing anisodiametric particles is far higher than that of sols with spherical particles, which has been confirmed by experiment by *E. Eirich* and co-workers [9], using models. Dissolved single chain molecules will likewise considerably increase the viscosity, whether they be considered as rigid rodlets or as flexible, randomly kinked thread-like objects. A primitive representation of the viscosity-increasing action of thread-like particles is given in Fig. 24, showing such a particle in a stationary field of flow. The particle is subjected to the simultaneous action

[2] Though, to be sure, the dimension definition accords with the conception of colloidal solution, it is not sufficient. The existence of the solution also presupposes certain reciprocal effects of energy between the solvent and the solute, just as in ordinary solutions. (See, for instance, the lucid exposition by *A. Gillet* and *N. Andrault de Langeron* (Introduction à l'Étude des Colloïdes, Liège 1936, p. 65—88) and also § 6 of this Chapter).

[3] *Wo. Ostwald*, Kolloid-Z., 32, (1923) 2; Kolloid-Z., 90, (1940) 372.

[4] See polemics: *Wo. Ostwald*, Kolloid-Z., 67, (1934) 330. *H. Staudinger*, "Organische Kolloidchemie", Braunschweig (1940), p. 71; J. Prakt. Chem., 160, (1942) 245.

[5] *E. Eisenschitz*, Z. physik. Chem., A. 103, (1933) 133.

[6] *W. Kuhn*, Z. physik. Chem., A. 161, (1932) 1, 27.

[7] *E. Guth* and *O. Gold*, Kolloid-Z., 74, (1936) 147.

[8] *M. L. Huggins*, J. Phys. Chem., 42, (1938) 911; J. Phys. Chem., 43, (1939) 439; J. appl. Phys., 33, (1939) 4848.

[9] Also compare survey in *R. Simha*, Meeting of the Amer. Chem. Soc. Cincinnatti O.; Ref. Cellulosechemie, 18, (1940) 92.

of various layers of the liquid moving at different velocities and will therefore exert a "braking influence". The tendency of the particle to orientate itself in the direction of flow, with consequent diminishing braking action, is thereby counteracted by its Brownian movement.

A satisfactory quantitative theory of the viscosity of dilute solutions of chain molecules has recently been produced by *W. Kuhn* and *H. Kuhn* and at the same time by *J. J. Hermans.* (cf. p. 102) and others. The relation between chain length and viscosity implicit in this theory is borne out by experimental evidence. In this respect there is no objection to the assumption of a molecular dispersion.

Whereas the viscosity of dispersions of spherical particles or spherical molecules like rubber latex and gummigut suspensions, solutions of ovalbumin and glycogen[10] is governed by the law of *Einstein* and increases in proportion to the concentration, the viscosity of solutions of anisodiametric particles increases far more than proportionally with the concentration; and the more anisodiametrical the particles are, the greater will be the viscosity.

Experience has taught us that the colloidal solutions of those highmolecular substances which chemical analysis has shown to be constituted of more or less spherical molecules always behave like dispersions of isodiametric particles as far as their viscosity is concerned, whereas the behaviour of all substances with chain molecules is similar to that of dispersions of thread-like particles.

Apart from particle shape, other factors undoubtedly contribute towards increasing the viscosity of more concentrated solutions (cf. p. 52).

§ 3. SOLVABILITY OF CELLULOSE

Whenever we speak of "cellulose" we should do well to remember that the word by no means stands for a homogeneous chemical compound, but for a variety of organic or artificial objects. They are, admittedly, all built up of chain molecules of a like nature, but both the average chain length (molecular size) and distribution of the chain lengths in the preparation and particularly the supermolecular structure may be entirely different in different specimens. Other telling factors are presumably the size and percentage of the crystalline regions and the degree of perfection their lattice order has attained.

Comparing native and regenerated cellulose preparations, yet more factors may become apparent (such as, maybe, individual points of permanent junction between the molecules[11] (Cf. Part I, Chapter V). Finally, native cellulose invariably contains other substances and contaminations which

[10] *Bancelin*, Compt. rend. hebd., 152 (1911) 1382.
H. Staudinger, I. Joseph and *E. O. Leupold*, Ann., 488, (1931) 150.
H. Staudinger and *F. Zapf*, J. Prakt. Chem., 157 (1940) 1.

[11] There are examples of insolubility in the customary solvents of derivatives retaining the fibrous form prepared from native cellulose. *H. Staudinger* and *G. Daumiller*, Ann., 529, (1937) 223.

have to be eliminated by certain refining processes. These may cause certain changes to take place in the cellulose substance and some degree of degradation is sometimes unavoidable. We shall only concern ourselves here with the general behaviour of the most common cellulose preparations, usually to some extent degraded.

There is probably no specific solvent for cellulose in the sense in which benzene, for instance, is the true solvent for rubber. Though cellulose swells to a limited extent in water, it does not dissolve in it[12]. This swelling is the result of penetration of the water between the individual cellulose chains in the amorphous regions, as we hope to show later more circumstantially. The water does not penetrate into the crystalline, or approximately crystalline portions of the micellar frame, as first concluded by *J. R. Katz*[13] from the fact that the X-ray diagram showed no change. (Later on it was discovered that a minute quantity of water had found its way to the lattice of cellulose II; Chapter I, § 4).

There are many known methods by which cellulose can be dispersed to a solution. Quite superficially, they are divided into two classes, i.e., the direct and indirect dispersion methods. By the former the cellulose is converted by substitution of one or several hydroxyl groups to a derivative, which can then be dispersed in a suitable solvent (e.g., nitrocellulose in acetone, methylcellulose in chloroform, cellulose xanthogenate in water). By the direct methods the dispersion can take place in a single operation (dissolving in cuprammonium, in concentrated mineral acids, in certain tetra alkylammonium bases), but, as will be explained in § 4, even in such cases a chemical reaction is involved.

Although, often as a result of secondary reactions, these methods may sometimes be suspected of involving a certain degree of decomposition of the chain molecule, in present views it frequently does not take place. So far as the cellulose preparations with which we are dealing are concerned, preliminary decomposition of the chains is in any case no indispensable condition for the process of dissolving. Many cellulose preparations can be repeatedly dissolved and precipitated again without displaying any serious signs of disintegration. It can, however, be proved in nearly all cases that an intramicellar reaction precedes solution. The obvious assumption is, therefore, that solution is conditional upon this process. To this we shall also revert more fully.

§ 4. ON THE PROBLEM OF MONOMOLECULAR OR POLYMOLECULAR DISPERSION

If we accept the micellar system as presented in the first Chapter (Figs. 13, 15, 16 and 18) to account for fibre structure, we shall have to assume that the methods of solvation mentioned will break down this structure to a

[12] *Th. Lieser* has recently reported on aqueous cellulose solutions prepared in a special way, the nature of which, however, requires further investigation; these solutions are in any case unstable and irreversible.

[13] *J. R. Katz*, Physik., Z. 25, (1924) 321; Ergebn. d. exakt. Naturw., 3, (1924) 363.

solution without necessarily disintegrating the chain molecules; yet the processes involved are not directly evident. The easiest case would be if the dispersion progressed down to the individual chain molecules present in the material and if these were then to float about in the solution as independent particles. In that case the dissociation of the fibre would be complete and exhaustive. This, however, is where the differences of opinion and theoretical difficulties already mentioned begin, and these we shall now have to consider. The old extreme view that the dispersion agent merely, pulls the "micellae" (i.e., the lattice-ordered particles) apart, but fails to dissolve the molecular association in the "micellae", may at any rate be considered as refuted, since the notion of individual "micellae" for the solid fibrous condition has proved to be entirely erroneous, the lattice-ordered particles being not individuals, but agglomerates formed by mutual molecular chains. One might, of course, imagine a dispersion of polymolecular particles out of the fibre, but this would entail the assumption either of the simultaneous disintegration of chains at certain places [14], or at least of certain chain sections, previously held together in a lattice order, being disrupted. But in that event it is not clear why the lattice order should be maintained at other equivalent places. Fig. 25

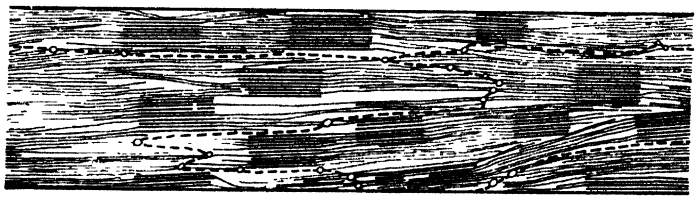


Fig. 25. Diagram of dispersion of a xanthated fibre after *W. Schramek.*
- - - - - - - - - Places of cleavage.
o o o o o o o o o Oxidizable primary valency bridges in the cellulose molecules.
Faint print: Sections of disturbed lattice order.

shows how *W. Schramek* imagines the formation of separate polymolecular particles, while chains disintegrate, when a fibre is converted to cellulose xanthate upon being dissolved. He thereby assumes that the xanthation reaction brought about by the solution and causing conversion only in the intermicellar "amorphous" regions is heterogeneous. In that case it is easy to see that the dispersed particles would have the character of "fringe micellae" (Fig. 14). Earlier still, *O. Faust* [15] propounded a similar theory (also see p. 335).

J. W. McBain and *D. A. Scott* [16] favoured the view of a dispersion of

[14] E.g., see *W. Schramek,* Papierfabrikant, 36, (1938) 226, who actually makes this assumption.
[15] *O. Faust,* Kolloid-Z., 46, (1928) 329.
[16] *J. W. McBain* and *D. A. Scott,* Ind. Eng. Chem., 28, (1936) 470.

polymolecular particles by certain methods of solvation and in recent times this has been defended also by *Th. Lieser* and his associates [17] (in the cuprammonium and viscose-procedure and also in solutions of methylcellulose in water). *Lieser* does not accept disintegration of the chains, but also favours the idea of the heterogeneous course of the chemical reaction brought about by the solution, contending that this affects only the surface and not the interior of the crystalline regions. *Lieser's* polymolecular particles are then "islands" likewise unaffected by the reaction. With our present picture of micellar structure, however, something more is needed to explain how such particles are torn out of their association in the fibre without disintegration of the chains. (In point of fact, the whole notion is applicable merely to those cases in which only a portion of the reactive hydroxyl groups has taken part in the reaction. *Lieser* himself has to assume molecular dispersion wherever there has been stoichiometrically comprehensive reaction).

Recently *Lieser* [17a] has advanced further experimental arguments in support of his theory. In his opinion the states of dispersion in solutions of cellulose and its derivatives must vary considerably all according to circumstances.

As the writer sees it, later developments point to the untenability of the polymolecular dispersion theory in the literal sense as represented by *Lieser* [18]. Nevertheless *Lieser's* views deserve special attention, as he holds [18a] that only those dispersion processes which produce a polymolecular dispersion are suitable for the manufacture of artificial fibres. Against this we have to remember that, with proper precautions, artificial fibres possessing normal properties have been made from solutions of cellulose in concentrated sulphuric acid (for which *Lieser*, too, assumes molecular dispersion). All the same, the view that, all according to circumstances, different states of dispersion may exist in cellulose solutions may be correct in a somewhat different, more general sense, and it behoves us to find out what the consequences may be to the manufacture of artificial fibre. The question of the connection between the "structure" of the solution and the technically important properties of the fibres spun from it has hitherto enjoyed but scant serious theoretical attention [19]. Yet there are several experimental observations hitherto not understood, for which such a connection might account.

To cite some examples: *G. G. Jones* and *F. D. Miles* [20] noticed that the strength

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[17] *Th. Lieser*, Ann., 483, (1930) 132; 511, (1934) 128; 522, (1936) 56; 528 (1937) 276; 532, (1937) 95, and especially Kolloid-Z., 81, (1937) 234; Die Kunstseide, 19, (1937) 191; Cellulosechemie, 18, (1940) 73, 121.
Th. Lieser and coworkers, Z. physik. Chem., B. 74, (1941) 708; Ann., 548 (1941) 195 ff.

[17a] *Th. Lieser* and co-workers, Z. physik. Chem., B. 74, (1941) 708; Ann., 548 (941) 195 ff. *Th. Lieser*, Chem. Ztg., 67, (1943) 197.

[18] *H. L. Bredée*, Kolloid-Z., 94, (1941) 81, recently advanced an objective refutation of some of the experimental arguments made by *Th. Lieser* and *W. Schramek* in favour of their views (cf. these authors' replies which are also printed at the end of that work).

[18a] *Th. Lieser*, Cellulosechemie, 18, (1940) 121.

[19] Apart from the often studied influence of the molecular size. What is meant is such questions as those referring to the state of dispersion, the reciprocal positions and the shape of the molecules, or the polymolecular particles in the spinning solution.

[20] *G. G. Jones* and *F. D. Miles*, J. Soc. chem. Ind., 52, T 251 (1933).

of nitrocellulose films may greatly depend upon the solvent with the aid of which they were made. A distinctive "crystallinity" of the film was ascribed to it. Similar differences were observed by *G. Centola*[21], also *J. Desmaroux* and *M. Mathieu*[22] in the production of films from solutions of varying concentration[23]. *A. V. Blom*[24] found even greater differences in the strength of cellulose acetate films in the function of the solvent. *E. Heuser* and *H. Y. Charbonnier*[25] report appreciable differences in the mechanical properties of hydrate cellulose films produced from viscose of different alkali contents and ascribe them to a different degree of dispersion of the solution[26]. We would, however, above all refer to the very fine investigations carried out by *G. Centola* and *M. Mathieu*, already referred to, who have also developed some important propositions with which we shall have occasion to occupy ourselves more than once in this book. Although, therefore, there are several indications that the state of solution of cellulose and its derivatives may vary with the prevailing conditions and although we should take note of such variations, the question still remains whether those differences can be summarily disposed of by ascribing them to differences in dispersity. First of all, a little closer study will show that this idea can by no means be simply and clearly defined with respect to solutions of high-molecular substances with chain molecules (p. 51); secondly, differences in the state of solution might just as plausibly be attributed to the spatial arrangement, or to the shape of the particles just before gelatination (take, for example, the more or less convoluted shape of the chain molecules). At the beginning of this chapter it was stated that research in this field is attended with immense difficulties; accordingly, it will be by no means an easy matter to find a decisive and satisfactory solution to such problems as these. None-the-less, their importance should not be lost to view.

Another point to be remembered is that, if the solutions should contain polymolecular particles, this does not necessarily mean to say that they were formed as such in the original fibrous structure; it is reasonable to assume that they might have been formed by secondary association processes (see below).

The present general trend of opinion in regard to the monomolecular or polymolecular dispersion of cellulose and its derivatives is that most solvents — where extremely dilute solutions are concerned — give rise to monomolecular dispersion, except for certain experimentally recognizable special cases (see below). This is especially so in the case of many solutions of

[21] *G. Centola*, Atti del X Congr. Intern. di Chimica, Roma IV, (1939) 117.
[22] *J. Desmaroux* and *M. Mathieu*, Compt. rend. hebd. 194, (1932) 2053.
[23] Also see *M. Mathieu*, Trans Faraday Soc., 29, (1933) 122.
M. Mathieu, La Gélatination de la nitrocellulose, Paris 1936.
[24] *A. V. Blom*, Z. angew. Chem., 53, (1940) 40.
[25] *E. Heuser* and *H. Y. Charbonnier*, Meeting of the Amer. Chem. Soc., 9—13 IX. 1940; (ref. Cellulosechemie 18, (1940) 118.
[26] The differences found by the author in the process of orientation and in the mechanical properties of isotropic filaments produced from vicose of different cellulose concentrations will be discussed in the third part of this book. (p. 476).

trisubstituted cellulose esters and ethers in organic solvents. Where there is no extreme dilution, on the other hand, more complicated states of solution and phenomena are to be expected, when three points of view are conclusive.

First of all, it follows from purely kinetic-statistical reasoning that the probability that, in not extremely dilute solutions of chain molecules, a molecule will be surrounded only by molecules of the solvent and may thus be regarded as "free" in this sense, must soon dwindle as the concentration increases. For then at various places of the chain there will be, in addition to solvent molecules, fragments of other chain molecules as well. The chain molecules can then no longer be regarded as "free" and moving independently of each other", the more so as the effects of forces between the molecules cannot fail to arise at the places of contact [27].

In the second place, associated molecules are liable to make their appearance under certain circumstances, in the same way as in solutions of low-molecular substances. We have only to think of the well-known signs of association in many solutions of substances containing hydroxyls, such as monovalent and polyvalent alcohols and the carboxylic acids.

In the third place, there may be marked binding of the solvent molecules to the chain molecules. This may likewise occur in low-molecular solutions, especially if solution takes place with distinctly positive heat effect [27]. This is called solvation. In the more concentrated solutions two chains, separated by a thin layer of solvent, may then compete for the solvent molecules, which likewise sets up certain attractive forces between these chains.

Thus there may be "mechanical interlinking" of different kinds between the dissolved chain molecules, resulting in a structure of the solution. They are partly responsible for the high viscosity of these solutions and it is even possible to deduce an elasticity modulus belonging to this class of interlinking from the structural viscosity (i.e. the dependence of the viscosity upon the rate of flow [28]).

The presence of molecules temporarily interlinked and reciprocally orientated in a certain way must be assumed even in purely low-molecular — and especially in polar — liquids [29].

To a certain extent it is a matter of taste as to whether these association agglomerates and group formations in low-molecular and macromolecular solutions are termed polymolecular particles. Though there is nothing against it in principle, there are two things to be borne in mind.

First of all, in the case both of low-molecular and high-molecular substances,

[27] *K. H. Meyer* and *A. J. A. van der Wijk*, Kolloid-Z., 101, (1942) 52.

[28] E.g., see *E. Eisenschitz* and *B. Rabinowitz*, Ber., 64, (1932) 2522. also compare *P. H. Hermans, J. J. Hermans* and *D. Vermaas*. Kolloid-Z., 105, (1944) 199. *J. J. Hermans*, Kolloid-Z., 106, (1944) 22, 95.

[29] *C. v. Raman*, Indian Journ. Phys., 3, (1929) 225, 399.
G. W. Stewart, Phys. Rev., 31, (1929) 174; 31 (1929) 153; 35, (1930) 726.
O. Kratky, Kolloid-Z., 68, (1934) 347.
S. S. Kistler, J. Phys. Chem., 36, (1932) 2948.
W. Kast and *H. A. Stuart*, Z. angew. Chem., 53, (1941) 12.
H. A. Stuart, Kolloid-Z., 96, (1941) 149.

these phenomena depend upon internal equilibrium. These assembled molecules do not form persistent groups; the process is rather one of repeated formation and dissolving [30]. Moreover, the average particle size is variable, depending on such things as temperature and concentration [31].

Secondly, in the case of high-molecular substances with chain molecules the matter is complicated by the fact that single sections of the chains are also liable to take part in such associations and group formations, with the result that one molecule may be involved in several agglomerations. This might lead to a state of affairs in which all the chains in a solution interlink to some degree in permanent alternation, so that all dissolved molecules might be considered as a kind of network of associations pervading the entire solution [32]. The liquid nature of the solution is, however, maintained owing to the permanent alternation of the points of junction.

The terms "particle size" and "dispersity" here lose their original signification and need to be defined afresh. It will, however, also be clear that, where "polymolecular particles" are concerned, the ideas here associated with them are totally different from those presented by *Lieser* and *Schramek* which have been discussed. The polymolecular particles of those authors were rather groups of molecules formed from the beginning and deriving from the original fibrous structure which, at best, conglomerated to still larger particles as concentration increased, yet would not be split up into single molecules with progressive dilution. Even if the views of these authors are rejected, the alternative need not be dogmatic assumption of a monomolecular dissolution under all circumstances without any cohesion between the particles. Here lies actually the crucial point of the contention around the doctrine of "micellar solutions" (a form we have decided to avoid, as being confusing).

The propagation of the view that a molecular dispersion exists in at any rate extremely dilute solutions of cellulose derivatives and other high polymers is due largely to the numerous investigations, always resting on this point of view, by *H. Staudinger* [33]. From his standpoint the process of solution of high-molecular ("macromolecular") substances does not differ fundamentally from that of low molecular ones; and many physico-chemical investigations

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[30] Also see, *K. H. Meyer* and *A. J. A. v. d. Wijk*, Z. Elektrochem., 47, (1941) 353; Helv. chim. acta, 20, (1937) 1321, 1331.

[31] Thus the "Micellæ" formed in soap solutions are labile structures very dependent upon temperature and concentration (cf. *McBain*, J. Amer. Chem. Soc., 57, (1935) 1926). According to *G. S. Hartley* ("Aqueous Solutions of Paraffin-chain Salts". Paris 1936), these particles have quite a different structure from that of "crystals". See also the recently published invesigations of *J. Stauff* (Kolloid-Z., 96, (1941) 244 and *H. Kiessig* (Kolloid-Z., 96, (1941) 252 and the discussion notes of K. Hess (Ber., 74, (1941) 119, 136).

[32] Cf. *K. H. Meyer* and *A. J. van der Wijk*, Kolloid-Z., 101, (1942) 52. More explicit representations of these states of solution will be given in Part III.

[33] These citations refer to both this author's books "Die hochmolekularen organischen Verbindungen, Kautschuk und Cellulose", Berlin 1932, and "Organische Kolloidchemie", Braunschweig 1940). (Further documentary references there). For a critical commentary on the views of *Th. Lieser* see *H. Staudinger*, Ber., 101, (1937) 2514 and, against that, *Th. Lieser*, Z. physik. Chem., B. 74, (1941) 708; Ann. 548, (1941) 195.

of the last few years, particularly those based on thermodynamic principles, tend to substantiate this view [34]. Only, the solubility of high-molecular substances is often more limited, as in the majority of cases solution will only take place if accompanied by positive heat effect, a limitation which does not apply to low-molecular substances (for the grounds see next section).

Staudinger calls solutions of macromolecular substances "Molecule colloids". He distinguishes between homopolar molecule colloids (organosols), to which solutions of cellulose derivatives in organic liquids belong, and heteropolar molecule colloids (hydrosols), under which category are classified the protein solutions and also aqueous solutions of cellulose xanthate and of cuprammonium cellulose. The latter contain polyvalent cations or anions, as the members of the chain contain ionogenic groups [35]. Both groups would therefore be comparable to low-molecular non-electrolytes and electrolytes. *Staudinger* also allows for interaction between the dissolved molecules. Whereas in the case of solutions of approximately globular particles (spherocolloids in *Staudinger's* terminology) the viscosity of equally concentrated solutions, in obedience to *Einstein's* viscosity law, is virtually independent of the particle size (or of molecular weight), it increases very noticeably with the molecular weight in the case of such solutions with strongly anisodiametric molecules (linear colloids). *Staudinger's* explanation of this phenomenon is that the range of activity of the chain molecules in solution is not, as it is approximately with spherical particles, equal to the volume of the dissolved molecules, but that it is a function of molecule length. As a result, he assumes, a strong hindrance to movement is developed in the molecules' reciprocal movement. A better explanation would be, however, as we have shown, that the anisodiametric molecules, with their, relatively speaking, far larger surfaces, are far more liable to produce mutual interaction in the solution [36].

It is only in very dilute solutions (sol solutions), in which these effects must gradually vanish, that there can be any question of freely moving chain molecules, and conformity to simpler physico-chemical laws may be expected. *Staudinger* applies his well-known "viscosity law" to such solutions only, calling the more concentrated solutions gel-solutions, which are calculated to exhibit far more complicated phenomena. In point of fact, the interaction and interlinking between the individual molecules in this case increase to such an extent that there is a certain resemblance to gels when it comes to firmer and also now permanent linkage (cf. p. 75 and 79). In many respects these solutions behave like "a felt saturated with liquid" [37] and not like a suspension

[34] Reference should likewise be made to many investigations carried out in *K. H. Meyer's* laboratory.
[35] *Staudinger* classifies the aqueous solutions of substances such as starch and glycogen under a third group, viz., the molecule colloids containing hydroxyls. Cellulose, which is closely akin to these, does not dissolve in water at all. Cf. Chap. I § 2.
[36] Cf. *K. H. Meyer*, Die hochpolymeren Verbindungen, Vo. II, p. 530 ff. (1940).
[37] *K. H. Meyer* and *A. J. A. van der Wijk*, Kolloid-Z., 101, (1942) 52.

of free rodlets or filaments. It is neither correct to say that the colloidal particles are the macromolecules, nor that the solution contains "free" polymolecular colloidal particles. These solutions contain a species of molecular framework approximating a micellar system in *A. Frey-Wyssling's* sense (see p. 36); they have a structure (though difficult to define exactly and quantitatively), which we must take into consideration for reasons already given [38].

The stability of these structures may increase and may pass through continuous transitions to the gel state in the narrower sense (cf. p. 38 ff. and p. 80). There is a series of continuous transitions between "gel solutions" with incipient, and downright gels with immediately recognizable mechanical cohesion [39].

In view of the often stressed analogy to the low-molecular states of solution, it need hardly be said that the association phenomena of the macromolecules as well will depend not only on the concentration and temperature, but also on the choice of solvent. There are several well-authenticated cases in which this influence of the solvent has been clearly apparent.

S. Lee and *I. Sakurada* [40] recently investigated association phenomena in solutions of cellulose derivatives by dielectric measurements and discovered that the solvent has a noticeable effect upon the dipole association. Reference should also be made to investigations by *M. Takei* and *H. Erbring* [41]. Specially convincing evidence of the influence of the solvent used upon the particle size is produced by *E. Steurer* in a recent publication [42]. By means of osmotic measurements he established the fact that ethyl cellulose (still containing 10% non-etherized free OH groups) was dissolved to a molecular dispersion in a selection of solvents (chloroform, dioxane and mixtures of benzene and ethanol), whereas in others (chemically pure benzene and toluene) continued to remain associated even with very strong dilution. In this case an average particle size was deducible from the osmotic data, showing that from 2 to 4 molecules had associated to form polymolecular particles. It needed the addition of only 0.3% of ethanol to the benzene solution to break up this association again completely. The osmotic particle size proved to be independent of the temperature in the non-associating solvents, but in the associating ones it was found to decline with rising temperature and was therefore variable to temperature.

There are many scattered references in the literature to the marked effect

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[38] The numerous factors which determine the interaction of the particles in concentrated solutions were recently reviewed by *J. de Booys* and *H. L. Bredée* (Kolloid-Z., 99, (1942) 171.

[39] A fine exemple is provided by the experiments carried out by *E. Heymann* (Trans. Farady Soc., 31, (1935) 846) on the temperature-sensitive reversible sol-gel transformations of aqueous methyl cellulose solutions (also cf. *E. Heymann*, The Sol-Gel Transformation, Paris 1936); further, the work of *V. A. Kargin* and *A. A. Stépanova*, Acta physicochim. U.R.S.S. 6, (1937) 183.

[40] *S. Lee* and *I. Sakurada*, J. Soc. Chem. Ind. Japan, 43 (1940) 171 B.

[41] *M. Takei* and *H. Erbring*, Kolloid-Z., 101 (1942) 59.

[42] *E Steurer*, Kolloid-Z., 96, (1941) 333; Z. physik. Chem., A. 190, (1941) 1, 16.

of trivial changes in the composition of the solvent upon the viscosity. As in the *Steurer* case, the solutions in question are usually of partly substituted cellulose derivatives still containing free hydroxyl groups. These cases, it seems to us, may likewise be explained under the terms of changes in the state of association of the solution.

H. Suida [43] states that very small amounts of water added to solutions of ethyl and acetyl cellulose will considerably reduce the viscosity. The addition of 0.08% of water to a dry 2% benzene solution of ethyl cellulose reduces the viscosity to one-sixth of its original value. It may be assumed that an association going back to unsubstituted hydroxyl groups in the hydrocarbon solution is greatly restrained by the addition of water, as the active places are occupied by water molecules. The addition of alcohol has a similar effect [44]. Dry "acetone-soluble" acetyl cellulose dissolves with difficulty in dry acetone, but easily after the addition of small amounts of water or alcohol. *S. Nisizawa* found that the structural viscosity of nitrocellulose solutions in alcohol-ether increases as the ether content increases. The addition of water increases the viscosity and the structural viscosity, whereas the addition of small amounts of salts (KI, $FeCl_3$) again reduces the structural viscosity. Other substances as well were found which have a contrary effect.

Staudinger [45] is among those citing similar cases. He considers it possible that chain molecules interconnected by "coordinative covalencies" may occur in aqueous solutions of cellulose xanthate, in which hydroxyl groups are known to be split off gradually (ripening) [46].

G. V. Schulz [47] concluded from investigations on the osmotic pressure of partly substituted methyl cellulose that, in concentrations of less than 0.5%, simple thread molecules are present in the solution. In higher concentrations he finds deviations which, though not yet explainable with certainty, might point to the formation of molecular aggregates. He considered, furthermore, that special attention should be given to these anomalies and particularly to their influence upon the properties of the filaments and films produced from such solutions.

It might be pointed out that, as set forth in the foregoing, the views held by the *Staudinger* school and the theories of those researchers who accept associations or other agglomerations in solutions of so-called molecular colloids are not as sharply opposed as would seem at first sight [48]. The emphasis on certain anomalies, particularly with partially substituted cellulose derivatives, provides a link, as it were, with the views of *Th. Lieser* on distinct states of solution in various solvents, to which we referred at the beginning of this Chapter.

[43] *H. Suida*, Cellulosechemie, 12, (1931) 310.
[44] Cf. the work of *E. Steurer* mentioned in footnote 42.
[45] *H. Staudinger* and *F. Reinecke*, Ann., 535, (1938) 47.
[46] *H. Staudinger*, "Organische Kolloidchemie", Branschweig, 1940, p. 71.
[47] *G. V. Schulz*, Z. physik. Chem., A. 177, (1936) 453.
[48] See e.g., *Wo. Ostwald*, Diskussions Bemerkungen, Z. angew. Chem., 49, (1936) 549. *J. W. McBain*, Nature, (1935) 1033.

Nor should the fact be lost sight of that we have before us various experimental results which point to time effects in the dispersion of high-molecular substances. In macroscopic dissolution, aggregates of several molecules — that is, polymolecular particles — may at first go into solution which only later disintegrate gradually in the solution. This is manifested by delay, or time-lag, in the transition from concentrated to more dilute systems. *R. O. Herzog* and *B. Lange* [49] were able to show by observing the depolarization of *Tyndall* light that, after the solution of a number of cellulose derivatives (and other high-molecular substances), it often takes a certain time before complete equilibrium sets in. The depolarization angle measured points to a diminution of the particle size. Very convincing examples are provided by the careful investigations of *M. Mathieu* [50], who found that more than a week elapses after the prepartion of a dilute solution of nitrocellulose in acetone before a state of equilibrium is attained. During this period the viscosity of the solution and the crystallinity of the films obtained from it by evaporation diminish. These are further signs of delayed dispersion. *O. Gerngross, C. Herrmann* and *R. Lindeman* [51] were able to show by X-ray photography that, on the "melting" of aqueous gelatine gels, (intramicellarly swollen) "crystalline" (or lattice-ordered) particles are present immediately after the transition to the liquid state, which then gradually continue to disintegrate [52]. *R. Rachowin* and *M. Schlachover* [53] established the probability of an increase in the "dispersity" after the dissolving of cellulose xanthogenate in the viscose process. This view is strongly supported by very admirable investigations by *G. Centola* [54], while *J. J. Stöckly's* [55] very readable paper on the process of dissolution in the manufacture of cellulose is founded on similar views. In this connection recently published work by *O. Kratky* and co-workers [56], to which we shall revert in Part III (p. 336), is particularly noteworthy. *J. Löbering* [57] describes analogous phenomena in solutions of cellulose in mineral acids [58].

However, considering that in all these cases we are dealing with very highly swelled gels at the moment of dissolving, which themselves disintegrate as soon as they are subjected to relatively slight mechanical strain, it is scarcely surprising that primary detachment of the smallest portions of gel should take place, especially when the process of dissolving is accompanied by mechanical "stirring".

In conclusion, we wish to advance the weightiest arguments available at

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[49] *R. O. Herzog* and *B. Lange*, Ber., 62, (1929) 491.
[50] *M. Mathieu*, La Gélatination de la nitrocellulose, Paris 1936.
[51] *O. Gerngross, C. Herrmann* and *R. Lindeman*, Kolloid-Z., 60, (1932) 276.
[52] Also compare *O. Gergross, O. Graf Triangi* and *P. Köppe*, Ber., 63, (1930) 1609.
[53] *R. Rogowin* and *M. Schlachover*, Cellulosechemie, 14, (1933) 40.
[54] *G. Centola*, Atti del X Congr. Intern. di Chimica, Roma IV, (1939) 117.
[55] *J. J. Stöckly*, Kolloid-Z., 105, (1943) 190.
[56] *O. Kratky* and co-workers, Kolloid-Z., 96, (1941) 301.
[57] *J. Löbering*, Kolloid. Beih., 50, (1939) 235.
[58] Also see *S. A. Glückmann*, Acta physicochim. U.R.S.S., 13, (1940) 379.

present time in favour of the monomolecular character of the dispersion of the majority of dilute cellulose solutions.

1°. The osmotically determined molecular weights [59] and the specific viscosity of the very dilute solutions are dependent only in a very slight degree upon the temperature and the solvent. If there were associative agglomerations, this dependence should be more marked, as it actually is in other typical cases of association [60].

2°. The molecular weight determined osmotically and viscosimetrically (see Chapter III) usually remains unchanged despite the introduction of foreign groups into the molecule (e.g., by acetylation, methylation, etc.), despite, that is, what *H. Staudinger* calls "polymer-analogous conversions" [61]. This was confirmed by *E. O. Kraemer* [62] even with the use of an ultra-centrifuge.

3°. Many cellulose derivatives in solution can be spread to monomolecular films on a surface [63].

Summary

Extremely dilute solutions of cellulose and its derivatives consist of molecular dispersions. The exceptions to this rule are incompletely substituted cellulose derivatives with residual free hydroxyl groups in certain solvents.

In concentrated solutions, however, it has to be assumed that interaction and interlinking takes place between the molecules, on the effect and character of which there is as yet no unanimity of opinion. The interlinking between the molecules may be compared to the association which takes place in low-molecular substances, with this difference that the "cohesion" between the molecules will be confined to certain sections of the chains, even in the case of long chains. Every individual molecule will have "free" chain sections in addition to the associated ones and may interlink at various places with several other molecules. Thus we have solutions with a structure. The characteristic feature of associated aggregates is that they are in equilibrium with the non-associated molecules, that is to say that the points of cohesion

[59] *A. Dobry*, Compt. rend. hebd., 199, (1934) 289.
H. Staudinger and *E. Husemann*, Ann., 527 (1937) 195; 530 (1937) 1.
H. Staudinger and *G. V. Schulz*, Ber., 70, (1937) 1577.
For 1—3 % solutions of nitrocellulose in acetone *G. V. Schulz*, Z. physik. Chem., A. 180 (1937) 1, has moreover pointed out that the absence of any real association may be inferred from the dependence of the osmotic pressure upon the temperature. Also compare *E. Steurer*, Kolloid-Z., 96, (1941) 333; Z. physik. Chem., A. 190, (1941) 1, 16.

[60] *H. Staudinger*, "Die hochmolekularen organischen Verbindungen, Kautschuk und Cellulose", Berlin 1932. *H. Staudinger* and *W. Heuer*, Z. physik. Chem., A. 171, (1934) 139
For dependence of association upon temperature see:
K. L. Wolf and *W. Herold*, Z. physik. Chem., B. 27, (1935) 58.
G. Berger, Z. physik. Chem., B. 28, (1935) 102.
E. Steurer, Kolloid-Z., 96, (1941) 333; Z. physik. Chem., A. 190, (1941) 1, 16.

[61] *H. Staudinger* and *W. Scholz*, Ber., 67, (1934) 84.
H. Staudinger and *E. Husemann*, Ann., 527, (1937) 195.
H. Staudinger and *G. Daumiller*, Ann., 529 (1937) 223; 530, (1937) 1.

[62] *E. O. Kraemer*, Essay in book by *The. Svedberg* and *K. O. Pedersen*, "Die Ultrazentrifuge", Dresden and Leipzig 1940, p. 385.

[63] *J. E. Katz* and *P. J. P. Samwel*, Ann., 472, (1929) 241; and particulary *N. K. Adam*, Trans. Faraday Soc., 29, (1933) 90.
For a critical and comprehensive discussion of spreading experiments see: *H. Mark*, Physik und Chemie der Cellulose, Berlin 1932, p. 102.

are permanently changeable, forming and separating, re-forming and separating again continuously. This is how the liquid character is maintained and why there is no permanent cohesion between all the molecules in the fluid. (The relaxation time of the bonds is small). The total number of association bonds becomes for the time being a function of the concentration, the temperature and the composition of the solvent. Similar views have recently been propounded by *S. A. Glückmann* [64] and *K. H. Meyer* and *A. J. A. van der Wijk* [65].

The specific structure of solutions deserves special attention from the point of view of the technique of film and filament production. (Hitherto this subject has been neglected.)

§ 5. CHEMICAL ASPECTS OF THE PROCESS OF SOLUTION

As stated in § 3, chemical reaction plays a part in all known processes for the solution of cellulose. This is quite evident in the indirect processes, but in the direct ones as well a compound is always formed, primarily with the "solvent"; either there is likewise substitution of hydroxyl groups, or else a molecular (addition) compound is formed, which afterwards dissolves. This was proved in an impressive manner by *Alf af Ekenstamm* [66], for instance for solutions of cellulose in concentrated mineral acids [67]. The primary formation of compounds when dissolving in concentrated salt solutions [68] and in tetra-alkyl ammonium bases [69] was proved by X-ray diagrams.

We may therefore conclude that an *intramicellar* reaction always precedes the process of dissolution. The reagent penetrates between the individual chain molecules while their lateral distances are widened. The commencement of this process is quite clear, of course, if the cellulose can be shown to have gone through complete stoichiometrical reaction (as, for instance, with trisubstitution products), but also if the X-ray diagram of the crystalline portion shows more or less clear "crystalline" interferences (the diagram of the new compound), as often is observed. Nor can there be any doubt about an intramicellar reaction when the original cellulose interferences give place to a faded diagram, which points to lack of lattice order owing to intramicellar penetration of the reaction.

There have been a few cases in which no outward proof was forthcoming of complete stoichiometrical reaction and when the X-ray pattern showed no clear change, though solution may nevertheless have taken place, when, although intramicellar reaction was not conclusively proved, neither was its

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[64] *S. A. Glückmann*, Acta physicochim. U.R.S.S. 13, (1940) 379.
[65] *K. H. Meyer* and *A. J. A. v. d. Wijk*, Kolloid-Z., 101, (1942) 52.
[66] *Alf af Ekenstamm*, Ber., 69, (1936) 549, 553; "Ueber die Cellulose-Lösungen in Mineralsäuren", Lund 1936.
[67] *K. Hess* and *M. Ulmann*, Ber., 74, (1941) 119, 136, recently identified compounds between cellulose and conc. hydrochloric acid.
[68] E.g. Lithium rhodanide, *J. R. Katz* and *C. Derksen*, Rec. trav. chim., 50, (1931) 149.
[69] *W. A. Sisson* and *W. R. Saner*, J. Phys. Chem., 43, (1939) 687.

failure to materialize. In such cases doubt exists as to whether the core of the crystalline regions has really remained unaffected, or whether the quantity of the new compound formed is still too small to be manifested in the diagram, for numerous observations have shown that a new diagram does not become perceptible until extensive conversion of the original compound into the new one has taken place [70]. It is cases such as these which in the long run gave rise to the assumption of polymolecular dispersion (cf. § 4). As an example we may mention the viscose reaction, in which sodium cellulose I becomes soluble after a relatively small quantity of carbon disulphide has acted upon it, when the X-ray pattern of the sodium cellulose does not change [71].

Schramek and *Lieser* assume that a micellar surface reaction takes place. Such views have undoubtedly been encouraged by the fact that *K. Hess* and *C. Trogus* [72] have widely circulated the opinion that nearly all reactions of cellulose in the solid state take place in this way, that is to say, in respect of the micellar frame, proceeding gradually inwards ("micellar-heterogeneous" reaction). Accordingly, preparations in which the reaction has not been exhaustive invariably contain a micellar system only superficially converted. Latterly, however, it has been becoming increasingly apparent that there is another, more probable explanation of the facts. *F. D. Miles* [73] and *M. Mathieu* [74], for instance, were able to prove that intramicellar reaction takes place despite incomplete nitration of the cellulose (with as yet no perceptible "nitrate diagram"). J. *Sakurada* and *T. Morita* [75] have shown that, with acetylation in the fibrous form, although conversion in the "amorphous fringes" of the fibre may take place sooner, because this is where the reagent first penetrates, solution does not take place until the intramicellar conversion has also been completed. *G. Centola* [76] has similar evidence for acetyl cellulose. Other experimental data recorded by *G. Centola* [77] likewise support the probability of exhaustive intramicellar reaction in the solution of cellulose xanthogenate. It may therefore be assumed that intramicellar reaction is inherent in the preliminaries to dispersion. The reason is plain: The cohesion between the chain molecules in the crystalline regions of the unchanged cellulose is very strong, for it rests, among other things, upon "hydrogen bonds", the valency of which is of the order of chemical bonds (see Chapter I, § 2 and § 3). No "ordinary" solvents exist capable of overcoming these combinations. Dispersion cannot take place without the contributive energy of a chemical reaction.

Although every intramicellar exhaustive reaction does not entail dispersion,

[70] *K. Hess*, Z. angew. Chem., 47 (1934) 30.
[71] *W. Schramek* and *F. Kütner*, Kolloidchem. Beih., 42, (1935) 331.
[72] *K. Hess* and *C. Trogus*, Z. physik. Chem., B. 15, (1931) 1208; Z. angew. Chem., 47, (1934) 30.
[73] *F. D. Miles*, Trans. Faraday Soc., 29, (1933) 110.
[74] *M. Mathieu*, Trans. Faraday Soc., 29, (1933) 122. Compt. rend. hebd., 200, (1935) 143.
[75] *J. Sakurada* and *T. Morita*, J. Soc. Chem. Ind. Japan, 41, (1938) 381 B.
[76] *G. Centola*, Ann. Chim. Applicata, 26, (1936) 788; Atti der X Congr. Intern di Chimica, Roma, IV, (1939) 129.
[77] *G. Centola*, Atti der X Congr. Intren di Chimica, Roma IV, (1939) 129.

the converse is true. Primary intramicellar reaction and the process of solution are strictly distinct processes which do not always take place under the same conditions, even in the so-called direct dispersion method. This was verified very elegantly by *Alf af Ekenstamm* [78] with reference to the solution of cellulose in mineral acids.

Solution depends upon whether intramicellar swelling also sets in. To this end the composition of the surrounding solution must more often than not be different from the optimum composition for the formation of the compound. Thus, according to *Alf af Ekenstamm,* to dissolve hydrate cellulose in phosphoric acid, it must first be saturated with 11.6 n. acid (formation of the compound) and then dissolved in a 14 n. acid (swelling). It is not possible to dissolve direct in the latter acid.

A necessary condition to intramicellar swelling is that it can take place with positive heat effect (see also § 6). When cellulose esters and ethers are dissolved in organic liquids — say, cellulose nitrate in acetone — a compound is often first formed with the solvent (verifiable by X-ray spectrography) before swelling and solution take place.

Obviously, all these facts point clearly to a primary separation of all the chain molecules.

Contrary to intermicellar swelling (e.g., cellulose in water, see § 2), which is always limited, that which precedes the process of solution is an *unlimited swelling;* it passes steadily over into the dissolved state. It is the characteristic first step in the process of solution of all high-molecular substances with chain molecules and dwindles as the chains shorten in length, until it vanishes. *Staudinger* [78a] has more to say on the subject.

An excellent summary of X-ray behaviour during the formation and solution of cellulose derivatives and of the theories relating to the subject was published by *W. A. Sisson* including a comprehensive bibliography [78b].

§ 6. THE NATURE OF DISSOLVING AND SWELLING

In the previous section we have seen that, after the necessary intramicellar reaction preparatory to solution, cellulose preparations can be dispersed in a suitable solvent by a process of swelling which gradually merges into that of dissolving. We shall now examine the nature of these processes of dispersion and swelling.

§ 6.1. *Comparison between the Process of Solution in Low-Molecular and High-Molecular Substances*

According to thermodynamics, the free energy decrease, ΔF, of the system in any isothermic process occurring spontaneously and at constant

[78] *Alf af Ekenstamm,* Ber., 69, (1936) 549, 553.
"Ueber die Cellulose-Lösungen in Mineralsäuren", Lund 1936.
[78a] *H. Staudinger,* "Organische Kolloidchemie", Braunschweig 1940; p. 70.
[78b] *W. A. Sisson,* Ind. Eng. Chem., 30, (1938) 530.

pressure is a measure of the activity or the "driving force" of the process:

$$\Delta F = \Delta U - T \Delta S \qquad (2.1)$$

The (negative) quantity ΔF = the free energy decrease; ΔU = the change in heat content of the system, being negative if the process is exothermic and positive if it is endothermic. T is the absolute temperature and ΔS the entropy change of the system. The latter is positive if the entropy increases. The meaning of the entropy term in a process of mixing can be made clear by reference to the mixing of two ideal gases, which is known to take place without either the absorption or the emission of heat. Thus, ΔU being zero,

$$\Delta F = - T \Delta S \qquad (2.2)$$

The decrease of free energy corresponds to an increase in the entropy = ΔS only, i.e. to an increase in the thermodynamic probability of the system. The course of the process is governed merely by thermal motions or, expressed differently, by the diffusion tendency of the two specimens of molecules. Homogeneous mixture of the two gases is more probable than the coexistence of the two disparate components.

If two miscible fluids A and B are brought together in one vessel, they mix spontaneously by diffusion. Formula (2.2) will apply if mixing takes place without heat effect ($\Delta U = O$), when it is called an *athermal mixture*. The aim in this case, too, is a state of maximum statistic disorder. The thermodynamic probability and, with it, the entropy of the system tend to reach a maximum value. Examples of these athermal mixtures are rare (e.g., benzene-toluene).

The heat effect ΔU of ideal gases, when mixed, is exactly zero, because their molecules, true to definition, exercise no cohesive power upon each other at all. $\Delta U = O$ in a system such as benzene-toluene because the mutual attraction between the molecules in benzene, in toluene and in the mixture of the two is evidently the same.

In the majority of cases, however, mixing proceeds either exothermically or endothermically. The energy effect can then be represented as the algebraic sum of the expenditure of energy required to remove a molecule of component A from the neighbourhood of its kind, of the expenditure of energy needed to produce a "void" in component B large enough to receive a molecule A, and the increase in energy when molecule A enters that void.

A positive heat effect ($\Delta U < O$) signifies that the molecules in the mixture exert greater mutual attraction than those in the separate components. The energy effect therefore furthers the blending process; the thermal diffusion tendency is strengthened by the neutralization of attractive forces. A negative heat effect ($\Delta U > O$) is a sign that attractive forces have to be overcome in the mixture; that is to say that the cohesion in the unmixed components is greater than the attractive forces between the molecules of different kinds in the mixture. If, despite this, mixing takes place, i.e., if

nevertheless $\Delta F < O$, the pure thermal diffusion tendency is said to be great enough to raise the molecules to the required degree of higher potential energy ($T \Delta S - \Delta U > 0$).

Let us now apply these theories to the solution of a solid substance in a very large amount of solvent. In this case the cohesive forces holding together the molecules of the solid substance have first to be overcome, and this requires some supply of energy. Then we have the energy effect on mixing and the diffusion tendency.

The condition of a low-molecular and of a macromolecular substance with chain molecules before and after solution is represented in Fig. 26 and 28.

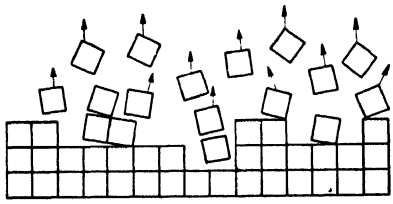


Fig. 26. Diagram showing process of solution of a low-molecular substance.

The energy effect resulting from the interplay between the cohesion forces and the solvation energy will be of the same order of magnitude per unit of weight in the case of the large molecules, but, reckoned per mole, will be far greater than in the case of the small molecules. In both cases solution leads to a state of greater statistical disorder and there is consequently a gain in entropy. It is not clear, however, whether there is any real difference between the ultimate gain in entropy calculated per mol or per unit of weight. There is, however, another, very real difference, which may be perceived at once. The diffusion tendency — i.e., the velocity with which mixing may take place — calculated per mole is of the same order of magnitude (kT) in both cases but, calculated per unit of weight, is much smaller in the case of the macromolecular substance. The large molecules have very little mobility (cf. page 43). Now if the macromolecular substance dissolves exothermically, there will be nothing to prevent the energe reaction from proceeding with relative rapidity, but access of entropy (the cleaving apart of the molecules, i.e., their dispersion) is always a slow process. This is how swelling comes into existence.

As soon as the cohesive forces have been overcome, the small molecules of the low-molecular substance quickly distribute themselves in the solution. With the macromolecular substance, however, the process takes a different course, in that first the molecules of the solvent penetrate into the macromolecular substance, as a result of which the heat of solution is already largely liberated, the forces of attraction between the two kinds of molecules being in the main neutralized. A better way of putting it might be to say that the molecules of the solvent are drawn in by energy. The second phase in the process of solution (dispersion) takes place gradually at first and very slowly (see next section).

Dealing with cellulose and its derivatives, solution is actually connected with

a positive heat effect; in other macromolecular systems the latter may be zero, or even negative. The process then depends entirely upon the entropy gain. Recent investigations have shown that the molecular entropy of mixing of linear macromolecules is very much greater than that of mixing small molecules, owing to the larger number of different configurations which the former may assume in the solution as a result of the flexibility of the chains [79]. Though this greater entropy gain undoubtedly favours solution, it works out very slowly, as already stated. In cellulose it is never great enough to promote solution alone and dissolving only occurs if assisted by a positive heat effect of sufficient magnitude.

This somewhat bare outline may help to explain why macromolecular substances never dissolve at once and why solution is always preceded by a relatively slow process of swelling [80]. In this case swelling is a partial process inherent in the process of solution and, therefore, is in no way mysterious (cf. remarks on time-lag on p. 55).[81]

§ 6.2 *Further Consideration of Swelling, or the Dissolution of a Micellar System*

The local inequality of the cohesive forces between the chain molecules is essentially characteristic of a micellar system such as that described for cellulose. They are at their most powerful in the crystalline regions, there representing the lattice energy of the cellulose crystal. They are less potent in the amorphous regions. Here we shall come upon a complete spectrum of cohesive forces according to the local reciprocal position and arrangement of the chains.

It will be evident from what has been said that there will be swelling agents as well as dissolving agents. At times a liquid will penetrate as far into the system as its ascendency over the forces of cohesion permits, but it will not be a true solvent unless it also completely overcomes the cohesion of the lattice.

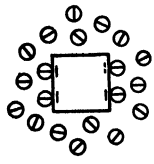


Fig. 27. Orientation of the solvent molecules in relation to the molecules of the dissolved substance as the result of polar forces.

Figure 28A illustrates the continuous transition from a crystalline region (left) to a fimbriate amorphous region of the micellar frame (right), in the latter of which the chains may possibly no longer be parallel, but slightly divergent. The increasing distance between the chains in the figure is meant to symbolize the diminishing cohesion between them, though in reality there will be junction points of varying degrees of stability in the amorphous regions.

[79] *K. H. Meyer*, Z. physik. Chem., 44B, (1939) 383; *M. L. Huggins*, J. Am. Chem. Soc., 64, (1942) 1712; Ann. New York Acad. Sci., 44, (1943) 431; Ind. Eng. Chem., 35, (1943) 216; *P. J. Flory*, J. Chem. Phys., 10, (1942) 51; *G. Gee* and *L. R. G. Treloar*, Trans. Farad. Soc., 38, (1942) 147, 276, 418.

[80] *J. R. Katz*, Ergebn. d. exakt. Naturw., 3, (1924) 320.

[81] It should be pointed out that macromolecular substances containing spherical molecules, such as glycogen, often dissolve without swelling. Here once again the cohesive forces in the solid substance, calculated per mole, are far smaller, owing to much less surface development of the molecules.

The molecules of a dissolving or swelling agent first press forward along the amorphous regions which occur everywhere in the fibre, forcing the chain molecules apart as they do so. If the predominating conditions of energy are such as not to allow the junction points of maximum cohesive strength to be overcome, the process comes to a standstill at junction points of a certain stability. In this case the liquid is merely a swelling, not a dissolving agent, and this is where we have *limited swelling,* as for example in cellulose and water. Because the crystalline regions do not swell and, therefore, do not change, the X-ray diagram undergoes no modification (intercrystalline, or intermicellar swelling).

The initial phase of swelling is usually governed entirely by factors of energy. It is often even found that the entropy factor has a counteracting effect; this we shall now explain.

In Fig. 28 an orientated adsorption of the first layer of bound solvent molecules on the chains is assumed. This orientated adsorption may be imagined as follows: The members of the chain contain polar groups (as cellulose and its derivatives invariably do) to which the solvent molecules attach themselves, either by induced polarization, or, since they contain dipoles themselves, in an orientated position and with positive heat effect. The orientated adsorption results in diminution of the partial entropy of the solvent, as the thermodynamic probability of the aligned molecules is less than that of their "amorphous" state in the pure liquid. *G. V. Schulz* [82] has demonstrated the actual probability of this decrease in entropy of the solvent in the initial stage of swelling in the nitrocellulose-acetone system (cf. § 7). It also occurs in the cellulose-water system (Part II, Chap. II, § 1).

If the "affinity" of the solvent to the macromolecular components (i.e., the free energy change) is great enough, the process continues and the solvent molecules also penetrate into the crystalline regions, a fact which is, of course, reflected in the X-ray diagram, which changes (intracrystalline, or intramicellar swelling). One of two things may then occur, viz.,

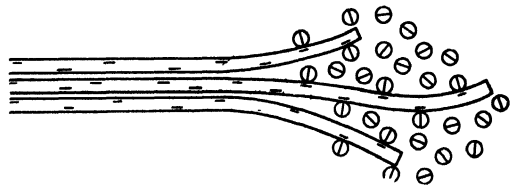


Fig. 28 A. Diagram showing the process of solution of a micellar system. Intermicellar swelling.

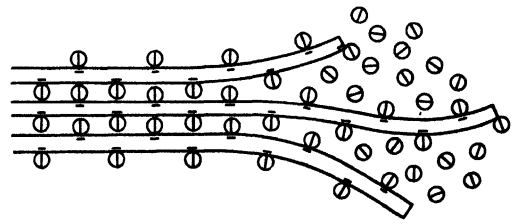


Fig. 28 B. Stage following that shown in Fig. 28 A. Intramicellar swelling.

[82] *G. V. Schulz,* Z. physik. Chem., A. 184, (1939) 1.

a. Only a stoichiometrical number of molecules penetrates into the lattice and swelling proceeds no further (Fig. 28 B).

b. After this first phase, more molecules penetrate and swelling proceeds until the micellar system has dissolved completely *(unlimited swelling)*. It is in this second case only that the liquid is a true solvent.

In case a) a new, fairly sharply defined X-ray diagram is usually produced, being that of the addition compound of the macromolecular substance with the solvent, of which there are many known examples (cellulose in concentrated sodium hydroxide, nitric acid, perchloric acid, hydrazine, lithium thiocyanate, cellulose II in water, nitrocellulose in ketones, etc.). Once these compounds have been formed with heat effect and the cohesive forces in the lattice of the original substance overcome, the cohesion in the new lattice will still be too powerful. The affinity of the "solvent" to the macromolecular substance will have been neutralized to the extent that when more molecules of the former penetrate, they have insufficient energy to overcome the lattice forces. When dealing with solvents consisting of several components, this may, however, sometimes be rectified by a subsequent change in the composition of the former, as in the case of the solution of cellulose in mineral acids observed by *A. af Ekenstamm*, quoted in § 5 (also see below).

It was seen in § 5 that the formation of a chemical compound always precedes the solution of cellulose. When it has been formed, it depends once again upon the energy and entropy conditions dealt with in the previous section whether swelling comes to a standstill or proceeds. Nevertheless, in one respect a new situation arises after intramicellar swelling has taken place, for then the energy required to separate the molecular chains in the crystalline regions is considerably diminished. Further swelling then often depends entirely upon entropy. It might be said that a new substance is in process of dissolving, i.e., the addition compound of the cellulose with the solvent which is formed during intramicellar swelling. The heat of solution of this compound is far less than that of the original cellulose crystallites.

In accordance with the foregoing it has been observed in a few well-authenticated cases that, after the strongly exothermic absorption of the first doses of swelling agent by the original substance, all further swelling and solution are endothermic. Whereas the first phase of swelling shows a negative temperature coefficient (that is to say, is furthered by decline in temperature), the continued process of swelling displays a positive coefficient of temperature (is fostered by increase in temperature). These facts have been demonstrated most effectively and instructively by the very exact direct calorimetric determinations carried out by *E. Calvet* and co-workers [83] in

[83] *E. Calvet* and co-workers, Compt. rend. hebd., 212, (1941) 542; 213, (1941) 126; 215, (1942) 138.

the nitrocellulose-acetone system. After approximately 6 moles of acetone per C_6 group have been absorbed with considerable positive heat effect (23 kcal), very appreciable cooling is observed as the absorption of acetone proceeds. 18.5 kcal are re-absorbed by the system up to infinite dilution (and solution). Accordingly, the integral heat of solution of nitrocellulose in acetone amounts only to 4.5 kcal.

M. Mathieu [84] has shown by radiography that with 6 moles of acetone per C_6 the formation of the coordinative additive compound nitrocellulose-acetone is completed. Its composition corresponds to approximately 50% nitrocellulose, the point at which *G. V. Schulz,* in his thermodynamic analysis of the system (see § 7), likewise found some discontinuity in the character of the solvent binding.

The fact that the compound dissolves with negative heat effect goes to show that, according to formula (2.1), the entropy factor is in this case the driving force of the process [85].

When mixed solvents of graded solvent power are used, the transitional stages from slight, limited swelling, at one extreme, through increasing degrees of swelling up to solution, at the other end, are often passed through collectively. It is a fact established empirically, and also predicted by *J. N. Brønsted* [86] on theoretical grounds, that the last step along this path (i.e., the transition from limited to unlimited swelling) will then quite suddenly follow a minute change in the composition of the solvent. As that author demonstrated, the conditions for the transition from limited to unlimited swelling are exceedingly sensitive to the molecular weight of the high-molecular substance, whereas there is nothing to show that the molecular weight affects the first phases of swelling in any way (cf. § 7). E.g., polystyrene of very high molecular weight swells with positive heat effect in acetone, but does not dissolve in it. Polystyrenes of low molecular weight likewise swell with positive heat effect in acetone; afterwards, however, they dissolve in it and the second process is demonstrably connected with negative heat effect.

Brønsted also gives us to understand that a macromolecular substance is either completely soluble or insoluble in a given solvent; in other words, can only swell to a limited extent. There is no such thing as "saturated solutions" such as low-molecular substances give us; instead, we have the state of

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[84] *M. Mathieu*, La Gélatination de la nitrocellulose, Paris 1936.

[85] It should be pointed out that the effects described here are by no means specific to macromolecular systems; they occur equally with ordinary substances. Thus the hydration of anhydrous calcium chloride takes place with positive heat effect, while the subsequent solution of the hydrate in water proceeds with negative heat effect. The only distinctive difference which marks analogous processes in macromolecular substances is the far slower rate at which they take place, which is due to the slow diffusion of the large molecules. Although the thermal impulses act continually upon all members of the chain, yet they do so very irregularly and therefore seldom in the same direction. This alone would easily account for the fact that it takes some considerable time for this partial process, governed as it is by entropy, to run its full course.

[86] *J. N. Brønsted*, C.r. Laboratoire Carlsberg (Sect. chim.) 22, (1938) 99.

limited swelling which, in a certain sense, is conversely a saturated solution of the solvent in the macromolecular substance [87].

It will now be clear that swelling and solution are very kindred processes, comprehensible both from the thermodynamic and the molecular-kinetic points of view, the macromolecular substances requiring no specious "colloid-chemical" interpretations or special laws other than those evoked for the low-molecular substances.

In cases of limited swelling it might be said that just those sections of the chain molecules are dissolved which, owing to their particular position in less well ordered regions, have more free energy. They have not yet dissolved in other regions of better lattice order. These places represent the "junction points" (cf. p. 36) which are responsible for the mechanical cohesion in the swollen gel. The "dissolved" chain sections in the gel acquire increased mobility. They are subject in an intensified degree to the thermal movement (micro-Brownian movement of individual chain sections) and the chains may here accordingly be more or less kinked. This representation may serve to explain certain elastic phenomena in gels. It will also be clear that the degree of limited swelling which a given micellar system attains in a liquid depends upon its structure and, in particular, upon the spatial arrangement into which its component molecules fall. In this sense, too, the peculiarities of swelling may provide important clues to the structure of such systems and we shall have more to say about this later on.

In the foregoing we have seen that the entropy of mixing in solutions of linear macromolecules is considerably greater than that calculated for the "ideal" case of a mixture of two species of molecules, which goes to show that the macromolecules undergo appreciable configurational changes upon dissolution. The chain elements being able to rotate fairly "freely" around the primary valence bonds, individual chains, more or less at random, are apt to become convoluted. *E. Hückel* [88], who early held the view that abnormal values of the entropy of mixing might occur and might be explained in this way, has pointed out that the inner mobility of the molecules may depend upon the concentration of the solution. The questions involved have yet to be settled, but they are of paramount importance to the elucidation of the "structure" of the solutions, which item, in turn, has considerable bearing upon the problems of gel structure. They are implicated in the subject of this book.

It is necessary to point out again that the dispersed chain molecules in concentrated solutions will exert directing forces upon each other, which will tend to bring about a mutual orientation and parallelization of neighbouring chains ("Ordnung in kleinsten Bereichen" = order in smallest regions). This is inferred not only from geometrical considerations, but also from the model

[87] Also compare recent investigations by *M. L. Huggins* and *P. J. Flory*, (loc. cit. footnote 79), who give an even more exact interpretation of this behaviour.

[88] *E. Hückel*, Z. Elektrochem., 42, (1936) 657.

experiments carried out by *H. A. Stuart*. According to *R. Rehaag* and *H. A. Stuart* [89], a tendency to assume "close" order is always present in low-molecular liquids and is appreciably enhanced in the case of anisodiametric molecules [90]. *J. J. Stöckly* [91], considering cellulose xanthate in the process of dissolving, makes a similar assumption. He gave the name "mesophases" to the persistent regions consisting of still roughly parallelized molecules, though devoid of three-dimensional lattice order.

With chain molecules in concentrated solutions, therefore, it will be necessary to reckon with a tendency of all chains to straighten and for neighbouring molecules to take up a more or less parallel position (also see p. 127). With increasing dilution the factors responsible for this tendency will gradually disappear and the chains, falling into a less orderly arrangement, will be more apt to kink. We shall revert to this hypothesis in Part III (p. 436) in connection with certain properties of gels produced from solutions of varying concentration.

§ 7. OSMOTIC PRESSURE. DEPARTURE FROM THE VAN 'T HOFF LAW. SOLVATION

Let us return to the thermodynamics of solutions and see whether we can arrive at a better understanding of their behaviour.

The change in free energy ΔF_1 of the solvent [92] when one mole is added to a very large quantity of the solution, is equal to the (negative) maximum work done upon dilution.

$$\Delta F_1 = - PV_1 \qquad (2.3a)$$

V_1 = partial molecular volume of the solvent in the solution, P = osmotic pressure. It can be measured osmotically. In concentrated solutions the swelling pressure P_S takes the place of the osmotic pressure, with which, thermodynamically, it is identical:

$$\Delta F_1 = -P_S V_1 \qquad (2.3b)$$

To determine ΔF_1 one can measure the vapour tension depression of the solvent in the solution [93].

$$\Delta F_1 = RT\ln (P/P_0) \qquad (2.4)$$

(P = vapour tension of the solution; P_0 = saturation pressure of the pure solvent). The thermodynamic behaviour of the systems can be studied by measuring the osmotic pressure of the very dilute solutions, the vapour tension depression in the realm of higher concentrations and gels, and the dependence of these quantities on temperature. The change in heat content and the entropy change may be derived from this dependence on temperature

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[89] *R. Rehaag* and *H. A. Stuart*, Physik Z., 38, (1938) 1027.
[90] Also see *H. A. Stuart*, Kolloid.Z., 96, (1941) 149.
[91] *J. J. Stöckly*, Kolloid-Z., 105, (1943) 190.
[92] The subscript 1 denotes solvent; 2 the solute.
[93] For the basis of this formula see, e.g., *J. R. Katz*, Nernst Festschrift, Halle 1912 p. 201; Cellulosechemie, 11 (1930) No. 2.

with reference to the following two thermodynamic equations, given without comment:

$$\Delta U_1 = -\frac{d(\Delta F_1/T)}{d(1/T)} \qquad (2.5)$$

$$\text{and } \Delta S_1 = -\frac{d(\Delta F_1)}{dT} \qquad (2.6)$$

G. V. Schulz[94] has in this way recently carried out a comprehensive examination of the nitrocellulose-acetone system in concentrations ranging from 0.1 to 75% of acetone. We shall be reverting to these investigations in a few moments.

If we know the thermodynamic quantities expressed in (2.5) and (2.6), we are in a position to decide which is the dominating factor when the solvent is absorbed, i.e., the action of molecular forces, or the tendency to reach a state of greater thermodynamic probability.

ΔU_1, viz. the action of molecular forces of attraction, is always a marked characteristic of solutions — even very dilute ones — of high-molecular substances with chain molecules and it is the main reason for their not behaving like "ideal dilute solutions"; indeed, they usually fail in many respects to conform to the *Van 't Hoff* laws for dilute solutions. For the latter apply only on the assumption that

$$\Delta U_1 = O \qquad (2.7)$$

(hence that no further heat effect takes place when a dilute solution is further diluted) and also on the supposition that ΔS_1 is equal to the "ideal mixing entropy" ΔS_1^*, both of which are true for athermal mixtures of low-molecular liquids, the mixing of ideal gases and also for the dilute solutions of many low-molecular substances. A second reason for the departure from the *Van 't Hoff* laws may therefore reside in the fact that

$$\Delta S_1 \neq \Delta S_1^*$$

For small concentrations of the second component and ideal dilute solutions thermodynamics states that

$$\Delta S_1^* = RN_2 \qquad (2.8)$$

(N_2 representing molecular fraction of the dissolved substance). By inserting equations (2.3a), (2.7) and (2.8) in the thermodynamic fundamental equation

$$\Delta F_1 = \Delta U_1 - T \Delta S_1 \qquad (2.9)$$

we get the expression

$$PV_1 = RTN_2 \qquad (2.10)$$

which, if N_2 is small, is identical with *Van 't Hoff's* law, when V_1 = the volume of the solution:

$$P = RTN_2/V_1 = RTc/M \qquad (2.11)$$

(c = concentration of the dissolved substance; M = its molecular weight). Therefore, if we substitute a constant k for RT/M,

$$P = kc \text{ and } P/c = k \qquad (2.12)$$

[94] *G. V. Schulz*, Z. physik. Chem., A. 184. (1939) 1.

holds for a given substance. Thus, if P/c, the "reduced osmotic pressure", is plotted against the concentration, the result is a horizontal straight line. Up to the highest dilutions at which osmotic pressure can be measured, solutions of high-molecular substances with chain molecules produce, not a straight line, but a curve that ascends with the concentration. Therefore, with reference to *Van 't Hoff's* equation, their osmotic pressure is too high (as also, consequently, their vapour tension depression, rise in boiling point, etc.). As Wo. *Ostwald*[95] has explained, in this case the empirical equation:

$$P = ac + bc^n \qquad (2.13)$$

takes the place of (2.12). We shall revert to this in Chapter III when we discuss the estimation of the molecular weight from the osmotic pressure.

It has been emphasized that, in themselves, the departures from *Van 't Hoff's* laws are not surprising and are merely due to either of the two conditions: $\triangle U \neq 0$ *or* $\triangle S \neq \triangle S^*$, without entailing the assumption of any special state of solution[96]. For example, if, instead of (2.7), $\triangle U_1 < O$ (and on further dilution, therefore, there is still some noticeable positive heat of dilution), then, according to equations (2.9) and (2.3a), higher osmotic pressure should be noted than is to be expected on the basis of the *Van 't Hoff* law. The same applies when $\triangle S_1 > \triangle S_1^*$. The deviations certainly cannot be explained by association or aggregation of thread molecules in the colloid-chemical sense, as in that case they would be the very opposite (i.e., osmotic pressure too low instead of too high).

The departures from *Van 't Hoff's* laws are often very considerable and are greater in proportion as the chains are longer. Thus the reduced osmotic pressure of a nitrocellulose of 450000 mol. weight dissolved in acetone in a concentration of only 5 grams per litre is already more than two and a half times that presupposed by formula (2.11): Thanks to the work done by *E. Calvet*, to which we referred in § 6, we can enter more fully into this well-authenticated case; for, from those investigations we know that $\triangle U_1 > O$. If only for this reason, therefore, the osmotic pressure must be less than that of the *Van 't Hoff* law, which means to say that $\triangle S_1 >> \triangle S_1^*$. Consequently the increase in entropy upon dilution must certainly be much greater than the ideal mixing entropy. This accords with the hypothesis that the solvent molecules have less freedom of movement as the concentration increases and that their position is affected by the dissolved chain molecules. (Directed adsorption; see below.)

As will be shown in Chapter III, the molecular weight can always be derived from the osmotic pressure by extrapolation, that is, so long as the mixing entropy is still contributing noticeably to the free energy of the solvent; for, according to (2.8) and (2.10), the dependence of this free energy upon the

[95] *Wo. Ostwald*, Kolloid-Z., 49, (1929) 60; Z. physik. Chem., A. 159 (1932) 375.
[96] *G. V. Schulz*, Z. physik. Chem., A. 158 (1932) 237; A. 160, (1932) 407; A. 177 (1936) 453; A. 180, (1937) 1.
O. Kratky and *A. Musil*, Z. Elektrochem., 43, (1927) 326.

molecular weight of the dissolved substance rests entirely upon the mixing entropy. It is evident on the other hand that the energy contributed is governed primarily by the weight ratio of the components and not by the molecular weight

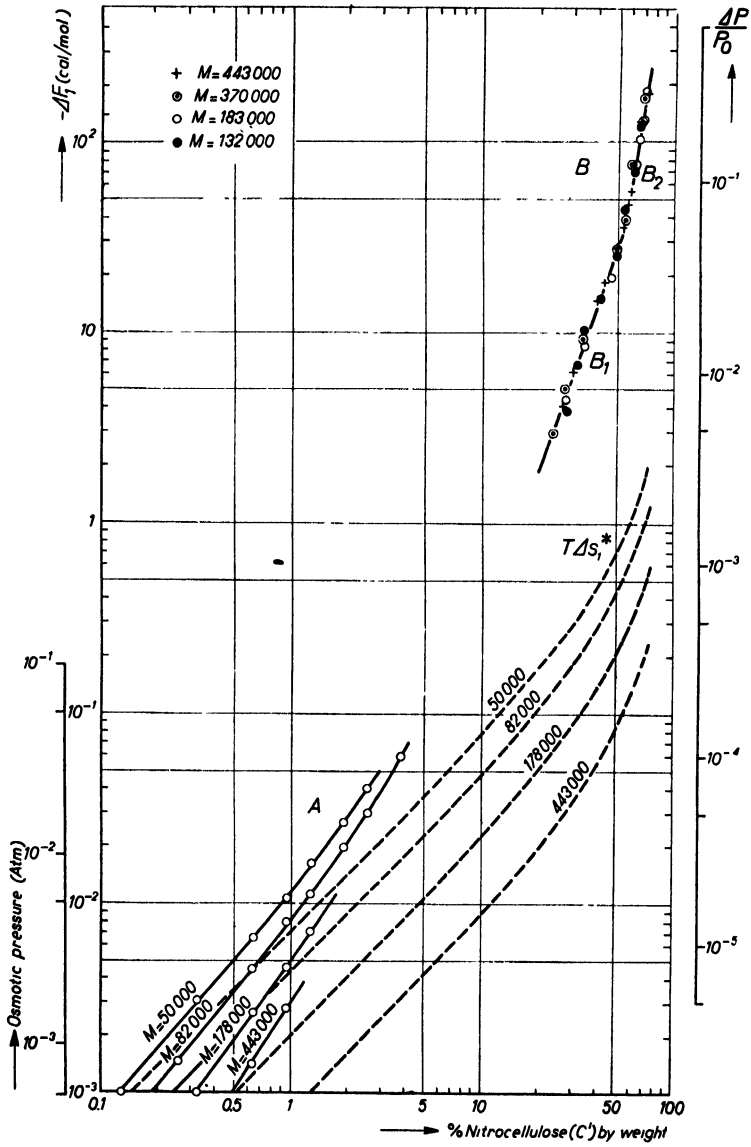


Fig. 29. Free energy decrease (ΔF_1) of the solvent in solutions of nitrocellulose-acetone of varying concentrations. A. Osmotic measurements. B. Vapour pressure measurements. Broken lines: Calculated values of the mixing entropy $T\,\Delta S$. ΔF_1 is dependent upon the molecular weight of the nitrocellulose in the A region only. In the B region the curves converge. After *G. V. Schulz* (1939)

(for it depends upon the action of forces between all the members of the chain and the solvent). If $T\ \Delta\ S_1^*$ becomes small against $\Delta\ U_1$ the osmotic pressure, or the swelling pressure, will depend upon the length of the chains.

Fig. 29 represents the relevant conditions in the nitrocellulose-acetone system according to estimations by *G. V. Schulz* [97] for four nitrocellulose preparations of increasing molecular weight. The change in the free energy $-\Delta F_1$ of the acetone is plotted against the concentration (continuous lines). (Both coordinates were chosen logarithmically, because they cover several orders of magnitude). The corresponding osmotic pressure and the relative vapour tension depression are also recorded. The broken lines indicate the (calculated) amount of mixing entropy $T \Delta S_1^*$.

G. V. Schulz first distinguishes the area marked A, covering from 0.1 to 5% of nitrocellulose, where it was still easy to measure the osmotic pressure (between 10^{-3} and 10^{-1} at.). In this range ΔF_1 is still very dependent upon the mixing entropy and, therefore, upon the molecular weight. As the concentration increases, however, the curves of the four preparations gradually converge, because the energy member is gaining the upper hand over $T \Delta S_1^*$. There is a hiatus between 5 and 20% of nitrocellulose, due to experimental difficulties.

In the B area of 20 to 75% of nitrocellulose the dependence upon the molecular weight has vanished within the margin of error ($T \Delta S_1^*$ becomes smaller than 1% of ΔF_1), with the result that there is but a single curve left, which was obtained by determinations of the dependence of the vapour tension depression upon temperature. In agreement with results formerly obtained by *J. R. Katz* [98], the active forces operating between the molecules of the two components are alone responsible in the B area for the absorption of the solvent by the swelling nitrocellulose gel. In the region of 55% nitrocellulose there is a break in the curve, which points to the fact that above this the solvent is bound differently from below it. It may be that above 55% ΔF_1 becomes $> \Delta U_1$ and so the entropy of the solvent diminishes upon absorption in the gel (cf. p. 63). *J. R. Katz* [99], *R. Fricke* and *J. Lüke* [100] came across similar phenomena with other substances, such as casein, cellulose and agar-agar.

G. V. Schulz [101] maintains that the difference between the B_1 and B_2 areas is that the solvent molecules in the latter are fixed to certain places, just as they are in a crystal lattice. The system cannot here be regarded as a solution without qualification; rather is it in the nature of a molecular addition compound between the components.

In the same publication *G. V. Schulz* [101] arrives at interesting and important conclusions as to the range of the forces operative in the B area between the molecules of the two components. While referring to the original investigations, we shall only briefly touch on some of the results. On the

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[97] *G. V. Schulz*, Z. physik. Chem., A. 180, (1937) 1; B. 40, (1938) 319; A. 184, (1939) 1.
[98] *J. R. Katz*, Ergeb. d. exakt. Naturw., 3, (1924) 320; 4, (1924) 363. Physik. Z. 251, (1924) 321.
[99] *J. R. Katz*, Kolloid-Beih., 1, (1917) 116.
[100] *R. Fricke* and *J. Lüke*, Z. Elektrochem., 36, (1930) 309.
[101] *G. V. Schulz*, Z. physik. Chem., A. 184 (1939) 1.

assumption — certainly correct at a first approximation — that the active forces between the molecules are alone responsible for the work performed in the absorption of the solvent, *G. V. Schulz* was able to show that the forces of attraction nearest to the chains are of approximately the same order of magnitude as the well-known forces of *Van der Waals—London*, but that with distance they diminish in strength more slowly than the latter. The *London* potential which, for small molecules, decreases in inverse ratio to the 6th power of the distance, should decrease with the 5th power for chain molecules, whereas *Schulz* finds an exponent in between 3 and 4. This relatively marked energy of interaction at long distances is readily understood when we are concerned with a potential of dipolar forces and when there are orientated molecular layers, through polarisation, between the active molecules which propagate the attraction to a certain extent [102]. It has been stressed frequently [103] that there is often extensive orientation of the solvent molecules in lyophilic gels and it has been pointed out at various times that it even becomes visible in X-ray diagrams. *J. R. Katz* and *J. C. Derksen* [104], for instance, noticed it in the case of gelatin and agar-agar, while *N. H. Kolkmeyer* and *J. C. L. Favejee* [105] believe they have established the same for starch and cellulose [106].

Table II shows how great is the difference between the decline of the forces of attraction after the 6th and that after the 3rd to 4th power. It provides numerical information on the decline in differential potential in calories per grammolecule of monomeric residue of swollen substance as a function of the distance in å, notably for highly polar nitrocellulose in acetone and rubber (non-polar) in benzene. For comparison, the corresponding values for carbon dioxide are given in the last colum. Whereas the potential of attraction in the last-named case almost vanishes at a distance of between 10 and 15 å, it still has, to the nearest approximation, 2½% of its value at a distance of 50 å in the case of nitrocellulose. (The distance 50 å corresponds to a solution of roughly 4% of nitrocellulose in acetone.)

TABLE II

Differential Potential in Cal per Grammolecule of Monomeric Residue of Swollen Substance Dependent upon Distance (according to G. V. Schulz).

Distance (å)	Nitrocellulose-acetone	Rubber-Benzene	CO_2
5	—	71.3	64.7
10	—	5.9	2.3
12.5	70	—	—
15	45	1.3	9×10^{-2}
20	20.6	0.53	1.6×10^{-2}
30	7.0	0.12	1.2×10^{-2}
50	1.7	0.02	6.5×10^{-3}

[102] *G. Briegleb*, "Zwischenmolekulare Kräfte und Molekülstruktur", Stuttgart 1937.
[103] *P. Koets* and *H. R. Kruyt*, Kolloid-Z., 82, (1938) 315.
[104] *J. R. Katz* and *J. C. Derksen*, Collegium (1932) 931.
[105] *N. H. Kolkmeyer* and *J. C. L. Favejee*, Nature, 132, (1933) 602; Z. Kristallogr. A 88, (1934) 226.
[106] Also see *K. Hess*, Ber., 69, (1937) 1800.

As a result of the extensive potential of attraction, the chain molecules envelop themselves in a layer — as a rule roughly monomolecular — of solvent molecules very firmly attached to certain places, which is already present in the B_2 area and, moreover, in another, though far less firmly bound shell of the same (solvation). The solvent envelope prevents the close approach of neighbouring chain molecules, their average kinetic energy being insufficient to enable them to break through. The "effective volume" of the molecules thus enhanced may also affect viscosity.

The rôle of solvation and the extension of the solvent shells have nevertheless often been overestimated in colloid chemistry and they certainly cannot be alone responsible for, say, the very high viscosity of cellulose solutions. *A. Dobry* [107] has demonstrated experimentally that only the first (probably monomolecular) layer of solvent shells is bound tightly enough to contribute to the hydrodynamic effective volume of the molecules.

In conclusion we must direct attention to an observation made by *G. V. Schulz* [108], which has an important bearing upon our subject. Artificial cellulose fibres are formed as gels from a solution. It is an established fact that the characteristic "consistency" of the gels and, in particular, those mechanical properties which are of technical interest, undoubtedly depend upon the chain length. Since the interaction of energy between the two components in the B area has proved to be independent of the molecular weight, the forces of attraction between the molecules cannot in themselves be responsible for the dependence of these properties of consistency upon molecular weight. Consequently, these must be due rather to some *factor of the shape of the molecules.* Hence this factor brings us back to the domain of geometrical factors and therefore offers more favourable prospects of a satisfactory solution. We shall revert to this matter in Part III.

As we shall see later, it seems probable that the mechanism of the swelling and de-swelling of regenerated cellulose is intimately connected with the steric configuration of the molecules.

The swelling of cellulose and its derivatives in concentrated solutions of strong electrolytes is accompanied by certain special phenomena. For instance, as the concentration of the electrolyte increases a maximum of swelling power is sometimes reached (e.g., cellulose and sodium hydroxide solutions, when the swelling maximum is reached at 10—11% NaOH). For further details and the interpretation of these phenomena we refer to the books of *E. Valkó* [109] and *K. H. Meyer* [110], in which this subject is dealt with.

§ 8. GENERAL REMARKS ON THE STRUCTURE OF CELLULOSE GELS

8.1 Introduction

In the two preceding sections we have recognized the process of swelling

[107] *A. Dobry,* J. chim. phys., 35, (1938) 20.
[108] *G. V. Schulz,* Z. physik. Chem., A. 184, (1939) 1.
[109] *E. Valkó,* Kolloidchemische Grundlagen der Textilveredlung, Berlin 1937, p. 183.
[110] *K. H. Meyer,* Die hochpolymeren Verbindungen, Leipzig 1940.

as a necessary transitional stage in the dissolving process of macromolecular substances with chain molecules. We have to some extent brought into line thermodynamic views of energy distribution with kinetic and geometric representations in terms of a model. So far, however, we have only considered the case of ordered and approximately parallel chains of molecules in the unswollen state as found in native cellulose fibres. The presentation of the structure of the gel given at the same time was, therefore, the picture of a fibre swollen to a gel.

In contrast to this, artificial cellulose fibres are formed by de-swelling a gel produced from a solution and we must therefore give our attention to the processes of gelatination and de-swelling. We shall here deal in more general terms with gel formation and gel structure and shall enter more fully into details in the third part of this book.

8.2 Gel Formation from a Solution

It will be evident that cellulose gels — which can be obtained merely by the coagulation of a cellulose solution — will not exhibit any preferred orientation, but rather that they are isotropic, like the solution itself. Such isotropic gels, if allowed to de-swell under proper precautions, produce isotropic cellulose, even in the dry state, and this may subsequently be swollen again isotropically.

Certain structures exist in artificial fibres which resemble those of native fibres, in that their chain molecules are more or less aligned in the direction of the fibre axis. As explained in Part III, this orientation of the chains is the result of treatment which forms part of the manufacturing process, namely the mechanical deformation of the primarily formed isotropic gels. For the moment, however, we shall pass over this matter of orientation and first consider the process of gelatination, itself.

In principle, the formation of a gel from a solution represents, in reverse the processes through which a gel goes from unlimited swelling to a solution. It takes place when conditions arise in which the dissolved substance becomes insoluble. For the reasons given earlier on page 65, il will therefore generally react very sensitively to the slightest changes in the composition of the dispersion medium, the temperature, etc., always apart from the time factor (for, just as in the process of dissolution, there will be some retardation).

Whereas the regions with a lattice order are the component parts of the structure which resist the longest during the process of solution, it is to be expected that, conversely, these crystalline regions will be the first to be formed during gelatination. In point of fact, gelatination may best be described as a form of crystallization; similarly, having defined the process of swelling as "local dissolution", we might now say that gel formation is a "local crystallization" of the chain molecules.

We have seen (p. 56) that a temporary interplay of local bonds between

the chains is to be assumed in concentrated solutions of polymeric chains and that the chain sections at the junction points must lie parallel. The nearer the solution approaches to gelatinizing conditions, the more numerous and the more firmly attached will these bonds become [111]. Once the distinct solubility limit for highly polymeric substances has been exceeded, these bonds are stabilized and become strong, temporarily established local "junction points" (cf. p. 36). As a result, all the molecules henceforth remain clustered, forming a network which pervades the entire liquid, the fluid character of which has given place to a solid (also cf. pp. 39 and 53).

Obviously, these junction points evolved from parallel chains may also now be considered as regions with a lattice order, or at least as a tendency to such — in a sense as "nuclei of crystallization". The process is entirely comparable to those which primarily take place in the precipitation of a low-molecular substance. That the crystallization does not at first proceed any further, but is impeded, is due on the one hand to the restricted power of diffusion of the large molecules and, on the other, to the fact that a single molecule is liable to take part in the formation of several spatially separated centres of crystallization.

Fundamentally, the structure of an isotropic cellulose gel will have the appearance of that shown in Fig. 15. Gels are coherent micellar frames in *Frey-Wyssling's* sense (p. 35 ff) and, in the case of linear polymers, the frame must be thought of as consisting of chain molecules. These form a network with junction points, which might be defined as "interlocking points" of the network and which are interconnected by chains of molecules.

If the junction points actually do represent regions of an approximate lattice order, it will depend upon their longitudinal and lateral dimensions whether X-ray diagrams appear and how sharply defined these will be. (cf. p. 21 ff). In freshly formed gels, particularly those formed from dilute solutions, they may be composed of so few chain sections, or be so short, that they are not capable of producing crystalline interferences. They might then be compared to the nuclei of crystallization of low-molecular substances which are likewise composed of few molecules. Upon the ageing of the gel, or its de-swelling, they are likely to spread and become detectable by X-rays. Thus an isotropic gel freshly produced from viscose shows imperfect crystal interferences, but they become more distinct when the gel is allowed to de-swell, or if it is heated. Unlike technically produced artificial fibres, in which, for the above reasons, there is usually a distinct preferential orientation, isotropic gels naturally thereby produce a *Debye-Scherrer* diagram, indicating a wholly random orientation of the crystalline regions.

The size of the primarily formed crystalline regions might be expected also to stand in some relation to the rate of gelatination. *G. Centola* [112] has made

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[111] Also see *P. J. Flory*, J. Phys. Chem., 46, (1942) 132.
[112] *G. Centola*, Atti del X Congr. Intern. di Chimica, Roma, IV (1939) 117.

some interesting observations on this point; he has also cited some examples substantiating the influence of the solvent.

It should be remembered that the junction points, or crystalline regions, primarily formed during gelatination often represent the lattice of an addition compound with the solvent [112a]. In that case, solvent molecules have penetrated in between the chains. Similar compounds are formed inversely during the swelling of an unswelled substance. Cellulose in aqueous media first shows an unstable compound of high water content (cellulose hydrate II, see Chapter I § 4), which later loses water and is not formed during the process of swelling.

It is essential to point out that the portion of the total structure interconnecting the junction points is to be considered as being in a molecularly dispersed state. In the swollen state, in particular, one should imagine in the amorphous regions single molecular chains surrounded by solvent molecules. For it is precisely upon this that the close relationship between swelling and solution, which was dealt with in § 6, rests, and in this lies the distinction between these systems and other, likewise gel-like systems of coarser structure consisting of interlaced fine crystal needles or dendrites [113].

This picture of the molecular structure of gels of high-molecular substances squares with the fact that high-molecular substances made up of approximately spherical molecules do not swell; nor do they form typical gels when separating from their solutions [114]. It also harmonizes with the theories developed many years ago by colloid chemists on the presumed structure of gels. See, for instance the articles by *S. C. Bradford* [115], *D. J. Lloyd* [116] and *E. Manegold* [117], and also the book by *A. Gillet* and *N. Andrault de Langeron* [118]. The view that many typical sol-gel transformations are undoubtedly related to crystallization processes (in so far as they are not due to the formation of chemical cross links) is gradually gaining ground [119] and there are many facts in support of it. We cannot enter into this matter more fully now [120], but would point out that all those conditions which increase the size of the separating crystals in low-molecular substances (such as lowering the

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112a This may be regarded as proved beyond doubt, at any rate so far as gelatin gel is concerned. *J. R. Katz*, Rec. trav. chim. 51, (1932) 835. *J. C. Derksen*, Thesis. Amsterdam (1935).

113 From a system of this kind it should be possible to squeeze all the swelling liquid by mechanical pressure diminishing in proportion to the size of the crystals, which can be done no more than partially with a "true" gel.

114 Cf. *H. Staudinger*, "Organische Kolloidchemie", Braunschweig 1940. Colloid chemists recognized long ago that gel formation is always accompanied by anisodiametric particle shape; see *W. Reinders*, Chem. Weekbl., 27, (1930) 166; *H. R. Kruyt*, Chimie et Ind., 42, (1939) Number 4.

115 *S. C. Bradford* in J. Alexander's Colloid Chemistry, New York, Vol. I, (1926) p. 751.

116 *D. J. Lloyd*, J. Alexander's Colloid Chemistry, New York Vol. I, (1926) p. 767.

117 *E. Manegold*, Kolloid-Z., 96, (1941) 186.

118 *A. Gillet* and *N. Andrault De Langeron*, Introduction à l'Etude des Colloïdes, Liège 1936, p. 65—88.

119 This statement refers only to high-molecular substances with chain molecules and may not always apply to certain inorganic colloids.

120 See also *K. H. Meyer* and *A. J. A. v. d. Wijk*, Z. Elektrochem., 47, (1941) 353; Helv. Chim. acta, 20, (1937) 1321, 1331.

concentration, increasing the solvent power of the dispersion medium) give rise to a coarser gel frame in high-molecular substances [121].

In the preceding pages we have only outlined qualitatively the structure of gels, i.e., the formation of local centres of crystallization interlinked by free chain sections. The details of gel structure, size, number and distribution of the crystalline regions, their mutual orientation at short distances and similar data respecting intercrystalline regions and their nature (e.g., the flexibility of the chains and their shape) leave us with a number of variations not dealt with. It will also be evident that the ultimate special structure will be determined by numerous factors. First of all the microstructure of the gel will be influenced by the structure of the solution at the moment of coagulation, as for example by the degree of order at short distances ("Ordnung in kleinsten Bereichen"), by the state of association (p. 48, 53) and the degree of convolution of the chains, which, again, may depend upon the dilution and nature of the solvent, etc. We shall come upon more specialised examples later. The structure of the gel will furthermore be determined by the conditions of gelatination, by its age and by its subsequent de-swelling, if any.

Neither these factors in their variety, nor the effect they have can be taken in at a single glance, and it is only by further systematic investigation into the properties of the solutions and by the examination of gels produced under various conditions that one can hope to arrive at some explanation of further particulars.

Obviously there must be some close relationship between the macroscopically determinable physical and mechanical properties of the gels and their particular microstructure, and the problems we have touched on (to be dealt with again in Part III) are of decisive importance in the scientific investigation of artificial fibres. At this juncture we shall deal briefly with the following points.

We have already discussed the connection between the extension of the junction points and the appearance or distinctness of the X-ray interferences. The size of the "meshes" of the gel framework, or its density of packing, will be intimately related with the degree of swelling. Swelling and de-swelling must go together with changes in the configuration of the frame yet to be defined. In this respect the nature of the intercrystalline molecular regions between the junction points, their flexibility and shape are just as important as data on the crystallized regions themselves and will also contribute decisively in determining the mechanical and deformatory properties of the gels (cf. p. 73).

It was stated at the end of the preceding section that the steric configuration of the molecules must undoubtedly influence the consistency of the gels and

[121] See *S. C. Bradford*, J. Alexander's Colloid Chemistry, New York Vol I, (1926) p. 751; *D. J. Lloyd*, J. Alexander's Colloid Chemistry, New York, Vol. I, (1926) p. 767. *E. Heymann*, Trans. Faraday Soc., 31, (1935) 846.

the mechanism of swelling and de-swelling. That statement may be viewed in a new light from what has just been said.

When dealing specifically with gels from regenerated cellulose in the third part of this book, we shall start from the basic arguments advanced here which, in essentials, may be regarded as legitimate, for which reason we have introduced them now [122].

At present we shall merely touch on a few points designed to show that these basic views square with much of the actual experience with gels.

8.3 Some Phenomena observed in Gels in the Light of the Foregoing

The features of unlimited and limited swelling were discussed comprehensively in the preceding section. In the latter case the solvent is unable to overcome the forces of cohesion in the crystalline regions, i.e., in the junction points, and so mechanical cohesion in the gel is maintained [123].

It may often happen that a limited process of swelling is transformed by change in temperature to an unlimited one. Thus gelatin and agar gels which show limited swelling in the cold, are liable to liquefy with increase in temperature. This might be explained as the melting or dissolving of the crystalline junction points. Melting being an endothermic process, increase in temperature favours it.

The reverse often applies to cellulose and its derivatives, when unlimited swelling (dissolution) is encouraged by the lowering of temperature. E.g., regenerated cellulose preparations become soluble at low temperature in 2 n sodium hydroxide solution; methyl cellulose solutions solidify with increase in temperature to a gel which, on cooling, liquefies again. It was shown in § 6 how cases of this kind can be explained by negative temperature coefficients of solubility.

With these thermo-reversible gels the temperatures of gel liquefaction and re-solidification are often far apart. The melting point of an agar gel, for example, is appreciably higher than the temperature at which the liquefied gel gelatinizes on cooling. This hysteresis is related to the difference in melting point of larger and smaller crystallites, a fact already familiar in low-molecular substances. As a gel coagulates, the junction points formed are very small at first and the solidification point therefore corresponds to

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[122] These views also incorporate the theory of gels as solid solutions (a time-honoured theory, to the establishment of which *J. R. Katz* contributed in large measure) and that of the essential crystalline nature of gels. To this must be added the significance of steric factors, of mass distribution between crystalline and intercrystalline substance and of the flexibility of the molecular chains. Then there is a fluid transition to the "molecular felt structures" as assumed for other high-molecular substances such as rubber and polystyrene, for the characterization of which *F. Horst Müller* was chiefly reponsible.

[123] Limited swelling may also be conditioned by chemical cross links between the chains, when these primary bonds perform the task of the junction points. E.g., rubber vulcanized by the addition of styrene polymerized in the presence of small quantities of divinyl benzene. The same may occur with cellulose, e.g., after cross-linking of the molecules by the action of formaldehyde.

that of the smallest crystallites. We might put it this way: Considerable supercooling is needed to bring these "nuclei" into being at all[124]. Once the gel is formed, junction points grow in due course to larger ones, which by that time have a higher melting point. Therefore, upon re-heating, a higher temperature is required to melt them. Similar considerations apply, ceteris paribus, to the thermically reversible gels of the methyl cellulose in water type. The indeterminate character of the gelatination and melting points may therefore be explained by the simultaneous presence of crystallites of different sizes. *K. H. Meyer*[125] affirms that the crystallite size affects the solubility of high-molecular substances in particular to a very considerable extent.

Like crystallization, gelatination can be stimulated by inoculation and similarly displays an "autocatalytic" character[126], *S. N. Banjeri* and *S. Ghos*[127] found with gelatin, for example, that the addition of gel particles assisted coagulation.

A solution rarely solidifies suddenly to a gel. There is much to show that junction points between the molecules are already in process of forming in a sol nearing the stage of gelatination. Ever larger aggregates are being formed, which gradually assemble in a coherent frame. The more dilute the sol, the more clearly is this process revealed. With extreme dilution flocculation takes place instead of gelatination. In this case the locally formed aggregates cannot associate in a coherent frame.

Conversely, it has been found that, in the liquefaction of gels, aggregates may for some time still be identified in the sol, even containing crystalline particles, an example being gelatin (cf. p. 55). Once again, the more dilute the gel, the more noticeable was this phenomenon. Apparently the aggregates formed prior to gelatination dissolve again as such. *J. L. Ouweltjes*[128], for instance, was able to show that the viscosity of gelatin gels directly after melting is particularly high if the gels are dilute. Progressive aggregation also probably takes place in viscose solutions during the subsequent maturing which eventually leads to coagulation. Though the thermal effects measured in sol-gel transformation have usually been slight, their sign is in agreement with the theory of crystallization[129]. According to *S. A. Glückmann*[130] the smallness of the thermic effects is in complete accord with the theories propounded if it be realized that the junction points between the molecules have been largely prepared by the association in the solution. These links need relatively little strengthening — that is, their length

[124] It would not be contradictory to state that macromolecular substances with chain molecules can only crystallize from a solution if sufficient crystallization centres are formed by adequate supercooling. Though crystallization begins, it remains incomplete for the reasons given and the temperature therefore does not rise to an equilibrium temperature as it would do in low-molecular solutions.

[125] According to *K. H. Meyer*, Die hochpolymeren Verbindungen, Leipzig, Vol. II, (1940) p. 530 ff.

[126] *V. A. Kargin* and *A. A. Stepanova*, Acta physicochim. U.R.S.S. 6, (1937) 183.

[127] *S. N. Banjeri* and *S. Ghos*, Z. anorg. Chem., 194, (1930) 305.

[128] *J. L. Ouweltjes*, Thesis, Amsterdam 1942.

[129] *E. Heyman*, The Sol-Gel Transformation, Paris (1936), p. 17,

[130] *S. A. Glückmann*, Acta physicochim. U.R.S.S., 13, (1940) 379.

of life requires but little prolongation — to produce the almost continuous transformation to the gel. It should also be borne in mind that an exothermic addition compound with the solvent usually takes part in the primary formation of the lattice, the heat of crystallization of which is less than that of the macromolecular substance itself.

As to the optical properties, all transitions may take place between optically almost empty systems with a weak *Tyndall* effect and those with a strong *Tyndall* effect. In the former case the junction points are small and the gel frame is largely of molecular dispersion; these systems are to be considered as monophasic (cf. p. 36). To the degree that the junction points, or the supports of the frame, grow, turbidity increases and the appearance of X-ray interferences becomes more frequent. In the case of cellulose and its derivatives, which usually have a more marked tendency to crystallize, the *Tyndall* effect is stronger throughout.

Gels allowed to coagulate freely in three dimensions are optically isotropic. If the isotropic gel is subjected to deformation, it becomes doubly refractive, owing to the then anisotropic disorder of the molecules in the deformed gel frame. We shall revert to this later.

As the gels are de-swollen (or as they shrink on drying), the gel frame contracts and therefore becomes compressed.

We have now to consider two points of view, one being that possibly the crystalline junction points grow to some extent, thereby entailing an increase in the percentage of crystalline substance [131]. In any event, the number of junction points (including many of a non-crystalline nature) will increase considerably. This is probably why gels, once dried, swell far less when re-soaked than originally.

The second point of view is that the very considerable de-swelling of these gels can hardly be visualized without assuming a change in the shape of the fibrillar elements of the gel framework (crumpling of molecular chains) [132]. The changes in gel structure resulting from de-swelling concern us very materially and we shall deal with the matter in greater detail in Part III, when we shall also consider the equally important effect of the concentration of the gelatinizing solution upon the degree of swelling and structure of the gel. It looks as though it may be possible at the present time to tackle most of these problems by consistently pursuing the fundamentals here set forth, with the aid of the available knowledge of low-molecular systems and the results of recent progress in other high-polymers. Thus the characteristic elasticity of gels might be correlated with the molecular disperse structure of the gel framework with reference to the physics of rubber elasticity.

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[131] *O. Kratky* and co-workers, Kolloid-Z., 96, (1941) 301.
[132] *P. H. Hermans*, Kolloid-Z., 96, (1941) 311.

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CHAPTER III

LENGTH, END GROUPS AND SHAPE OF THE CHAIN MOLECULES

§ 1. GENERAL REMARKS AND BASIC CONCEPTS. POLYMERIC UNIFORMITY AND MOLECULAR WEIGHT SPECTRUM

The chain molecules of cellulose as at present known consist of a long row of equal, interconnected glucose residues and therefore exhibit polymeric uniformity ("Polymereinheitlichkeit"). For a comprehensive description of a molecule it is necessary to know the length of the chain and the constitution of the end groups. According to page 8, the formula of cellulose is:

$$[C_6H_{10}O_5.\ (C_6H_{10}O_5)n.\ C_6H_{10}O_5]\ OH$$

The link number N of the chain is $n + 2$; it is usually denoted by P (degree of polymerisation). The molecular weight of the monomeric residue $C_6H_{10}O_5$ is 162 and the molecular weight of the chain is therefore

$$M = 162\,P + 17$$

$M = 162\,P$ may be written for larger values of D.P. In all probability, only cellulose preparations obtained by partial hydrolysis correspond to the above formula.

Nothing is known with certainty about the nature of the end groups in native cellulose as deposited in plants; nor have we adequate knowledge of the chain length of native cellulose, though it is undoubtedly very considerable. According to *Alf af Ekenstamm* [1] P is at least 3000.

With one exception (end-group determination by exhaustive methylation, cf. § 4), all methods by which chain length can be estimated require operations with samples previously purified and dissolved by chemical processes, thereby involving the risk of a partial breakdown or change in the nature of the end groups. *K. Hess* and *F. Neumann* [2] found that, by applying the end-group method referred to above with great care to native fibres, their end-group content was small enough to fall within the margin of error.

According to more recent investigations carried out by *G. V. Schulz* and *E. Husemann* [3], cotton cellulose consists of molecules of uniform length

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[1] *Alf af Ekenstamm*, Ber., 69, (1936) 549, 553 "Ueber die Cellulose-Lösungen in Mineralsäuren", Lund 1936.
[2] *K. Hess* and *F. Neumann*, B. 70, (1937) 710.
[3] *G. V. Schulz* and *E. Husemann*, Z. physik. Chem., B. 52, (1942) 23.

(P = 3100 ± 100) and, by analogy with other biochemical experience, it seems probable that a definite chain length actually is formed in the living plant. *E. Husemann*[4] maintains that native xylanes — substances accompanying cellulose in wood — likewise have a uniform chain length.

The polymeric uniformity of native cellulose has been doubted more than once in the past. According to *E. Schmidt* and co-workers[5], both wood cellulose and cotton cellulose contain one carboxyl group to every 100 glucose groups, so that the carboxyl content is 0.23%. Whereas *Schmidt* took the carboxyl group to be the end group and therefore estimated the degree of polymerisation at 100 or thereabouts, *H. Staudinger*[6] regarded it as a foreign group built into the structure at regular intervals (in which case native cellulose would be a polybasic acid). *M. Lüdtke*[7] states that cotton fibres do not originally contain carboxyl groups, but that these are introduced by the oxidation of CH_2OH groups when the fibres are freed from foreign substances by purifying processes. Even the most carefully purified preparations he found to contain at least one COOH to 400—500 glucose residues, i.e., approximately 0.06%.

L. Brissaud[8] tried to determine the carboxyl content by the evolution of carbonic acid on heating with concentrated hydrochloric acid. *M. Rebek*[9] attempted to base a quantitative determination of the carboxyl groups upon the binding of crystal violet base and found 0.03 — 0.04% COOH in cotton, which is one carboxyl group to about 1000 glucose residues. *A. M. Sookne* and *C. H. Fugitt*[10] describe a method by which the carboxyl content can be determined rapidly by electrodialysis.

Later investigations have established the presence of a certain percentage of carboxyl in practically all cellulose preparations, but the quantity of COOH groups depends very largely upon the origin of the material and its preliminary treatment. This experimental evidence at the same time cleared up the apparently contradictory results obtained by earlier investigators.

These investigations were carried out by means of a method recently devised by *O. H. Weber*[11] for the estimation of carboxyl. It is based on the binding of methylene blue by the carboxyl groups and the reversible separation of this dyestuff by acids. (In his report on the work the author also criticizes the relevant older papers). It had become evident from related research carried out by *E. Husemann* and *O. H. Weber*[12] that the glucose number i.e., the number of glucose residues relative to one COOH group and the

[4] *E. Husemann*, J. Prakt. Chem., 155, (1940) 13.
[5] *E. Schmidt*, Cellulosechemie, 13, (1932) 129; Papierfabrikant, 31, (1932) 138; Ber., 68, (1935) 542; Ber., 70, (1937) 2345;
E. Schmidt, M. Hecker, W. Jandebeur and *M. Alterer*, Ber., 67, (1934) 2037;
E. Schmidt, W. Jandebeur, M. Hecker, R. Schneag and *M. Alterer*, Ber., 69, (1936) 366.
[6] *H. Staudinger*, Papierfabrikant, 36, (1938) 388.
[7] *M. Lüdtke*, Biochem. Z., 285, (1936) 78.
[8] *L. Brissaud*, Mém. des Poudres, 28, (1938) 43.
[9] *M. Rebek*, Kolloid-Z., 92, (1940) 217.
[10] *A. M. Sookne* and *C. H. Fugitt*, Textile Res., 10, (1940) 380.
[11] *O. H. Weber*, J. Prakt. Chem., 158, (1941) 33.
[12] *E. Husemann* and *O. H. Weber*, J. Prakt. Chem., 159 (1941) 335.

degree of polymerisation are roughly of the same magnitude in native cellulose fibres (cotton, ramie) and that high-molecular monocarboxylic acids, probably with terminal COOH, are therefore present. The cellulose obtained from wood, straw and reed and also kapok, on the other hand, have a glucose number ranging between 90 and 130 and therefore contain several (8—12) COOH groups per macromolecule, probably built in at regular distances.

From the fact that native cellulose in a solution of sulphuric acid decomposes with abnormal rapidity at the beginning of hydrolysis, *Alf af Ekenstamm* [13] came to the conclusion that this cellulose contains, in addition to the ordinary glucosidic links, some that split off far more quickly. This inference was later challenged by *G. V. Schulz* and *H. J. Löhmann* [14]. Shortly after, however, *G. V. Schulz* and *E. Husemann* [15] showed that probably alien groups are built into the molecule of cotton cellulose at regular intervals of about 510 glucose residues and that next to those groups lies a very easily hydrolysed glucosidic bridge bond. The hydrolysis constant of these bonds is about 1500 times that of normal bridge bonds. There was as yet no clue to the nature of the alien groups; they may possibly contain a carboxyl group (glucuronic acid residues), or maybe a xylane residue has interposed.

Carboxyl groups built laterally on the chain may also be thought of as having accrued through oxidation of the primary alcohol groups of the glucose residues. As a matter of fact, oxidized preparations often exhibit a high carboxyl content.

The accretion of carboxyl groups likewise takes place during the maturing of alkali cellulose, during which oxidative decomposition is known to take place. Probably only one COOH group here occurs per point of cleavage and consequently only one of the fragments receives a COOH as end group. In this way all the molecules in artificial viscose fibres produced from wood cellulose carry lateral and terminal carboxyl groups.

The COOH groups are responsible for the base exchangeability and also for a considerable portion of the ash content. In recent interesting investigations carried out by *D. Krüger* and *F. Oberlies* [16] their presence was also detected by their catalytic activity. It is of the utmost importance to the clarification of many a problem connected with the microstructure and behaviour of cellulose and with the changes that take place during degradation that as clear a picture as possible should be obtained of the number and distribution of the carboxyl groups. Further details are expected to be forthcoming very shortly.

The polyuronides occurring with the hemicelluloses in lignified cells have

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[13] *Alf af Ekenstamm*, "Ueber die Cellulosclösungen in Mineralsäuren", Lund 1936, (also: Ber., 69, (1936) 549, 553).
[14] *G. V. Schulz* and *H. J. Löhmann*, J. Prakt. Chem., 157, (1941) 238.
[15] *G. V. Schulz* and *E. Husemann*, Z. physik. Chem., B. 52, (1942) 23.
[16] *D. Krüger* and *F. Oberlies*, Ber., 74, (1941) 663. Also see *D. Krüger*, Klepzigs Text. Z., 44, (1941) 647.

likewise been recognized as polycarboxylic acids. The high carboxyl content of wood celluloses is probably due in part to the fact that there the cellulose is chemically linked with the other constituents of the wood (incrustations, chiefly lignin) through the carboxylic groups (in substantiation of which may be cited the difficulty with which cellulose is extracted from wood meal with, say, *Schweitzer's* reagent).

H. Staudinger's work [17] on the nitrates of native cellulose has given him reason to presume that native cellulose also contains bonds in the form of esters. On the basis of their experimental work on the methylation of native cellulose, *K. Hess* and *E. Steurer* [18] suspect the presence of chemical cross links between the chains ("Vernetzungsbrücken"). *Alf af Ekenstamm* (loc. cit.) expressed a similar view and went so far as to assume that the rupture of these links is a necessary preliminary to the dissolving of native cellulose at all. Further observations which might point to chemical cross links were made by *R. Signer* and *H. Gross* [19] and *F. Opderbeck* [20]. *I. Sakurada* and *S. Lee* [21] noticed signs of anomalous viscosity during the first dissolution of "fibre acetate" ("Faseracetat"). These "chemical fine details" of the structure of native cellulose are not yet altogether understood. Nor is it yet possible to foresee their effect, if any, upon the mechanical properties and the practical textile merits of native cellulose. We should, however, do well to give our attention to this matter.

According to other authors, yet other polysaccharidic structural units, such as pentose groups, may be built into the cellulose skeleton. More will be said about this in Part III, Chapter I. Ordinarily it is exceedingly difficult to detect departures such as these from the "normal" structure of cellulose molecules, but it is necessary to keep a keen look-out for them.

It is probable that almost every cellulose met with in practice always consists of molecules of different chain lengths, being therefore mixtures of polymeric homologues, as *H. Staudinger* [22] pointed out long ago. The cellulose objects met with in practice, which are always broken down to some extent, certainly do contain a molecular spectrum of the kind [23]. *G. V. Schulz* [24] made it clear that a distinction should be made between "polymolecularity" (i.e., non-uniformity of molecular weight, or spectrum of molecular weight) and "polydispersity", these terms being identical in meaning as applied to solutions only if the disperse particles are unimolecular. Whereas polymolecularity is a property of the substance, which remains the same whatever the state (micellar systems, solutions), polydispersity is merely a given condition of

[17] *H. Staudinger*, Cellulosechemie, 15, (1934) 66.
[18] *K. Hess* and *E. Steurer*, Ber., 79, (1940) 669.
[19] *R. Signer* and *H. Gross*, Z. physik. Chem., 165, (1933) 161.
[20] *F. Obderbeck*, Thesis Bonn., D. 5, 1937; cf. *S. Peat*, Ann. Reports Chem. Soc. London, 36, (1939) 271.
[21] *I. Sakurada* and *S. Lee*, Kolloid-Z., 61, (1932) 50.
[22] *H. Staudinger*, Ber., 59, (1926) 3021.
[23] *H. Staudinger*, Zellstoff-Faser, 33, (1936) 162.
[24] *G. V. Schulz*, Z. Elektrochem., 44, (1938) 102.

the substance. The term "heterogeneity" occasionally used in later technical literature to denote non-uniformity of chain length is misleading, since the same term is used to describe the composition of several phases.

It will be evident that for an adequate characterization of a cellulose preparation it is necessary to furnish fuller details of its polymolecularity, i.e., of the numerical distribution of the molecular chain lengths within it. As a rule it is not enough merely to give an average; for two objects with the same average molecular weight may produce entirely different chain length spectra and, therefore, possess different properties.

Fractionation will often achieve partial separation of molecules of varying chain length, since the process depends upon diminishing solubility in inverse ratio to chain length. For practical purposes sufficient information as to the distribution of chain lengths can be obtained by quantitative fractionation and determination of the average molecular weights of the individual fractions (§ 3), but before we go into this we must consider more closely what is meant by "average molecular weight".

§ 2. SPECTRUM OF MOLECULAR WEIGHTS AND AVERAGE DEGREE OF POLYMERIZATION

The available methods for the estimation of chain lengths (molecular weights) furnish only average values. If there has been no previous fractionation (§ 3), this average is mostly related to a broad spectrum of chain lengths. Therefore one and the same object tested by two different methods, each in itself reliable, may produce two different average values for the chain lengths, from which it will be clear that the definition of the average value is qualified by the nature of the method applied. Neglect of this point has given rise to many a disagreement and misunderstanding, yet the reason for these differences is a very simple one. The classical methods (osmotic pressure, vapour tension depression, etc.) measure the number of particles present per unit of weight of the substance; the effect measured diminishes as the molecular weight (MW) increases. Exactly the same applies to the end-group method. The point at issue with the viscosity method and the rate of sedimentation, on the other hand, is the length or the weight of the individual particles; the effect measured increases together with increasing MW.

For the following reason it will be readily understood why, therefore, different average values must necessarily be found for mixtures of different chain lengths. In solutions of the same concentration, small molecules, owing to their great number per unit of weight, have strong osmotic activity, but have little effect upon the viscosity, whereas long molecules, being few in number, exert but little osmotic influence but have a powerful effect upon the viscosity, in the sense of increasing it.

After *H. Staudinger* [25] had drawn attention to this matter, *E. O. Kraemer* and *W. D. Lansing* [26] and *W. Kern* [27] took over quantitative treatments, which were later elaborated by *G. V. Schulz* [28] and others.

We can only deal with the main principles of this matter here. For its considerable development in recent years, due particularly to *G. V. Schulz*, in connection with the theory of fractionation processes, we must refer to the original literature (see § 3 and separate list at the end of this Chapter).

A simple example will serve to explain the difference between the average degree of polymerization determined osmotically and viscosimetrically (P_O and P_V). Let the osmotic effect for a homogeneous substance with P degree of polymerization with a concentration of c grams per litre be E_O. This is proportional to the number of particles and therefore:

$$E_O = k_O \, c/P \qquad (3.1)$$

According to *Staudinger* the viscometrically measured effect E_V for chain molecules is proportional to the concentration and the length of the particles; therefore

$$E_V = k_V \, c.P \qquad (3.2)$$

(k_O and k_V are constants).

Let us take as an example a mixture of chain molecules of the following composition:

Percent. by wt	*Degree of polymerization*
12	100
24	200
64	400,

one gram of which we dissolve per litre. Our calculation of the effects of the individual fractions and of the mixture then is as follows:

Fractions		*Osmotic effect*	*Viscometric effect*
P	c (g/l)	k_O.c/P acc. to (3.1)	k_V.c/P acc. to (3.2)
100	0.12	0.0012 × k_O	12 × k_V
200	0.24	0.0012 × k_O	48 × k_V
400	0.64	0.0016 × k_O	254 × k_V
Mixture: 1.0 g/l		E_O = 0.0040 × k_O	E_V = 314 × k_V

From (3.1) and (3.2) it appears that $\bar{P}_O = 250$ and $\bar{P}_V = 314$.

The general formulæ are:

$$\bar{P}_O = c/\Sigma \frac{c_i}{P_i} \qquad \bar{P}_V = \frac{1}{c} \Sigma c_i P_i \qquad (3.3)$$

It is possible to prove that $\bar{P}_V$ must always $> \bar{P}_O$ The magnitude of the difference depends upon the scattering of the chain lengths in the mixture

[25] *H. Staudinger*, "Die hochmolekularen organischen Verbindungen, Kautschuk und Cellulose", Berlin 1932, p. 64 and 169.
[26] *E. O. Kraemer* and *W. D. Lansing*, J. Phys. Chem., 39, (1935) 153; J. Amer. chem. Soc., 57, (1935) 1369.
[27] *W. Kern*, Ber., 68, (1935) 1439.
[28] *G. V. Schulz*, Z. physik. Chem., B. 32, (1936) 27; B. 41, (1939) 466; B. 46, (1940) 137; B. 47, (1940) 155.

and is noticeable in the degree of such scattering. As a particularly striking example of this *W. Kern* (loc.cit) calculated that the two mixtures:

A. 33% P = 100 with 67% P = 200

B. 67% P = 100 with 33% P = 1000000

would show the same osmotic average degree of polymerization (150), whereas that measured viscometrically would exhibit 167 for mixture A and 33100 for B. Extreme cases of this kind, however, scarcely ever occur in actual practice, unless mixtures are intentionally made of substances very divergent in degree of disintegration.

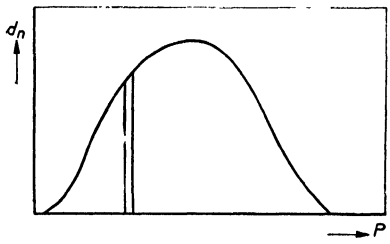


Fig. 30. Diagrammatic frequency curve.

The distribution of the individual lengths of chain must be known to control the conditions in a particular case. In all practical cases the statistical distribution of the chain lengths is a continuous function which can be represented in a frequency curve as a function of the degree of polymerization. A curve of this kind is given diagrammatically in Fig. 30. The surface of the infinitely narrow strip sketched in represents the number dn of gram-molecules in a monomeric residue of the substance, the degree of polymerization of which is between P and $P + dP$; dn is a function of P

$$dn = f(P)\, dP \qquad (3.4)$$

The total number n of all molecules in a gram-molecule of monomeric residue is

$$\int_0^\infty dn = n = \int_0^\infty f(P)\, dP \qquad (3.5)$$

The rational definition of the mean molecular weight $\overline{M}$ is the amount by which a given quantity of the material (in grams), has to be divided to get the number of gram-molecules it contains [29]. Let the molecular weight be M, the degree of polymerization P and the weight of the monomeric residue M'; then

$$M = M'.P \text{ and therefore } \overline{M} = M'.\overline{P}$$

$\overline{P}$ being the mean degree of polymerization. There are, therefore, in one moles. It follows from (3.5) and (3.6) that

$$n = M'/\overline{M} = 1/\overline{P} \qquad (3.6)$$

mole of monomeric residue (hence, M' grams):

$$\overline{P} = \frac{1}{\int_0^\infty f(P)\, dP} \qquad (3.7)$$

[29] This is the mean molecular weight with which also thermo-dynamics and the kinetics of reactions are concerned.

Since the average values $\overline{M}$ and $\overline{P}$ refer to the number of molecules, it is these which are obtained from the osmotic and end-group determinations.

In addition to the number of molecules, we want to know the mass in grams of the molecules of a given degree of polymerization per gram-molecule of monomeric residue of the substance. Since dn gram-molecules weigh $PM'dn$, this, according to (3.5), will be:

$$M'P\, f\,(P)\, dP \qquad (3.8)$$

and 1 gram of substance will therefore contain

$$P \,.\, f\,(P)\, dP \qquad (3.9)$$

grams. If (3.9) is represented by a graph as a function of P, the result is the mass distribution curve, which is thus derived from the distribution curve according to (3.4) and (3.9) by multiplication of the respective ordinates with P. This curve is directly related to the experimental results of fractionation, for it is obtained when one gram of an inhomogeneous preparation is divided into endless small fractions and the weights of the fractions are plotted against degree of polymerization. (For the practical determination of this curve see § 3). Upon transition to mass distribution the character of the curve is liable to change completely, an example of which is afforded by Fig. 31A, which refers to a styrene polymerisate, where curve I is the number distribution curve and II the mass distribution curve. (The ordinate scale is not shown).

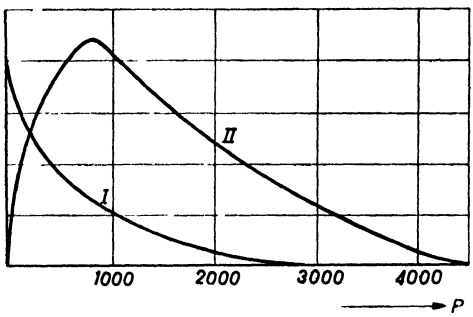


Fig. 31 A. Distribution of the degrees of polymerization in a styrene polymerisate (after *G. V. Schulz* and *E. Husemann*, 1936). I. Frequency distribution function. II. Mass distribution function.

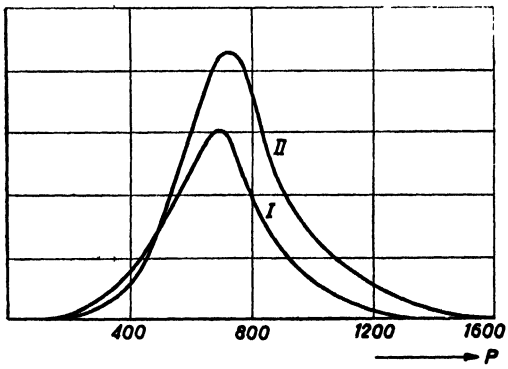


Fig. 31 B. Distribution of the degrees of polymerization in a nitrocellulose (after *H. Staudinger* and *G. V. Schulz*, 1935). I. Frequency distribution function II. Mass distribution function.

Here we have a maximum in the mass distribution, but none in the number distribution. A different type of curve is found in all cellulose and its derivatives, being similar to Fig. 30 as shown in Fig. 31 B for a nitrocellulose. If the frequency curve (I) has the character of a Gauss error

curve, as is usually the case here, the mass distribution curve II is of a like nature [30].

The determination of the average degree of polymerization by viscometrical means preduces a magnitude differing from that obtained according to (4). By simple means [31] it can be shown that

$$\overline{P}_\eta = \int_0^\infty P^2 \, . \, f\,(P)\; dP \qquad (3.10)$$

Comparison of $\overline{P}_\eta$ with the osmotic average value according to (3.7) will disclose a very considerable difference [32]. In the case represented by Fig. 31A, $\overline{P}_\eta$ is about twice as big as $\overline{P}$, whereas the difference in the case of Fig. 31B amounts only to roughly 8%.

Starting from (3.7) and (3.10), *G. V. Schulz* [33] demonstrated mathematically that differences of great magnitude need not be feared if the distribution curves are in the nature of a *Gauss* error curve, and the less so as the scattering of the chain lengths is less. The term $\overline{P} = P_{max}$ (the degree of polymerization of the curve maximum) may then be added. If preparations of the kind are then split up into fractions, the scattering diminishing further in each, the degree of polymerization of the fractions determined viscometrically may be recorded without appreciable error as equal to the average degree of polymerization $\overline{P}$.

According to *G. V. Schulz*, the formula

$$U = (\overline{P}_\eta/\overline{P}) - 1 \qquad (3.11)$$

("Inhomogeneity") can be introduced as a measure of the distribution of molecular weight in an object (or as its polymolecularity). Its strict definition from the distribution can be obtained by substitution of formulas (3.7) and (3.10) in (3.11):

$$U = \int_0^\infty f\,(P)\; dP \quad \int_0^\infty P^2 f\,(P)\; dP - 1 \qquad (3.12)$$

Equation (3.11) applies only, of course, where *Staudinger's* viscosity relation holds good (so not to spherical particles); but equation (3.12) is universally applicable. If a substance containing chain molecules of uniform length is

[30] If the cellulose objects ordinarily met with in practice be regarded as formed in consequence of the degradation of originally very large molecules (brought about by mere chance), the type of their distribution curves follows from calculations made by *W. Kuhn*, B. 63, (1930) 1503. The mass distribution curve is similar to that of Fig. 31 B, though unsymmetrical, with its maximum shifted somewhat to the left. See *G. V. Schulz*, Z. physik. Chem., B. 46, (1940) 137 and B. 47 (1940) 155. Fractionated products can be conveniently represented by *Gauss* curves.

[31] See *G. V. Schulz*, Z. Physik. Chem., B. 32, (1936) 27.

[32] *W. D. Lansing* and *E. O. Kraemer*, J. Phys. Chem., 39, (1935) 153 and J. Amer. Chem. Soc., 57, (1935) 1369 state that a third average value may occur in measurements made with the ultracentrifuge (sedimentation equilibrium).

[33] *G. V. Schulz*, Z. physik. Chem., B. 46, (1940) 137; B. 47, (1940) 155.

broken down by the rules of chance, its non-uniformity U gradually increases from the value 0 to the value $U = 1$ [34].

§ 3. CHAIN LENGTH AND SOLUBILITY; FRACTIONATION

To split up a polymolecular preparation into fractions of different average weights, use is made of the fact that the solubility of the members of a polyhomologous series decreases as the molecular weight increases. *B. M. Dunkel* [35] and *J. N. Brönsted* [36] state that the reason for this is that the difference in potential energy of a molecule in two different phases has to increase with the molecular weight, whereas the kinetic energy (kT) it has available to overcome this difference does not depend upon the molecular size. According to *G. V. Schulz* [37], the relation between the solubility c and the degree of polymerization is as follows:

$$c = K \cdot e^{-kP} \qquad (3\cdot13)$$

where K and k are constants [38]. The solubility is, therefore, dependent in a high degree upon P. *G. V. Schulz* [39] has dealt comprehensively with the theory according to which the solubility and precipitability of high-molecular substances are a function of the degree of polymerization and the theory of fractionation based upon it, without invoking other views, such as those published on the theory respecting low-molecular solutions [40].

Practice makes use of the difference in solubility of low- and high molecular cellulose decomposition products in sodium hydroxide in the determination of the α, β and γ cellulose fractions.

H. Staudinger [41] records that the α fraction, which is insoluble in NaOH of 17.5% at 20°, consists of degrees of polymerization of 150 and higher than these. The β fractions contains P = 10-150 and the γ fraction $P < 10$. For the characterization of technical preparations the custom is gaining ground to test their solubility in sodium hydroxide at other concentrations as well. Solubility in sodium hydroxide depends to a very great extent upon the concentration of the caustic solution; like swelling, it has a distinct maximum at about 10% NaOH and increases as the temperature drops. The higher the degree of swelling during the extraction, the higher-molecular are the fractions which go into solution [42]. Lithium hydroxide has even greater solvent power. Under optimum conditions at low temperature, celluloses are soluble in NaOH

[34] *G. V. Schulz*, Z. physik. Chem., B. 51, (1942) 127.
[35] *B. M. Dunkel*, Z. physik. Chem., A. 138, (1928) 42.
[36] *J. N. Brönsted* and *E. Warming*, Z. physik. Chem., A. 155, (1932) 343.
[37] *G. V. Schulz*, Z. physik. Chem., A. 179, (1937) 321.
[38] Also cf. *J. N. Brönsted* and *E. Warming*, Z. physik. Chem., A. 155, (1931) 343; *J. N Brönsted* and *P. Colmant*, Z. physik. Chem., A. 168, (1934) 381; *J. N. Brönsted*, C.r. Laborat. Carlsberg (chim.), 22, (1938) 99; *E. Broda* and *H. Mark*, Papierfabrikant, (1937) 471.
[39] *G. V. Schulz*, Z. Elektrochem., 43, (1937) 479; Z. physik. Chem., A. 179, (1937) 321; B. 46, (1940) 137; B. 47, (1940) 155.
[40] Also cf. the interesting investigations by *K. H. Meyer* and *A. J. A. v. d. Wijk*, Helv. chim. acta, 20, (1937) 1313, 1321, 1331.
[41] *H. Staudinger*, Die Kunstseide, 21, (1939) 6.
[42] *G. W. Saito*, J. Soc. chem. Ind. Japan, 43, (1940) 160, 194.

up to $P = 300$ and in LiOH up to $P = 500$[43]. Freshly reprecipitated preparations which have not been previously dried are still soluble up to considerably higher degrees of polymerization. Of the numerous publications which have appeared on the subject we shall mention only those by *C. Birtwell, D. A. Clibbens* and *A. Geake*[44], *S. M. Neale*[45], *G. Davidson*[46] *Th. Lieser*[47] and *G. W. Saito*[48].

Preparations of considerably higher molecular weight are still soluble in quaternary ammonium bases (e.g., *Staudinger* says up to $P = 1200$ in tetra ethyl ammonium hydroxide).

Alf af Ekenstamm[49] also has some interesting observations on the solution of cellulose in sulphuric acid and phosphoric acid. All cellulose preparations can be dissolved in phosphoric acid, with scarcely a hint of decomposition, but, in the case of high degrees of polymerization, this is only possible within a certain very narrow range of concentration of the acid (normality 14.02 — 14.15 normal at 20°). As, however, this range widens as P diminishes, the latter can be estimated in this way.

To determine a "chain length diagram" or the distribution curve of a preparation, it is split up into fractions of different molecular weights, either by fractionated dissolution or by fractionated precipitation. When using the former method the operator starts with a "bad" solvent, with which he first dissolves the low-molecular components. Then the dissolving power of the solvent is gradually increased and the solute is drained off from time to time. In the second case a non-solvent miscible with the solvent is added in small portions at a time to a solution of the preparation and the precipitate formed in the meantime is separated off. These methods of fractionation for the determination of the distribution of chain lengths have latterly aroused great interest in technical circles and have proved exceedingly useful for experimental work in the artificial fibre industry.

For practical purposes nitrocellulose has been found to be particularly suitable for quantitative fractionation of the kind. Cellulose preparations were converted to nitrocellulose with the aid of a mixture of nitric acid and phosphoric acid[50], which is quite feasible without alteration to the length of the chains under certain suitable conditions. *H. Staudinger* (loc.cit.) and also *H. Dolmetsch* and *F. Reinecke*[51] state that the nitrocellulose should then

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[43] Such statements should be accepted with caution. *H. Staudinger* and *J. Jurisch* state in Kunstseide und Zellwolle, 21, (1939) 6, that the solubility limit of the low fractions depends upon the nature of the preparation and is also liable to vary in different native fibres.

[44] *C. Birtwell, D. A. Clibbens* and *A. Geake*, J. Text. Inst., 19, (1928) T 349.

[45] *S. M. Neale*, J. Text. Inst., 20, (1920) T 373; Shirley Inst. Mem., 8, (1929) 87.

[46] *G. Davidson*, Shirley Inst. Mem., 13, (1934) 1; J. Text. Inst., 25, (1934) T 174; 27, (1936) T 112.

[47] *Th. Lieser*, Ann., 528, (1937) 279.

[48] *G. W. Saito*, J. Soc. Chem. Ind. Japan, 43, (1940) 160, 194.

[49] *Alf af Ekenstamm*, Ueber die Celluloselösungen in Mineralsäuren, Lund 1936; compare: Ber., 69, (1936) 549, 553.

[50] *H. Staudinger*, Papierfabrikant, 35, (1937) 463.
H. Staudinger and *E. Mohr*, Ber., 70, (1937) 2296.

[51] *H. Dolmetsch* and *F. Reinecke*, Zellwolle, 5, (1939) 219, 299.

undergo fractionated solution but *J. Jurisch*[52] has since shown that far better results are obtained by a process of precipitation by which water is gradually added to the acetone solution of the nitrocellulose. To obtain the best results from fractionated precipitation, *G. V. Schulz*[53] (who, on the basis of a series of exhaustive investigations, has fully explained the principles underlying this process) holds that the following precautions should be taken:

1°. Let the solution be as dilute as possible.

2°. Operate at constant temperature.

3°. The formation of the precipitate should be very gradual, so that equilibrium may set in.

4°. Every effort should be made to precipitate a liquid phase (coacervate). (Far greater difficulties are encountered with solid precipitates).

Thus cellulose and cellulose acetate are not convenient starting materials but, as stated above, good results are obtained with solutions of nitrocellulose in acetone precipitated by the addition of water.

G. V. Schulz[54] has shown that an approximately correct determination of the distribution curve by fractionation can only be attained if there is sufficient scattering of the chain length, though even then, of course, the separation of the chain length cannot be anything like complete. Fig. 32, borrowed from *G. V. Schulz*[54] shows the mass distribution curves resulting from the separation of a sample with Gaussian distribution into four fractions (§ 2).

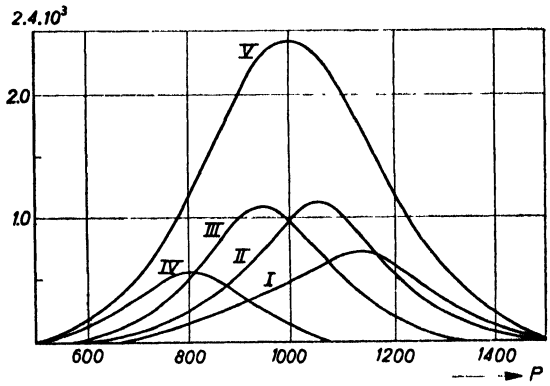


Fig. 32. Result of the decomposition of a substance with *Gauss* division into 4 fractions after *G. V. Schulz* (mass distribution curve).

It will be seen that the polymolecularity of the individual fractions is still considerable. Nevertheless fractionation provides a fairly satisfactory general impression of the molecular composition in cases of this kind. It is important to note that *G. V. Schulz*[54] was able to show that relative divisibility is independent of the molecular weight, i.e., that molecules with $P = 100$ separate from those with $P = 102$ to the same extent as do those with $P = 1000$ from molecules with $P = 1020$. The possibility of fractionation is therefore subject to no upper limit with respect to molecular weight.

[52] *J. Jurisch*, Chem. Ztg., 64, (1940) 269.
[53] *G. V. Schulz*, Z. physik. Chem., B. 46, (1940) 137; B. 47, (1940) 155.
[54] *G. V. Schulz*, Z. physik. Chem., B. 46, (1940) 137; B. 47, (1940) 155.

A few figures may serve to illustrate how the "chain length diagram", or the distribution curves, can be found by experiment and thus the polymolecularity of a sample. We shall confine ourselves to a simple procedure suitable for ordinary practical application. (For a more exact analysis of fractionation see *G. V. Schulz*[54]).

In actual practice the cellulose sample is not separated into infinitely small, but into finite fractions. The degree of polymerization is determined either by the viscometric or the osmotic method. As explained above, the two values may then as a rule be considered equal.

A numerical example is given in Table III. A sample is separated into eight fractions. The weight of each fraction per gram of the original substance is recorded in the first column. Thus if a fraction contains Δn gram-molecules, its weight represents $P \Delta n$ moles of the monomer (cf. the formulae in § 2). The measured average degrees of polymerization P of the fractions are recorded in column 2. Columns 1 and 2 therefore contain the experimental data of the fractionation. Column 3, $\Sigma P \Delta n$, gives the sums of the weights. These totalled weights are plotted against P as the step-ladder curve in Fig. 33 and the latter represents the fractionation diagram (chain length diagram). A continuous curve I is then drawn through the step-ladder curve so as to intersect with it as nearly as possible in the middle of the perpendicular sections of the latter.

This curve represents the integral function $\int P dn$[55].

TABLE III

Numerical example of a fractionation

	1	2	3	4	5	6	7	8	9
	$P\Delta n$	P	$\Sigma P\Delta n$	Middle of the Fraction	Diff. $P\Delta n$	Diff. P	$\frac{P\Delta n}{\Delta P} \times 10^5$	Pm	$\frac{\Delta n}{\Delta P} \times 10^6$
1	0.01	160	0.01	0.005	0.025	80	31	200	1.56
2	0.04	240	0.05	0.03	0.065	110	59	295	2.00
3	0.09	350	0.14	0.095	0.14	125	112	413	2.72
4	0.23	475	0.37	0.255	0.245	135	196	537	3.64
5	0.26	600	0.63	0.50	0.255	140	182	570	2.72
6	0.25	740	0.88	0.755	0.165	185	89	783	1.13
7	0.08	925	0.96	0.92	0.06	175	34	1012	0.34
8	0.04	1100	1.00	0.98					

$$\bar{P}_\eta = \Sigma P \Delta n \,.\, P = 611 \qquad \bar{P}_0 = 1/\Sigma \frac{P\Delta n}{P} = 535$$

[55] In this way the result becomes independent of the chance weight of the individual fractions. Although the step-ladder curve of every parallel experiment will be different, the integral curve will always be the same.

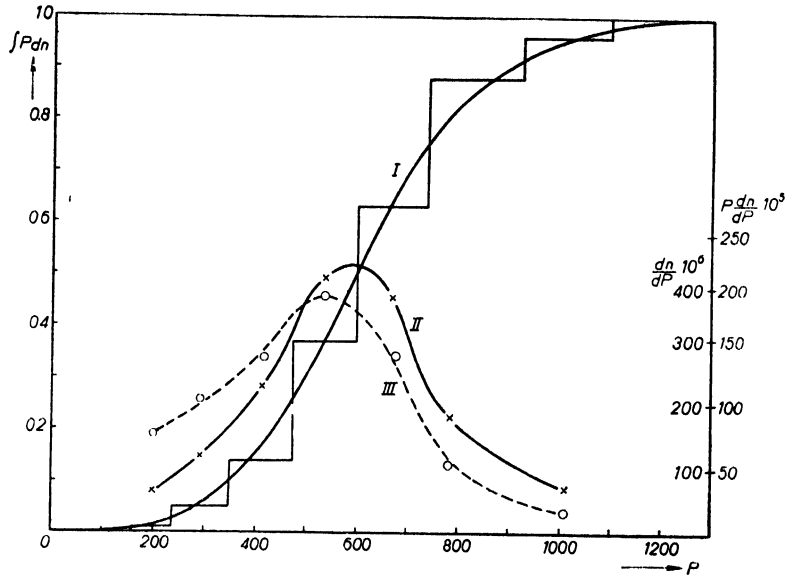


Fig. 33. Example for evaluation of a fractionation. Step-ladder curve: Chain length diagram; I. Interval curve; II. Mass distribution curve; III. Frequency distribution curve.

The mass distribution curve II and the frequency distribution curve III (see § 2) are found from this integral curve by first determining the middle of the fractions (the ordinates of the points of intersection between the step-ladder curve and the integral curve) and then the intervals of $P \triangle n$ (column 5) and the intervals diff. P of P (column 6). Column 7 gives the quotients of the figures in columns 5 and 6, which represent the differential quotients of the integral curve. Plotted against P, they produce the mass distribution curve II, whose maximum corresponds to the weight-average molecular weight. The latter is equal to the viscometrically determined degree of polymerization of the initial unfractionated sample. As will be evident from the equations (3.4) and (3.10) in § 2, it can be calculated thus:

$$\bar{P}_\eta = \Sigma P^2 \triangle n \qquad (3.14)$$

The values $\triangle n/\triangle P$, i.e., the ordinates of the frequency distribution curve III, will be obtained by dividing the figures of column 7 by the average values P_m of the degrees of polymerization P of the individual fractions (column 8). The degree of polymerization corresponding to its maximum represents the real average degree of polymerization $\bar{P}_0$ according to equation (3.3) (number-average). The latter can be calculated from the equation

$$\bar{P}_0 = 1/\Sigma \frac{P \triangle n}{P} \qquad (3.15)$$

The values of $\bar{P}_\eta$ and $\bar{P}_0$ calculated from the figures in the table are given at the foot of the latter. They can also, of course, be determined graphically from Fig. 33.

§ 4. METHODS FOR THE DETERMINATION OF THE CHAIN LENGTH

4.1 Introduction

The experimental evidence on the determination of the molecular weight of high-molecular native and artificial materials is very extensive and, until recently, was uncoordinated and in many respects contradictory. A survey of it is provided by the monograph published in 1936 by *M. Ulmann* [56], to which we may here refer. Latterly, however, there has been some healthy clarification of the subject. We shall now only discuss those methods and results which, according to current views, present a fairly reliable picture of the chain lengths of cellulose and its derivatives. This will entail consideration of the end-group method, the direct determination of the osmotic pressure, the viscosity method, the birefringence of flow method and the precipitation method. The indirect osmotic methods, e.g., the cryoscopic and vapour tension depression methods do not concern us, because the effects produced by solutions of high-molecular substances are almost negligible. The drop in freezing point of a relatively low molecular sample of 20000 molecular weight in an aqueous solution of 0.5% in water would be only 0.00047°, whereas the osmotic pressure would correspond to a water column of 62 mm. Moreover, remarkable and as yet unexplained anomalies are observed from time to time when high-molecular substances are subjected to the "indirect" osmotic methods. The same applies to the "isothermal distillation" method specially stressed by *M. Ulmann* (1936) himself. In this book we shall not give an account of the discussion and attempted explanation of these anomalies [57]. We shall only briefly deal with the determinations of molecular weights by the ultracentrifuge as suggested by *The Svedberg*. This method, which has proved so successful for proteins, gives rise to exceptional difficulties when applied to substances containing chain molecules.

4.2. End-Group Method

In theory, the presence of two end groups with different properties in the molecule of cellulose should make it possible to determine the average length of the chain by chemical means. Yet in each individual case it is necessary first to ascertain what the end groups are. Uncertainty — as there usually is — on this point seriously detracts from the practicability of end group determinations.

We have already seen (p. 82) that scarcely anything is known of the end group in native cellulose. Conditions are sometimes more favourable in degraded samples. One of the two end groups of cellulose decomposed by

[56] "Molekülgrössenbestimmungen bei hochmolekularen Naturstoffen", Dresden and Leipzig 1936.

[57] E.g., see *O. Kratky* and *H. Mark*, Fortschritte d. Chemie organ. Naturstoffe, 1, (1938) 255; *F. Klages*, Kolloid-Z., 93, (1940) 19.

acid hydrolysis is of an aldehydic nature — as in the case of glucose — and therefore has reducing properties. Attempts have been made to utilize the reactivity to alkaline copper solutions for the determination of the end group content [58], but the application of this method to any random sample cannot be expected to disclose any dependable connection with the chain length. Apart from this, the method has been shown by *W. Weltzien* and *N. Nakamura* [59] to be unsuitable for other reasons, and this is also clearly evident from an article recently published by *H. Staudinger* and *K. W. Eder* [60]. Another method derived from sugar chemistry for the estimation of the reducing end group is oxidation with hypoiodous acid (iodine number determination) as evolved by *M. Bergmann* and *H. Machemer* [61]. Apparently this method can be used in certain cases, *H. Staudinger* [62], for instance, having applied it effectively to hydrolysed acetyl cellulose. Nevertheless, this method has also been severely criticized in many quarters [63] and must therefore likewise be eliminated for general application.

A carboxyl group probably occurs in one of the end groups of cellulose subjected to oxidation in an alkaline medium and this carboxyl group can be determined by acid titration or by a method devised by *M. Rebek* or *O. H. Weber* (p. 83). In this way *W. Wehr* [64] established a simple relation between the acid number and chain length in the case of cellulose obtained by the denitration of nitrocellulose samples.

Recently *E. Husemann* and *O. H. Weber* [65] have shown that the aldehyde end group in a polymerhomologous series of celluloses, prepared by graded hydrolytic degradation from cotton, can be oxidized to a carboxylic acid group by boiling with soda alkaline copper hydroxide solution. Then, by determining the carboxyl content by the method evolved by *O. H. Weber* [66], they were able to determine the DP of the samples, which tallied with that found by the viscometric and osmotic methods.

The first end-group determination of cellulose preparations, which gave rise to a good deal of discussion, followed the method of exhaustive methylation devised by *W. N. Haworth* and *M. Machemer* [67]. On the assumptions of the formula given on page 8, the two end groups would contain four instead of

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[58] Copper number after *G. C. Schwalbe*, Ber., 40, (1907) 1347.
[59] *W. Weltzien* and *N. Nakamura*, Ann., 440 (1924) 290.
[60] *H. Staudinger* and *K. W. Eder*, Cellulosechem., 19, (1941) 125.
[61] *M. Bergmann* and *H. Machemer*, Ber., 63, (1930) 316, 2304.
[62] *H. Staudinger*, "Die hochmolekularen organischen Verbindungen Kautschuk und Cellulose", Berlin, 1932, p. 455, 462.
[63] *K. Hess, K. Dziengel* and *H. Maas*, Ber., 63, (1930) 1922; *K. Freudenberg, E. Plankenhorn* and *A. Boppel*, Ber., 71, (1938) 2435; Naturwiss., 26, (1938) 124; *S. Rogowin* and *M. Schlachover*, Z. angew. Chem., 48, (1935) 647; *A. R. Martin, L. Smith, R. L. Whistler* and *M. Harris*, J. Research Natl. Bur. Standards, 27 (1941) 449, have recently re-examined the iodometric method in detail and shown that it may give useful results, if carried out with the necessary precautions.
[64] *W. Wehr*, Kolloid-Z., 88, (1939) 207.
[65] *E. Husemann* and *O. H. Weber*, J. prakt. Chem., 161, (1942) 1
[66] *O. H. Weber*, J. prakt. Chem., 158, (1941) 33.
[67] *W. N. Haworth* and *M. Machemer*, J. chem. Soc. London, A (1932) 2270; cf. Ber., 65, (A) (1932) 43.

three methoxyl groups after exhaustive methylation of the sample. After hydrolysis there would be formed, in addition to trimethyl glucose, a quantity of tetramethyl glucose corresponding to the end group content, and this can be isolated and determined (by distillation of the methyl sugars previously converted to methylglucosides). This method is useful in many cases and has often done good service (notably in starch chemistry), but it calls for careful handling. *K. Hess and F. Neumann* [68] revised it and found that its discoverers had not carried it out properly and that the molecular weights they recorded were on the whole far too low. *Hess* and *Neumann* pointed out the necessity of excluding oxygen during methylation, as otherwise end groups are "oxidized into the substance". If properly carried out under suitable conditions, the method provides a convenient means of establishing degradation of cellulose. In native cellulose *Hess* and *Neumann* were unable to identify any end groups convertible into tetramethyl glucose by this method. For that matter, *K. Freudenberg* and *E. Braun* [69] had come to a similar conclusion before them [70].

Recently *M. L. Wolfrom* and co-workers [71] have used the mercaptal formation of the aldehyde group when reacting with ethyl mercaptan:

$$-CHO + 2\,C_2H_5SH \longrightarrow -CH(SC_2H_5)_2 + H_2O$$

in the determination of the end groups in cellulose. Sulphur is determined in the product. The correspondence found between sulphur content and viscosity of the products seems to indicate that the method yields reasonable results.

In subsequent work *Haworth* and others also failed to detect a measurable quantity of end groups in undegraded cotton [72].

We may sum up by saying that end groups may be determined in certain cases to good effect, but that the utmost care is always necessary and that the appropriate method has to be selected for each individual case.

4.3 *Osmotic Method*

At the present time the direct determination of the osmotic pressure of cellulose samples in very dilute solution is certainly the most reliable and best method for the estimation of chain length. It is, moreover, relatively easy to carry out. As already further explained in Chapter II, § 7, *Van 't Hoff's* law for osmotic pressure does not hold good for substances with

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[68] *K. Hess* and *F. Neumann*, Ber. 70, (1937) 710. Cf. also E. *Leckzyck*, Ber., 71, (1938) 829; *K. Hess* and others, B. 73, (1940) 505.

[69] *K. Freudenberg* and *E. Braun*, Ann., 460, (1928) 288.

[70] Also cf. *K. Hess, D. Grigorescu, E. Steurer* and *H. Frahm*, Ber., 73. (1940) 499, 509, 669, 980; *K. Hess* and *E. Steurer:* Ber. 79, (1940) 669 and *W. N. Haworth, E. L. Hirst, L. N. Owen, S. Peat* and *F. J. Averill*, J. chem. Soc. London, (1939) 1885.

[71] *M. L. Wolfrom* et al., J. Amer. Chem. Soc., 59, (1937) 282; 60, (1938) 1026, 3009; 61, (1939) 1072.

[72] *W. N. Haworth* et al., J. Chem. Soc. London, (1939) 1885.

chain molecules, however dilute the solutions. If the "reduced osmotic pressure" $\frac{p}{c}$ is plotted against the concentration, the result is not a straight horizontal line, as is the case with ideal dilute solutions in accordance with *Van 't Hoff's* relation

$$\frac{p}{c} = \frac{RT}{M}$$

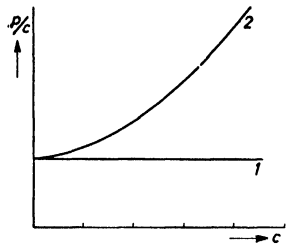


Fig. 34. Reduced osmotic pressure p/c in dependence upon the concentration. 1. Solution of ideal substance. 2. Solution of a high-molecular substance with chain molecules

but as a rule a rising curve (Fig. 34) running either convex or concave with respect to the c axis, or else in an approximately straight line [73]. According to *Wo. Ostwald*, this curve can be represented by the empirical relation:

$$\frac{p}{c} = a + b.c^{n-1}$$

To arrive at reliable values for the molecular weight one must, as this author has emphasized, determine the osmotic pressure at several concentrations, plot the result of the measurements in accordance with Fig. 34 and then graphically extrapolate to concentration nil as follows:

$$\lim_{c = o} \frac{p}{c} = \frac{RT}{M}$$

There is often the difficulty, especially where very high molecular weights are concerned, that the p/c values begin to increase considerably even at the lowest concentrations. As a result, the extrapolation is often very inaccurate, but we have to take this source of error into the bargain. The procedure of extrapolation recommended by *G. V. Schulz* [74] is erroneous, as clearly shown by *J. Duclaux* [75].

Careful experimental work on solutions of nitro-cellulose and acetyl cellulose enabled *A. Dobry* [76] to show that the values $lim \left(\frac{p}{c}\right)_{c = o}$ obtained by graphic extrapolation in measurements of a given sample in various solvents always give the same number and, therefore, the same particle weight. *H. Staudinger* and *F. Reinecke* [77], making similar measurements, obtained the same result. Hence it may be taken for a fact that molecular weights determined in this way actually do represent the true average molecular weight

[73] If association takes place in the solution, the curve may be a descending one.
[74] *G. V. Schulz*, Z. physik. Chem., 158, (1932) 237; A. 176, (1936) 317; 177, (1936) 453 J. prakt. Chem., 159 (1941) 130.
[75] *J. Duclaux*, J. chim. Phys., 41, (1944) 209; 42, (1945) 1.
[76] *A. Dobry*, J. chim. Phys., 32, (1935) 46; Bull. Soc. chim. P. et T., 2, (1935) 1882; Kolloid-Z., 81 (1937) 190, (where there is further literature).
[77] *H. Staudinger* and *F. Reinecke*, Ann., 535, (1938) 47; Ber., 71, (1938) 252.

of the object (also cf. p. 87). For theoretical reasons, however, the solvent may be expected to exert some influence and in certain cases the effect may even be considerable.

Probably the most accurate manner of plotting osmotic pressure data is according to the following equation given by *M. L. Huggins*[78] in which the solvent influence is accounted for:

$$\frac{p}{c} - \frac{RTd_1}{3M_1 d_2^3} \cdot c^2 = \frac{RT}{M_2} + \frac{RT}{M_1 d_2^2} (\tfrac{1}{2} - \mu_1)\, c \qquad (3.16)$$

where p is the osmotic pressure in atmospheres[79], c is the polymer concentration in grams per ml., R the gas constant (in cubic centimetres atmospheres per degree per mol), T is the absolute temperature, d_1 and d_2 are the densities of the solvent and the solute respectively, M_1 and M_2 are the molecular weights of the solvent and the solute and μ_1 is a constant dependent on the nature of the solvent and the solute. The second term on the left in this equation is negligible for many systems, but may be significant in others. By plotting the term or the terms on the left against c, a straight line should be obtained (at least at lower concentrations, whose intercept is inversely proportional to M_2, the number average molecular weight of the polymer):

$$lim \left(\frac{p}{c}\right) = \lim_{c=0} \left(\frac{p}{c} - \frac{RTd_1}{3M_1 d_2^3} \cdot c^2\right) = \frac{RT}{M_2} \qquad (3.17)$$

Where the need is for really reliable absolute determinations of the molecular weight, the osmotic method should be applied nowadays, though unfortunately its application is restricted to non-electrolytic solutions of the cellulose esters and ethers in organic solvents or water[80]. From the $lim \left(\frac{p}{c}\right)_{c=0}$ values obtained by extrapolation, the molecular weight can be calculated according to

$$M = 3.32.10^5\,(1 + 0.00367t) \cdot \frac{c}{p} \qquad (3.18)$$

(p = pressure in mm. water column, c = concentration in grams per litre, t = temperature in degrees centigrade.)

Although it is difficult to measure molecular weights above 100000, approximate estimations can be obtained, with care, up to about 400000 MW. A lower limit is set by the fact that the membranes in organic solvents are

[78] *M. L. Huggings*, J. Amer. Chem. Soc., 64, (1942) 1712; Ind. Eng. Chem., 35, (1943) 980.
[79] The pressure can be calculated in atmospheres by using the equation $p = (h_{obs} - h_\sigma) \times d_s/1033$ where h_{obs} is the observed height in cm of solution, h_σ is the capillary correction constant and d_s is the density of the solution in g/cm³, which should be known to about ± 0.005.
[80] *T. R. Bolam* gives a correction for particles behaving like polyvalent electrolytes in Kolloid-Beih., 39, (1934) 139.

impermeable to the dissolved molecules down to the limit of about $M = 20000$ only. It is therefore advisable to eliminate low fractions before taking osmotic measurements.

It should be borne in mind that osmotic molecular weight determinations are apt to produce distorted results if the dissolved substance tends so strongly to associate in the selected solvent that polymolecular aggregates are formed down to the lowest concentrations within the scope of measurement, in which case even the extrapolation formulæ given above fail. *E. Steurer*[81] recently drew attention to a striking example of this in solutions of ethyl cellulose in benzene. Unambiguous *lim p/c* values were obtained when smaller quantities of a polar solvent (0.3% ethyl alcohol) were added, or other solvents were used. In doubtful cases, therefore, several solvents should be tried out.

As far as apparatus is concerned, *A. Dobry*[82] and *G. V. Schulz*[83] have proposed arrangements which any laboratory could easily set up. The usually very slow establishment of equilibrium (some times taking several days) can be accelerated by giving the approximate height of ascent in the capillary that is expected. *O. Albert* and *O. Kratky*[84] have described an osmometer fitted with agitators by means of which equilibrium is established very rapidly[85].

Somewhat more complicated arrangements with pressure compensation are described by *P. van Campen*[86], *Ch. F. Boissonnas* and *K. H. Meyer*[87] and others[88]. *G. Gee*[89] described not long ago a comparatively simple osmometer suitable both for the pressure compensation and for the equilibrium method.

4.4. Viscosity Method

α. *Theoretical Basis.*

For quite some time the conditions governing the viscosity of dilute solutions of substances composed of chain molecules were not understood. According to the *Einstein* viscosity law deduced for spherical particles, the specific viscosity of a solution is independent of the particle size and increases proportionally with the concentration. It soon became evident that matters stand quite differently where substances containing thread molecules are concerned.

H. Staudinger had substantial experimental evidence to show that the specific viscosity of very dilute solutions of linear-polymeric substances increases

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[81] *E. Steurer*, Z. physik. Chem., A. 190, (1941) 1, 16; Kolloid-Z., 96, (1941) 333.
[82] *A. Dobry*, Kolloid-Z., 81, (1937) 190 (where there is further lit.).
[83] *G. V. Schulz*, Z. physik. Chem., 158, (1932) 237; A. 176, (1936) 317; 177, (1936) 453.
[84] *O. Albert* and *O. Kratky*, Oester. Chem., Ztg., Vol. 7/8 (1940).
[85] For experimental errors due to diffusion see: *W. W. Lepeschkin*, Z. physik. Chem., A. 186, (1940) 180; *G. V. Schulz*, J. prakt. Chem., 159, (1941) 130; more explicit discussion of errors: *E. Husemann* and *G. V. Schulz*, Z. physik. Chem., B. 52, (1942) 1.
[86] *P. v. Campen*, Rec. trav. chim., 50, (1931) 915.
[87] *Ch. F. Boissonnas* and *K. H. Meyer*, Helv. chim. acta, 20, (1937) 783.
[88] For further details see *M. Ulmann's* monograph: "Molekülgrössen-Bestimmungen hochpolymerer Naturstoffe", Leipzig and Dresden 1936.
[89] *G. Gee*, Trans. Faraday Soc., 36, (1940) 1162.

proportionally with the concentration and, moreover, in proportion to their molecular weight or their degree of polymerization, and it was upon this fact that he founded a method of molecular weight determination. This so-called *Staudinger* viscosity law was thereafter repeatedly attacked by experimenters and, even more so, by theorists.

Staudinger had taken the view that thread molecules in solution were rigid rods and defended this view for many years. This assumption was incompatible with the theories very fully developed by organic chemistry on the shape and flexibility of molecules and also conflicted with all the prevailing hydrodynamic theories. These stated that the specific viscosity of a suspension of rodlets of a given concentration increases in direct ratio to the second power of the proportion between length and width of the rodlets and so, for molecules of a polymerhomologous series, in proportion to the second power of the molecular weight.

According to the statistics, drawn up by *W. Kuhn* in 1932, of the freely suspended chain molecule with the free rotation of consecutive chain links towards each other which the doctrine of organic structure propounds, the molecule in the solution permanently assumes a varying kinked shape. The average external dimensions of this convoluted molecule can be calculated. Considering the convoluted molecule as such, and again as an anisodiametrical particle, it could be demonstrated that the ratio between its length and diameter increases by about $M^{1/2}$ (M = molecular weight). Therefore, in conformity with *Staudinger's* law, the specific viscosity should increase in proportion to $(M^{1/2})^2 = M$. This result was by no means satisfactory; for, on the one hand improved theoretical speculations produced somewhat different results, and, on the other, why, it was asked, should the molecule, kinked at random, be treated as a rigid, rod-like object? There was more reason to suppose that the convoluted molecule is an exceedingly mobile organization, readily changing shape in response to external effects and that, if caught in a field of flow, it will be liable to change its shape, in the sense that there will be a certain stretching of the chain in the direction of flow. From the theoretical point of view, this set a new hydrodynamic problem, viz., that of calculating by how much the inner friction would be increased by these conditions [90]. The first step in this direction was taken by *F. H. Müller* [91]. The calculation was then worked out in greater detail by *W. Kuhn* and *H. Kuhn* [92] and, at about the same time, by *J. J. Hermans* [93].

It was found that *Staudinger's* viscosity law must hold good for a really free kinked molecule subject only to the laws of chance, so representing an open

[90] *P. H. Hermans, J. J. Hermans* and *D. Vermaas*, Kolloid-Z., 105, (1944) 199.
[91] *F. H. Müller*, 4. Forschungstagung Zellwolle und Kunstseidering, Weimar, supplement to "Die Chemie" 47, (1943) p. 81.
[92] *W. Kuhn* and *H. Kuhn*, Helv. chim. acta, 26, (1943) 1394.
[93] *J. J.Hermans*, Kolloid-Z., 106, (1944) 22.

clew freely infiltrated by the solvent. If, however, the molecule is everywhere or in parts so dense as no longer to be infiltrated, modifications occur in the sense that the viscosity of the solution increases less than proportionally to the length of the chain. In the extreme case in which the clew is not infiltrated at all, its hydrodynamic behaviour is that of a rigid particle and, if *W. Kuhn*[94] is right, the viscosity should increase proportionally by $M^{0.6}$ to $M^{0.9}$.

According to *W.* and *H. Kuhn*[92], it is more common for the lower terms of a polymerhomologous series to behave like a freely infiltrated clew, the modifications towards the behaviour of non-infiltrated clews gradually taking place as the molecular weight increases. It will be readily understood that, where we have very long chains kinked at random, there is greater likelihood of various parts of the clew cohering either permanently or temporarily (inner association). This is an exactly similar process to that which takes place between neighbouring molecules in concentrated solutions. Therefore, if it takes place there will be modifications of *Staudinger's* law in a homologous series with increasing molecular weight, in that there will be too little increase in viscosity.

This offers an acceptable explanation of the much discussed departures from *Staudinger's* law which have so often been noticed in this — and never in the reverse — direction in experiments, and suggests other inferences as to the condition of the molecules in the solution (cf. § 5). With increasing chain length these departures will sooner occur according as the chains are more flexible. Cellulose chains being rather stiff ones and, hence, giving rise to rather "open" clews up to a relatively high molecular weight, it may be expected that cellulose and its derivatives are substances, which will follow *Staudinger's* equation particularly well over a fair range of chain length.

The current theoretical principles based upon the calculations of *W.* and *H. Kuhn* and of *J. J. Hermans* may now be considered reliable, especially as they can be successfully applied to the phenomena of birefringence of flow and have been substantiated quantitatively by appropriate examples in several directions. Furthermore, the size of *Staudinger's* viscosity constant can thereby be quantitatively equated with the average "degree of kinkiness" of the molecules. We shall revert to this in the appropriate sections.

β. *Discussion of the Practical Aspects of the Viscosity Method.*

The *Einstein* equation cannot be applied to solutions of high-molecular substances consisting of chain molecules. The quantity η_{sp}/c here increases very steeply with the concentration. In numerous papers *Staudinger* has

[94] *W. Kuhn*, Kolloid-Z., 68, (1934) 2; 101, (1934) 248.

attempted to show that η_{sp}/c, if determined for very dilute solutions, is approximately proportional to the molecular weight M according to the equations

$$\eta_{sp}/c_{gm} = K_m \cdot M \qquad \text{or} \quad \eta_{sp}/c = K_m P \qquad (3.19)$$

where c_{gm} and c are the concentration of the solution expressed in "Grundmolen" (mol. weight of the monomeric residue; cf. p. 82) and the concentration in g per litre respectively; P is the degree of polymerization and K_m a constant which is characteristic for the substance and the solvent in question.

The practical procedure resolves itself into determining the limiting value of η_{sp}/c at infinite dilution, which represents the differential quotient $d\eta_{sp}/dc$ for $c = 0$ and, therefore, the initial slope of the η_{sp} versus c curve [95]. The best method is to plot the experimental values of η_{sp}/c against c. According to *H. Staudinger* and *W. Heuer* [96] it may be of advantage to plot the logarithm of η_{sp}/c against the concentration. Another procedure of extrapolation was recently recommended by *G. V. Schulz* and *F. Blaschke* [97]. The quantity $\lim_{c=0} \eta_{sp}/c$ thus determined is now generally termed "intrinsic viscosity" and denoted by the symbol $[\eta]$ [98]. It should, however, be emphasized that, in order to obtain accurate results, it is also necessary to extrapolate the viscosity measurements to zero velocity gradient of flow. Though *H. Staudinger* and *M. Sorkin* [99] have already shown that the value of $\lim_{c=0} \eta_{sp}/c$ depends on the rate of flow and the more so according as the molecular weight of the linear polymer becomes greater, this point has often been overlooked. Recently a fundamental study of this point was published by *W. J. Lyons* [100] and this author has demonstrated that considerable errors can arise if the dependence of viscosity on the velocity gradient is neglected, since the effect does not disappear towards infinite dilution.

According to *Staudinger*, the determination of $[\eta]$ from viscosity measurements permits of determining the molecular weight in a very easy and simple way, provided the value of the constant K_m be known from comparison with other methods of molecular weight determination. In table IV we have

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[95] Cf. *M. L. Huggins*, J. Am. Chem. Soc., 64, (1942) 2716; *A. R. Kemp* and *H. Peters*, Ind. Eng. Chem. Ind. Ed., 33, (1941) 1263; 34, (1942) 1192.
[96] *H. Staudinger* and *W. Heuer*, Z. physik. Chem., A 171, (1934) 129; cf. also *H. Staudinger* and *M. Sorkin*, Ber., 70, (1937) 1993.
[97] *G. V. Schulz* and *F. Blaschke*, J. prakt. Chem., 158, (1941) 130; cf. also *A. Matthes*, Z. angew. Chem., 54, (1941) 517 and *H. L. Bredée*, J. prakt. Chem., 159, (1941) 146.
[98] "Grenzviskosität" according to *K. H. Meyer*, Hochpolymere Chemie, Leipzig 1940, Vol. II p. 23. See also the German nomenclature proposed by *W. Philippoff*, Kolloid. Z., 98, (1942) 90.
[99] *H. Staudinger* and *M. Sorkin*, Ber., 70, (1937) 1993.
[100] *W. J. Lyons*, J. Chem. Phys., 13, (1945) 43.

recapitulated the data given by *Staudinger* and co-workers for cellulose and its derivatives [1].

TABLE IV

K_m Constants of Cellulose and its Derivatives [1]

SUBSTANCE	SOLVENT	$K_m \cdot 10^4$
Cellulose	Schweizer's reagent	5
	Tetraethyl ammonium hydroxide	4.2
	Sodium hydroxide	5.5
	Copper-ethylene diamine	8.8
	Calcium thiocyanate	8.0
	Phosphoric acid	18—21 [2]
	Sulphuric acid	20
	Sodium hydroxide	7.0 [6]
Cellulose nitrate	Acetone	11 [7]
(12—13% N)	Butyl acetate	14
Cellulose triacetate	m-Cresol	6.3
	Chloroform	5.3
Cellite (40—43% $CH_3.COO$)	m-Cresol	8
	Acetone	9
Methyl cellulose		
24—54 % CH_3O	m-Cresol	14—12.5 [3]
36—45.6% CH_3O	Chloroform	11
30—45.6% CH_3O	Glacial acetic acid	10
22—33 % CH_3O	Water	11
Ethyl cellulose	m-Cresol	11
45—54.0% C_2H_5O	Chloroform	12.5
Butyl cellulose (2.3 OH subst.)	Chloroform	10.5 [4]
Benzyl cellulose (2.2 OH subst.)	Chloroform	10.5 [4]
Cellulose xanthates [5]		
10% S	2n Sodium hydroxide	4.6
15% S	2n Sodium hydroxide	3.9
20% S	2n Sodium hydroxide	2.8
23% S	2n Sodium hydroxide	2.5

[1] If not otherwise indicated, these data were borrowed from *H. Staudinger, F. Reinecke* and *G. Daumiller*, Ann., 535, (1938) 47; Ber., 70, (1937) 2512.

[2] On a former occasion *Staudinger* indicated 12.4. 10^{-4} for the K constant in phosphoric acid (Melliand Textilber., 18, (1937) 53. Compare also *Alf af Ekenstamm.*, Ueber die Cellulosclösungen in Mineralsäuren, Lund 1936; Ber., 69, (1936) 549, 553. *H. Staudinger* and *R. Mohr* gave the reason for the increase to about 20: Ber., 70, (1937) 2296.

[3] All according to methoxyl content.

[4] According to *H. Staudinger* and *F. Reinecke*, Ber., 71, (1938) 252.

[5] According to *H. Staudinger* and *F. Zapf*, J. prakt. Chem., 156, (1940) 261.

[6] According to *E. Schwarz* and *W. Zimmermann*, Melliand Textilber., 22, (1941) 525.

[7] According to later published data by *E. Husemann* and *G. V. Schulz*, Z. physik. Chem., B. 52, (1942) 1, - $K_m = 8.2 \times 10^{-4}$ applies to nitrated samples obtained by the hydrolytic decomposition of native cellulose, and $K_m = 10.2 \cdot 10^{-4}$ to those resulting from oxidative decomposition.

The experimental material on the basis of which *Staudinger* and his school attempted to found the viscosity method is very extensive (cf. the special references given at the end of this chapter). They relied in particular on the constancy of the degree of polymerization in polymerhomologous chemical transformations and on comparison with the osmotic method (cf. also p. 134).

Nevertheless, and regrettable as it may be, the limits of applicability of the viscosity method can by no means be traced at the present moment and the

accuracy of the values of the K_m constants as given in Table IV are open to doubt in the majority of cases. *Staudinger's* experiments, and even the viscosity method itself, have been more than once severely criticised. At present the situation cannot be considered as definitely clarified.

There is a consensus of opinion that [η] represents a characteristic constant for a given polymer-solvent system and that this quantity increases with the chain length of the polymer[8]. This is an important practical advantage, since it permits the arrangement of the members of a polymerhomologous series in the sequence of their average molecular weights, provided the influence of the molecular weight distribution in each object be correctly accounted for (cf. this Chapter, § 2, p. 87). For comparative work, therefore, the viscosity method is no doubt of considerable value and has, indeed, already rendered signal service in both technical and scientific work.

We shall now weigh the pros and cons and consider the more recent developments of the subject.

1°. Theoretical objections to *Staudinger's* law, as being devoid of a theoretical basis, are no longer relevant. It would seem, on the contrary, that it has a very good theoretical background now in the work of *W. Kuhn, M. L. Huggins* and of *J. J. Hermans*, though the theory is admittedly subject to some limitations. The most important of these is perhaps the failure of *Staudinger's* simple relationship to apply to a very large range of molecular weights and the fact that departures from it are to be expected at high values of M (and also for the lowest members of a polymerhomologous series). With high molecular weights the value of [η] will increase less than in proportion to M. All deviations so far reported actually are in conformity with this theoretical expectation.

2°. Experiments made by several other investigators have led to results consistent with *Staudinger's* rule. The molecular weight determinations of cellulose or cellulose derivatives with the ultracentrifuge (sedimentation equilibrium) carried out by *E. O. Kraemer, R. Signer* and *P. v. Tavel*[9] yielded results in approximate agreement with this rule, though partially leading to K_m values about half those given by *Staudinger*. (Departures found in polystyrene solutions[10] have been rejected by *Staudinger* on the ground that the molecules were branched and not linear.)

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[8] *A. Dobry*, Kolloid. Z., 81, (1937) 190, has shown that the value of [η] was also independent of the solvent used in a number of instances relating to cellulose nitrate and cellulose acetate and would thus even represent a constant characteristic of the polymer alone. This may not, however, be considered as a general rule, as was already recognized by *Staudinger* himself (cf. Table IV).

[9] *E. O. Kraemer*, Ind. Eng. Chem., 30, (1938) 1200; *P. Signer* and *P. v. Tavel*, Helv. chim. Acta, 21, (1938) 535.

[10] *R. Signer* and *H. Gross*, Helv. chim. Acta, 17, (1934) 59, 335, 726.

3°. Measurements made by *W. H. Carothers* and *E. O. Kraemer*[11] with polyhydroxydecanoic acids, having molecular weight known from terminal group titration, agreed well with the viscosity rule up to $M = 25000$. The same has been reported by *W. O. Baker, C. S. Fuller,* and *J. Heiss*[12] for polyhydroxyundecanoic acids up to $M = 25000$. These investigations are particularly noteworthy because the substances used were very well characterized and their molecular weights known from an independent, obviously reliable determination.

4°. From the viscosity and the molecular weights of fractionated cellulose nitrates determined by *H. Mosimann* in accordance with the method of sedimentation velocity in *The Svedberg's* ultracentrifuge[13], K_m constants between 10 and 11×10^{-4} can be calculated in the range of $P = 110$ to $P = 2300$. This tallies with the *Staudinger* value given in Table IV for cellulose nitrate in acetone. In a later paper, *Mosimann* reported that the relationship between M and $[\eta]$ is not a linear one[14]; the divergences; however, were not very serious[14a].

5°. The K_m constant for methylcellulose in water given by *Staudinger* was also found to agree well with the results of molecular weight determinations from sedimentation velocity and birefringence of flow (cf. Table V in the next section).

6°. *A. M. Sookne* and *M. Harris*[14b] investigated the relationship between viscosity and osmotic pressure of a series of carefully fractionated cellulose acetates in acetone and found a linear relationship between the molecular weight deduced from osmotic pressure and $[\eta]$ up to a DP of about 300. At higher molecular weights the linearity of the relation ceases. The K_m constant following from this work was, however, somewhat lower than the one given by *Staudinger.*

Several authors have pointed out (and this was recently stressed by *Baker, Fuller,* and *Heiss,* loc.cit.) that, in order to obtain satisfactory agreement down to the lowest members of a polymerhomologous series, an equation of the form

$$[\eta] = KP + B \qquad (3.20)$$

should be used[15]. Thus, instead of a single constant, two characteristic constants are needed for each solute-solvent system.

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[11] *W. H. Carother* and *F. J. van Natta,* J. Am. Chem. Soc., 55, (1933) 4714; *E. O. Kraemer* and *W. D. Lansing,* J. Am. Chem. Soc., 55, (1933) 4319.
[12] *W. O. Baker, C. S. Fuller* and *J. Heiss Jr.,* J. Am. Chem. Soc. 65, (1943) 2142, 3316.
[13] *H. Mosimann,* Helv. chim. acta, 26, (1943) 61.
[14] *H. Mosimann,* Helv. chim. acta, 26, (1943) 393.
[14a] Recently, *I. Jullander* came to the same conclusion; Thesis Uppsala (1945); J. Polymer Sci 2 (1947) 329.
[14b] *A. M. Sookne* and *M. Harris,* Ind. Eng. Chem. 37, (1945) 37.
[15] Cf. also *E. O. Kraemer* and *Van Natta,* J. Phys. Chem., 36, (1932) 3175; *K. H. Meyer* and *A. van der Wijk,* Helv. chim. acta, 18, (1935) 1067; *H. Staudinger* and *G. Daumiller,* Ann., 529, (1937) 219; *J. J. Flory* and *P. B. Stickney,* J. Am. Chem. Soc., 62, (1940) 3032; *R. M. Fuoss* and *D. J. Maed,* J. Phys. Chem., 47, (1943) 59.

Departures from *Staudinger's* simple relation have likewise been reported on more than one occasion.

1°. A number of cases where evidence was against proportionality of $[\eta]$ and M were recently listed by *K. H. Meyer*[16]. Compare also *G. V. Schulz* and *A. Dinglinger*[17] and *Staudinger's* answer to this criticism[18]. In some cases the departures were ascribed to branching of the molecules, e.g., those found in polystyrene solutions[19].

2°. *A. Matthes*[20] has recently reported considerable divergences in solutions of superpolyamides. Since he used unfractionated substances, the weight of this result cannot well be estimated.

3°. *N. Gralén* recently published extensive material on ultracentrifugal molecular weight and viscosity determinations of cellulose in cuprammonium solutions and came to the conclusion that the results were not consistent with *Staudinger's* rule. As this investigation appears to be an important one, we shall revert to it more fully in Section 4.7 (p. 115). As will be shown later, the inference from *Gralén's* data is that $[\eta]$ is approximately proportional to M up to $M \sim 7 \times 10^5$ $(P \sim 3000)$. The K_m constant of $1.7 \cdot 10^{-4}$ following from these data is, however, considerably smaller than that given by *Staudinger*. (There is evidence, however, that *Gralén's* figures may be too high; cf. § 4.7).

Various authors[21] have stated that, in the domain of high degrees of polymerization, the *Staudinger* equation should be replaced by the empirical expression:

$$[\eta] = KM^a \qquad (3.21)$$

where K and a are two constants characteristic of a given polymer-solvent system (a is always $\leqslant 1$).

Very few reliable values of K and a fitting this equation are available as yet. The following may be quoted:

	Temp.	K	a
Cellulose in cuprammonium hydroxide[22]	25°	1.7×10^{-4}	0.77
Cellulose nitrate in acetone[23]	27°	3.8×10^{-5}	1.0
Cellulose acetate in acetone[24]	25°	1.5×10^{-4}	0.82

[16] *K. H. Meyer*, Kolloid-Z., 95, (1941) 70.
[17] *G. V. Schulz* and *A. Dinglinger*, J. prakt. Chem., 158, (1941) 136.
[18] *H. Staudinger*, Kolloid-Z., 198, (1942) 330.
[19] *R. Signer* and *H. Gross*, Helv. chim. acta 17, (1934) 59, 335, 726.
[20] *A. Matthes*, J. prakt. Chem. 162, (1943) 245.
[21] *H. Mark*, Z. Elektrochem., 40, (1934) 449; *G. V. Schulz* and *B. Jirgensons*, Z. physik. Chem., B. 46, (1940) 105; *R. Houwink*, J. prakt. Chem., 157, (1940) 15; *J. J. Flory*, J. Am. Chem. Soc., 65, (1943) 372; *T. Alfrey*, *A. Bartovics* and *H. Mark*, J. Am. Chem. Soc., 65, (1943) 2319.
[22] Calculated from Gralén's data; cf. § 4.7; *W. Badgley*, *V. J. Frilette* and *H. Mark*, Ind. Eng. Chem., 37, (1945) 227 deduced $K = 8.5 \times 10^{-5}$ and $a = 0.81$ from the same observations. Cf. § 5.
[23] *M. L. Huggins*, Ind. Eng. chem. 35, (1943) 980.
[24] *A. Sookne*, *M. Harris*, *H. A. Rutherford* and *H. Mark*, J. Res. Natl. Bur. Standards, 29. (1942) 123; Polymer Bulletin 1, (1945) 17.

It should be emphasized that, even in using these figures, the molecular weights obtained may be in error to the extent of at least 30 per cent. and often even more.

The K for cellulose nitrate in acetone may be compared direct with *Staudinger's* value since a = 1. In *Staudinger's* equation:

$$\eta_{sp}/c = [\eta] = K_m P \qquad (3.22)$$

$[\eta]$ is based on the concentration in g/litre. The figures of K given here refer to the more usual measure of the concentration in g/100 ml. Hence we have the relationship:

$$K_m = KM_g/10$$

where M_g is the molecular weight of the monomeric residue. Considering cellulose trinitrate (M_g = 287), we obtain: $K_m = 3.8 \times 10^{-5} \times 28.7 = 10.9 \times 10^{-4}$, which tallies well with the value 11×10^{-4} from Table IV[24a]. The values for cellulose and cellulose acetate do not conform to those given in Table IV.

If $a \neq 1$, the values of K cannot be directly compared with those of K_m. Writing $[\eta] = K^*_m P^a$ (c in g/litre), we obtain

$$K^*_m = KM^a_g/10 \qquad (3.23)$$

($K^*_m = K_m$ only when $a = 1$).

The value of $[\eta]$, of course, always depends on the unit of concentration chosen. For practical purposes it may be of interest to list the following relationships.

Let c be the concentration in g per 100 ml. solvent
c_g „ „ „ in g per 100 g solvent
c_v „ „ „ in ml per 100 ml. solvent

and further: d = density of the solute and D = density of the solvent, then we have

$$\lim_{c \to 0} \eta_{sp} = [\eta] \cdot c \qquad \lim_{c \to 0} \eta_{sp} = [\eta]_g c_g \qquad \lim_{c \to 0} \eta_{sp} = [\eta]_v \cdot c_v \qquad (3.24)$$

These quantities are related to each other and to the K_m constant of *Staudinger* as follows[25].

$$[\eta]_g = [\eta] \cdot D \qquad [\eta]_v = [\eta] \cdot d \qquad (3.25)$$

$$[\eta] = PK_m/10 \qquad [\eta]_g = PK_m D/10 \qquad [\eta]_v = PK_m d/10 \qquad (3.26)$$

Owing to the very limited accuracy with which the constants K_m, K and a are known, the absolute values of M obtained by the viscosity method will

[24a] Note added in proof: This value applies to a nitrogen content of 13.5—13.6 %. The K_m constant has meanwhile been shown to vary considerably with the N-content. Cf. H. A. Wannow, Kolloid. Z., 102, (1943) 29 and particularly I. Jullander, Thesis Uppsala 1945; Arkiv för Kemi, Mineralogi och Geologi 21 A, (1945) 101 (in English).

[25] Only $[\eta]_g$ and $[\eta]_v$ are dimensionless quantities; both $[\eta]$ and K_m have the dimension m^{-1}[13].

be merely of the correct order of magnitude and will never represent accurate figures.

Viscometric determinations of cellulose in cuprammonium hydroxide and of cellulose nitrate in acetone will claim first consideration in artificial fibre research (particularly cellulose nitrate as regards fractionation; cf. § 3). Dilute cellulose xanthate solutions may also come into the picture for relative measurements [26]. The K_m constants hitherto published for these solutions, however, are still very uncertain. *E. Schwartz* and *W. Zimmerman* [27] have recommended viscosity determinations of regenerated celluloses in 10% sodium hydroxide solutions prepared at -5°. Regenerated celluloses would be soluble in this solvent up to $P = 600$.

Viscosity determinations in cuprammonium hydroxide require rigorous exclusion of oxygen and, therefore, a rather complicated apparatus. For the details we refer to the literature [28]. *W. W. Russel* and *N. T. Woodbury* [29] recommended the use of 1.96 N solutions in dibenzyl dimethyl ammonium hydroxide (Triton F) for viscosity determinations on cellulose and recently cupric ethylene diamine solutions have been recommended [30] which are not so sensitive to oxygen. Perhaps it is also of some interest to reconsider a proposal made by *A. af Ekenstamm* [31] to use solutions of cellulose in phosphoric acid.

The *Ostwald* viscometer is usually employed. For the selection of the correct dimensions of this apparatus and several measures to minimize the experimental error, we refer to papers by *G. V. Schulz* [32], *H. G. Bungenberg de Jong* [33] and *H. Mark*.[34] *A. af Ekenstamm* [35] has provided a formula for the correction of the density difference between the solvent and the solution. The influence of the velocity gradient in cuprammonium solutions has been discussed by *W. J. Lyons* [35a].

It should be mentioned in conclusion that several formulas have been suggested by means of which the intrinsic viscosity can also be calculated from viscosity determinations at concentrations higher than extreme dilution. Such formulas, by which $[\eta]$, or a constant proportional to $[\eta]$, can be calculated, have been

[26] To avoid errors due to the electroviscous effect in the case of these ionized derivatives 2 n sodium hydroxide should be employed as a solvent. Cf. *H. Staudinger* and *F. Zapf*, J. prakt. Chem., 156, (1940) 261.
[27] *E. Schwartz* and *W. Zimmermann*, Melliands Textilber., 22, (1941) 525.
[28] E.g., cf. *D. A. Clibbens* and *A. Geake*, J. Textile Inst., 19, (1927) T 77; *E. K. Carver*, Ind. Eng. Chem. Anal., Ed 1, (1929) 49; *D. A. Clibbens* and *A. A. Little*, J. Textile Inst., 27, (1936) T 285; *R. T. Mease*, J. Research Natl. Bur. Standards, 22, (1939) 271; *A. Lottermoser* and *F. Wultsch*, Kolloid. Z., 83 (1938) 194.
[29] *W. W. Russel* and *N. T. Woodbury*, Ind. Eng. Chem. Anal. Ed., 12, (1940) 151.
[30] *F. L. Strauss* and *E. M. Levy*, Paper Trade J., 114, (1942) 31.
[31] *A. af Ekenstamm*, Ueber die Celluloselösungen in Mineralsäuren, Lund 1936.
[32] *G. V. Schulz*, Z. Elektrochem., 43, (1937) 479.
[33] *H. G. Bungenberg de Jong*, First Report on Viscosity and Plasticity, Amsterdam 1935, p. 110.
[34] H. *Mark*, in *A. Weissberger*, Physical Methods of Organic Chemistry, New York 1945, Vol. I, p. 135.
[35] *A. af Ekenstamm*, Ueber die Celluloselösungen in Mineralsäuren, Lund 1936, p. 82.
[35a] *W. J. Lyons*, J. Chem. Phys., 13, (1945) 43.

given by *H. L. Bredée* and *J. de Booys* [36] and by *W. Philippoff* [37]. *A. Matthes* has shown how these formulas can be handled conveniently [38], but caution is necessary when applying them to solutions of moderate and high concentration [39].

W. J. Lyons has recently gone thoroughly into the question of determining $[\eta]$ from viscosity measurements with the aid of formulas accounting for the influence of concentration, in the case of cuprammonium solutions of cellulose [40]. He recommends the use of a modification of the *Philippoff* equation, which was developed empirically and has the advantage of yielding a uniform value for the intrinsic viscosity of a given solution regardless of changes in the velocity gradient at which the experiments are performed. This new equation:

$$\eta_{sp} + 1 = \left(1 + \frac{c}{\lambda}\right)^8 + \left([\eta] - \frac{8}{\lambda}\right) C \qquad (3.27)$$

has been found to agree well with data on cuprammonium solutions of cellulose in concentrations below 0.5 g per 100 cm³. The parameter λ is a function of the velocity gradient. Both $[\eta]$ and λ can be determined if measurements are taken at various concentrations. It could be shown that the form of equation (3.27) has a theoretical background in the reaction-rate theory of viscosity as given by *H. Eyring*.

4.5. *Birefringence of Flow Method*

The theory of the behaviour of kinked molecules in flowing solutions, referred to earlier as having been evolved by *W.* and *H. Kuhn* [41] and at the same time by *J. J. Hermans* [42], and perfected particularly by the former, has also supplied a firm foundation for molecular weight determination from optical data, which opens up very promising prospects for the future in several respects.

The straightening of optically anisotropic particles under the influence of a gradient of flow is known to be responsible for birefringence in solutions. Each monomeric residue of a polymer is to be regarded as an optically anisotropic structure. With a stationary solution, the directional distribution of the monomeric residues in the kinked chains is completely devoid of any average preferential orientation. If, however, the molecular chains are exposed to the effects of a flow gradient, the distribution of the monomeric residues becomes anisotropical and, as a result, birefringence occurs. A distinction

[36] *H. L. Bredée* and *J. de Booys*, Kolloid-Z., 79, (1937) 31, 43; 91, (1940) 39.
[37] *W. Philippoff*, Kolloid-Z., 98, (1942) 90.
[38] *A. Matthes*, Kolloid-Z., 54, (1941) 517.
[39] The viscosity of technical spinning solutions, for instance, is not merely determined by their concentration and the average DP, but may also depend on their previous history and other factors.
[40] *W. J. Lyons*. J. Chem. Phys., 13, (1945) 43.
[41] *W.* and *H. Kuhn*, Helv. chim. acta, 26, (1943) 1394.
[42] *J. J. Hermans*, Kolloid. Z., 106, (1944) 22; Rec. trav. chim., 63, (1944) 25, 205.

is necessary between the amount and the orientation of this birefringence (i.e., axial relation and position of the optical ellipsoidal index with reference to the direction of flow).

The phenomenon can be conveniently observed in a solution placed between two co-axial cylindrical surfaces one of which is rotated relatively to the other.

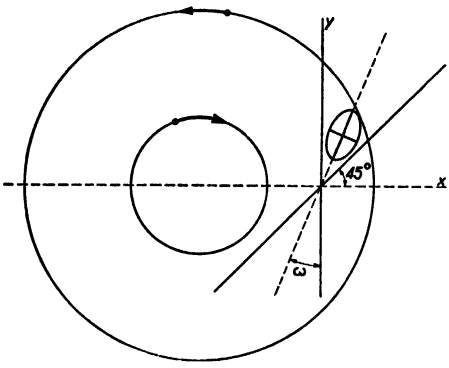


Fig. 35

Figure 35 shows in diagram the position of the ellipsoidal index relatively to the coordinate system x, y, the x-axis of which is radially and the y-axis tangentially to the rotating cylinder jackets. The y-axis thus lies in the direction of flow. The theory states that in low velocities of flow the main axes of the ellipsoidal index enclose angles of 45° with x and y. As the velocity of flow increases, the ellipsoidal index turns through an angle ω out of this initial position; the angle ω is denoted as the orientation of the birefringence of flow (hence the extinction angle with reference to the x-axis amounts to 45° + ω).

The amount of the birefringence is given by the difference $n_1 - n_2$ between the principal refractive indices (represented by the length of the main axes of the ellipsoidal index).

In the case of infiltrated clews (cf. p. 103), the theory gives for low velocity of flow:

$$n_1 - n_2 = q\,\eta_0 \,.\, c \,.\, K_\nu \,.\, P \qquad (3.28)$$

where q represents the gradient of flow (cm/cm.sec.), η_0 the viscosity of the solvent, c the concentration in grammolecules of monomeric residue/ml, P the DP and K_ν the *constant of birefringence of flow*. In the same way as explained for the viscosity and the osmotic pressure, it is possible to extrapolate to the limit $[(n_1-n_2)/q\eta_0 c]$ (for $q\eta_0 = 0$ and $c = 0$) from the experiments in which the gradient of flow and the concentration are varied. The value so obtained can, in analogy with the intrinsic viscosity, be denoted as the birefringence of flow number [ν]. We then have:

$$\lim \left(\frac{n_1-n_2}{q\,\eta_0 c}\right)_{q\eta_0 = 0;\ c = 0} = [\nu] = K_\nu \,.\, P \qquad (3.29)$$

Similarly, from the measurement of the angle of orientation ω (which depends upon the concentration) as a function of q, we get the *orientation number* [ω], which, according to the theory, must have the value of

$$\lim \left(\frac{\omega}{q\,\eta_0}\right)_{q\eta_0 = 0} = [\omega] = K_\omega . P^2 \qquad (3.30)$$

where K_ω represents the *constant of orientation*.

The constants K_ν and K_ω represent numerical values characteristic for every polymerhomologous series (provided the clews be freely infiltrated). They are determinable, of course, if objects are available whose molecular weights have been determined in some other way. If they are known, P can be determined by either method.

Nevertheless, by combining the birefringence of flow with viscosity measurements, it is possible to determine "absolute" molecular weights It is apparent from formulas (3.22) and (3.30) that

$$\frac{[\omega]}{[\eta]} = \frac{K_\omega}{K_\eta} \cdot P \qquad (3.31)$$

The theory asserts that the ratio between orientation and viscosity constants for infiltrated clews is as $10^3/RT$. (R = gas constant = 8.13×10^7 erg/degree; T = absolute temperature). We then get the relation

$$P = \frac{[\omega]}{[\eta]} \cdot \frac{RT}{10^3} \qquad (3.32)$$

Thus with the aid of these formulas it is possible to determine forthwith from measurements respecting the orientation of the birefringence of flow and from viscosity measurements the DP of one member of a polymerhomologous series and also to ascertain K_η and K_ω for the series in question in accordance with the formulas:

$$K_\eta = [\omega] \cdot [\eta]^2 \frac{10^3}{RT}; \quad K_\omega = [\omega] \cdot [\eta]^2 \cdot \frac{10^6}{(RT)^2} \qquad (3.33)$$

Table V gives some molecular weights determined by this method applied to methyl cellulose fractions according to measurements made by *A. Wissler* [43], compared with those found in the same objects by *R. Signer* and *P. v. Tavel* [44] using the ultracentrifuge.

TABLE V

Molecular Weights Determined by Combined Birefringence of Flow and Viscosity Measurements Applied to Methyl Cellulose Fractions, Compared with those found in the Ultracentrifuge

$\frac{\eta sp}{c}$	$\frac{\omega}{\eta_0 g} \cdot 10^4$	M calc. acc. to (3.32)	M in ultrac.	$K\eta 10^4$ calc. acc. to (3.33)
28	1.4	23500	24300	11.9
55	5.7	49000	54000	11.2
74	10.5	67000	72000	11.1

The last column of the table also gives the *Staudinger* K_m constants calculated according to (3.33) which tally well with the value given by that author for methyl cellulose in water (cf. Table IV).

[43] *A. Wissler*, Thesis, Bern 1941.
[44] *R. Signer* and *P. v. Tavel*, Helv. chim. acta, 21, (1938) 535.

The new prospects opening out for molecular weight determination which have been dealt with in this section are a great gain and hold out much promise. They will in all probability prove an incentive to a considerable amount of fresh experimental work.

It should be pointed out that the application of the birefringence of flow method demands very carefully fractionated objects, for, as particularly *J. J. Hermans* [45] emphasized, its results are highly sensitive to polymolecularity, a fact which, up to the present, has not been taken sufficiently into account.

4.6. Precipitation Method

G. V. Schulz was able to show, on the basis of his fundamental theoretical and experimental work on the solubility and precipitability of high-molecular substances, so often referred to here, that precipitation tests also offer a convenient means of determining molecular weights [46]. He determines the amount of a non-solvent which has to be added to the solution of the substance to produce lasting turbidity. There exists between the percentage of precipitant γ when cloud first appears and the degree of polymerization P of the solute the simple relation:

$$P = \frac{\beta}{\gamma - \alpha} \quad \textit{and therefore} \quad \gamma = \alpha + \beta/P,$$

where α and β are constants which can be established empirically [47] when the initial concentration of the solution and test temperature are given, for these two values re-enter into the factor β. E.g., if 50 cm³ precipitant has to be added to 100 cm³ of the solution up to cloud point, $\gamma = 0.333$.

If γ is plotted against $1/P$, the result is a straight line inclining to β, which cuts off a stretch α on the ordinate. The constants α and β can be ascertained by calibration with a series of fractions whose P has been determined by other means (say, osmotically). For the reliability of the results it is necessary that the polymolecularity of the individual fractions shall not be too large and that it shall be the same for all.

B. Jirginsons [48] has recently published a long article on the applicability and accuracy of the precipitation method, to which we here refer. The precipitation method produces particularly good results when a fluid and not a flocculent precipitate is formed, as in the case of the precipitation of a nitrocellulose solution in acetone by means of water. These liquid

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[45] *J. J. Hermans*, Rec. trav. chim., 63, (1944) 205.
[46] In particular see *G. V. Schulz* and *B. Jirgensons*, Z. physik. Chem., B. 46, (1940) 105.
[47] This equation applies only to unbranched chain molecules. $P = [\beta/(\gamma\alpha)]^{3/2}$ applies to spherical or strongly branched molecules. Thus inferences may be drawn from precipitation tests respecting molecular shape, not only by determination of the exponent in the above equation, but also from the dependence of the precipitability upon the concentration. *G. V. Schulz* and *B. Jirgensons*, Z. physik. Chem., B. 46, (1940) 105; cf. *E. Husemann*, J. prakt. Chem., 158, (1941) 163.
[48] *B. Jirginsons*, J. prakt. Chem., 161, (1942) 30.

precipitations may be regarded as a species of coacervates according to *H. R. Kruyt* and *H. G. Bungenberg de Jong*. On this matter we refer to the important investigations carried out by *A. Dobry*[49], from which it will also be seen how well suited are the coacervates to fractionation experiments.

The new *Schulz* method is not only of practical use, but is also theoretically most interesting. It relies on the fact that the transitional energy of a molecule between the two phases increases considerably with the molecular weight. This effect varies and depends upon the effects upon which the molecular weight determination from the osmotic pressure, the viscosity or the velocity of sedimentation is based. As the method has produced results tallying well with osmotic determinations in numerous cases [50], it is a valuable enrichment of our experimental stock and merits consideration for further trial and practical application.

4.7. Ultracentrifugal Method

The ultracentrifugal method, which has proved to be so serviceable a tool for molecular weight determinations in globular proteins, has as yet contributed little towards facilitating the determination of the molecular weight of linear polymers and is in this case beset with greater experimental and theoretical difficulties.

For details of the theory and the experimental procedure, we refer to the literature cited in the list of special references at the end of this chapter [51]. *The Svedberg's* ultracentrifuge is very expensive. A cheaper design of an air-driven centrifuge was described by *J. W. McBain* and *Leyda* [52]. Further literature and references to an apparatus built in Germany are to be found in a paper by *G. Schramm* [53].

There are two alternative methods, that of sedimentation equilibrium or of sedimentation velocity in combination with the determination of diffusion constants. Owing to the admirable achievements in the domain of the proteins and other biochemical objects, the results obtained with the ultracentrifuge are often regarded as decisive and particularly reliable. Where linear polymers are concerned, however, there is still reason for some scepticism.

The applicability of the equilibrium method is confined to the range of relatively low molecular weights and then the values obtained appear to be considerably lower than those resulting from sedimentation velocity and diffusion. This is particularly evident from the recent work of *N. Gralén* [54].

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[49] *A. Dobry*, J. chim. phys., 35, (1938) 387; 36, (1939) 9.
[50] E.g., see *G. V. Schulz* and *A. Dinglinger*, J. prakt. Chem., 158, (1941) 136 and *E. Husemann:* J. prakt. Chem., 158, (1941) 163.
[51] Cf. *The Svedberg* and *K. O. Pedersen*, Die Ultrazentrifuge, Dresden and Leipzig, 1940. For a recent survey cf. *N. Gralén*, Thesis, Uppsala 1944.
[52] *J. W. McBain* and *Leyda*, Nature, 141, (1938) 913; J. Am. Chem. Soc. 50, (1938) 2998.
[53] *G. Schramm*, Kolloid-Z., 97, (1941) 106.
[54] *N. Gralén*, Thesis, Uppsala 1944, compare *N. Gralén* and *The Svedberg*, Nature, 152, (1943) 625.

This author published some parallel determinations of cellulose in cuprammonium oxide and cellulose nitrate in amyl acetate by the equilibrium method and by the sedimentation velocity and diffusion method, with the results collected in Table VI:

TABLE VI

Molecular weight determinations by N. Gralén (M. 10⁻³)

	Equilibrium method		Sedimentation and diffusion
	I	II	
Cuprammonium solutions			
Aged alkali cellulose	96	136	210
Staple fibre (from sulphate cell.)	122	238	320
Cellulose nitrate in amyl acetate			
Unbleached Amer. linters	300	618	780
Sulphite cellulose	212	454	430

The equilibrium value depended on the formula chosen for calculating the experiments (I and II). There are, as may be seen, appreciable discrepancies, particularly in the case of the cuprammonium solutions. The figures for the cuprammonium solutions given in this survey, when combined with *Gralén's* viscosity data, would lead to the following K_m constants $\times 10^4$ (Table VI[A]).

TABLE VI[A]

Values of K_m calculated from Gralén's data

	Equilibrium method		Sediment. and diffusion
	I	II	
Aged alkali cellulose	5.3	3.8	2.5
Staple fibre	3.9	2.0	1.5

(The value used by *Staudinger* is $5.0 \cdot 10^{-4}$.)

According to *Gralén*, the values for sedimentation velocity are to be preferred, as there is reason to believe that the equilibrium molecular weight values are consistently too low.

A review of the literature shows that earlier ultracentrifugal molecular weight determinations on cellulose and its derivatives were almost invariably carried out in accordance with the equilibrium method, formula I also being used. A proportionality actually existing between [η] and M is deducible from these investigations. This also applies to the determinations carried out by *E. O. Kraemer* and *W. D. Lansing*[55] and by *Chawdbury* and *Bardhaw*[56] (on cellulose in cuprammonium oxide, cellulose acetate in acetone, cellulose nitrate in acetone) and those by *R. Signer, J. S. Liechti* and *P. v. Tavel*[57] and *A. Wissler*[58] (on aqueous solutions of methyl cellulose).

[55] *E. O. Kraemer* and *W. D. Lansing*, J. Phys. Chem., 39, (1935) 153; J. Am. Chem. Soc., 57, (1935) 1364; *E. O. Kraemer*, Ind. Eng. Chem., 30, (1938) 1200; Nature, 133, (1934) 870.

[56] *Chawdbury* and *Bardhaw*, J. Indian. Chem. Soc., 13, (1936) 240.

[57] *R. Signer, J. S. Liechti* and *P. v. Tavel*, Helv. chim. acta, 21, (1938) 530, 535.

[58] *A. Wissler*, Thesis, Bern, 1941.

The values of the K_m constants following from this work were about half those given by *Staudinger*, except in the case of methyl cellulose, where the two values agreed well, and in the case of the cuprammonium solutions, where there was a difference of only 25%. Roughly, the general agreement was passable.

This consistency of other molecular weight determinations with ultracentrifugal data obtained by a method now stated by *Gralén* to give unreliable values creates anew a rather difficult and uncertain situation with regard to the problem of the molecular weight of cellulose in general, especially now that this author has published an extensive series of molecular weight determinations from sedimentation velocity and diffusion, showing considerable deviations from those otherwise obtained. *E. Husemann* and *O. H. Weber* recently reviewed the situation before *Gralén's* data were published[59]. Comparing the mutually consistent values of osmotic, terminal group, and viscosity measurements (for celluloses and cellulose nitrates) with the available ultracentrifugal data, they came to the conclusion that the ultracentrifugal method still suffers from some impediments. As to the sedimentation equilibrium method, this has now received confirmation from the work of *Gralén*. The question, however, now arises as to whether the molecular weights obtained by this author by sedimentation velocity and diffusion, which, in the case of celluloses in cuprammonium hydroxide, are about three times larger than those following from other methods, are to be considered as the correct ones. These measurements were carried out with the best equipment existing and in a laboratory of high repute. The molecular weights were computed from the classical formula

$$M = \frac{RTs}{D\,(1 - V\varrho)} \qquad (3.34)$$

where s and D are the sedimentation and diffusion constants, V the partial specific volume of the solute in the solution and ϱ the density of the latter. In cuprammonium solutions there remains an uncertainty with regard to the correct value of V, but it is surely out of the question that the estimated and used value would have been incorrect to a degree sufficient to explain these great discrepancies. The earlier molecular weight determinations were based principally on osmotic measurements which might also be expected to yield reliable values. The reason for the very material descrepancies from *Gralén's* work has yet to be explained. In view of the importance of this work and of the fact that *Gralén* also deduced from his results the absence of any linear relation between M and [η] for cellulose dissolved in cuprammonium hydroxide — the solvent generally used for viscosity determinations in cellulose research, we shall now consider this point in greater detail. In Table VII the M and DP values obtained by *Gralén* from sedimentation velocity and diffusion are listed together with the values of [η] (in g per 100 ml)

[59] *E. Husemann* and *O. H. Weber*, J. prakt. Chem., 161, (1942) 1.

TABLE VII

Summary of Gralén's Results

	M × 10^{-3}	DP	[η]
1. Raw cotton	2400	10800	12.6
2. Unbleached American linters	2100	9300	13.5
3. Normally bleached Am. linters	690	3000	4.6
4. Chlorite bleached Am. linters	1700	7300	7.7
5. Natural flax fibre	3200	37000	16.8
6. Natural nettle fibre	2600	11600	13.5
7. Natural ramie fibre	2800	12400	10.5
8. Sulphite pulp	700	3100	5.6
9. Sulphate pulp	560	2500	4.7
10. Aged alkali cellulose	210	940	2.3
11. Over-aged alkali cellulose	62	270	0.6
12. Stable fibre from sulph te pulp	105	460	0.95
13. Staple fibre from sulphate	320	1400	2.1

In the upper part of Fig. 36 log *M* is plotted against log [η] and a straight line is drawn as well as possible through the observations.

This line therefore corresponds to equation (3.21) on p. 108 : $[\eta] = KM^a$. The observations are apparently roughly represented by this equation, though there is a great deal of scattering. The latter is illustrated even more graphically in the lower part of Fig. 36, where DP is plotted against [η]. The broken part of

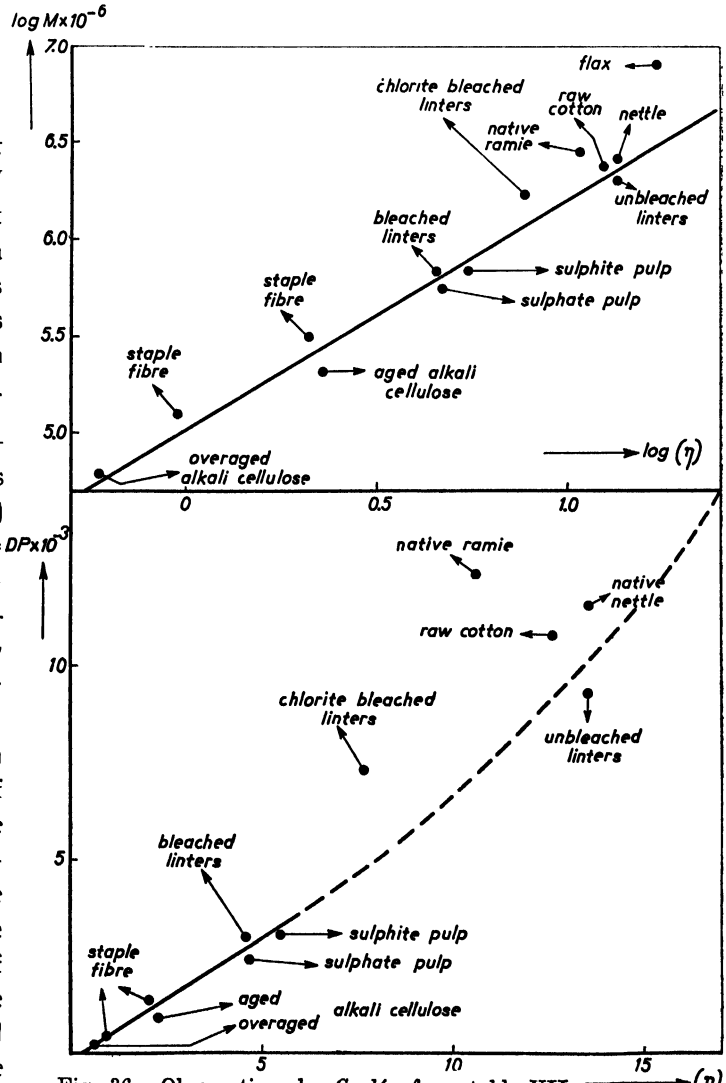


Fig. 36. Observations by *Gralén* from table VII plotted in an ordinary and in a logarithmic scale.

the curve in this figure corresponds to the line shown in the logarithmic plot. It is seen that the scattering is very considerable, especially in the region of the highest molecular weights. (It is somewhat masked in the logarithmic plot). The point for flax lies outside the figure and shows a very great deviation from the course of the curve. The consistency with the euqation $[\eta] = KM^a$ will be seen to be not very impressive.

It will be noticed, on the other hand, that, up to a *DP* of approximately 3000, the observations can be fairly well represented by the *Staudinger* equation $[\eta] = K_m P$, as shown by the full straight line in the lower part of Fig. 36. The latter corresponds to the equation:

$$[\eta] = 1.7 \times 10^{-4} P + 0.3 \qquad (3.35)$$

Below DP = 3000 there is no reason to prefer either of the two formulas. The linear relationship ceases at higher values of DP, as might be expected on theoretical grounds. Equation (3.21) then very roughly represents the observations, but no further than by giving a correct order of magnitude; some of the deviations exceed 100 per cent. The scattering of the results may be due either to experimental errors, or to differences in molecular weight distribution (non-uniformity), or else to both these factors.

In a recent review, *W. Badgley, V. J. Frilette,* and *H. Mark*[60] gave the equation

$$[\eta] = 0.85 \times 10^{-4} M^{0.81} \qquad (3.36)$$

as representing *Gralén's* observations. Our curve in the upper part of Fig. 36 corresponds to the equation

$$[\eta] = 1.7 \times 10^{-4} M^{0.77} \qquad (3.37)$$

It is illustrative of the very moderate degree of precision reached that both equations represent the observations with a not very different degree of accuracy, as may be seen from the figures in Table VII[A], giving values of $[\eta]$ calculated from *M:*

TABLE VII[A]

Intrinsic viscosities calculated from the M values in Table VII and those observed

	$[\eta]$ calculated from (3.36)	$[\eta]$ calculated from (3.37)	$[\eta]$ obs.
1. Raw cotton	12.6	14.1	12.6
2. Unbleached Amer. linters	11.5	12.6	13.5
3. Normally bleached Am. linters	6.2	5.75	4.6
4. Chlorite bleached Am. linters	9.5	10.7	7.7
5. Natural flax fibre	34.0	35.5	16.8
6. Natural nettle fibre	13.6	14.8	13.5
7. Natural ramie fibre	14.1	15.6	10.6
8. Sulphite pulp	4.57	4.52	5.5
9. Sulphate pulp	4.8	4.57	4.7
10. Aged alkali cellulose	1.76	2.14	2.3
11. Over-aged alkali cellulose	0.65	0.85	0.6
12. Staple fibre from sulphite pulp	1.0	1.26	0.95
13. Staple fibre from sulphate pulp	2.46	2.98	2.1

[60] *W. Badgley, V. J. Frilette* and *H. Mark,* Ind. Eng. Chem., 37, (1945) 227.

It may be realized from the foregoing how slight is the accuracy with which the available data can be cast into a single general formula.

A few words may be said on the K_m constant in equation (3.35), being $1.7 \cdot 10^{-4}$, in comparison with the value of $5 \cdot 10^{-4}$ put forward by *Staudinger.* The difference may be partly due to the fact that the ultracentrifuge data yield a weight average M. Admittedly, the viscometric M values also represent a weight average value, but *Staudinger* has gauged his K_m values on fractionated samples with the aid of osmotic pressure determinations, which yield a number average M. Now *Gralén's* experiments were carried out with unfractionated samples which, according to his estimations, consisted of a rather broad spectrum of molecular weights. The factor 2 may be deemed a reasonable figure for the possible difference between the weight average and the number average M. The *Staudinger* value would then reduce to $2.5 \cdot 10^{-4}$ and the remaining difference would be less alarming.

Finally, it should be borne in mind that *Gralén's* figures for unfractionated cellulose nitrates in acetone are not very different from those found in earlier work on nitrates. He concludes that nitration cannot be carried out without a partial breakdown of the chains, even when operating to *Staudinger's* directions claiming a nitration free from breakdown. As *Staudinger's* K_m values are partly based on nitrations assumed to exclude breakdown, the numerous data at present available on the degree of polymerization of cellulose and its derivatives cannot yet, apparently, be embodied in a single consistent scheme. A great deal of work on carefully fractionated samples will be necessary to clarify the subject [60a].

§ 5. SURVEY OF THE RESULTS OF MOLECULAR WEIGHT DETERMINATIONS

It appears from the work of *Gralén,* which was discussed in the preceding pages, that the degree of polymerization of native cellulose from the vegetable kingdom is of the order of 10000. Since this is, as yet, the sole investigation claiming such high values and as it would seem that this result still needs verification, a survey of the results of the numerous earlier publications on the subject may be appropriate here. See Tables VIII and IX.

[60a] (Note added to proofs). From recent work of *I. Jullander* (Thesis, Uppsala, 1945) it follows that P_{sd} as found from sedimentation and diffusion for cellulose nitrates is far too large as compared to P_o from osmotic pressure. From his work it can be deduced that the linear relation $P_{sd}/P_o = 1 + P_o \cdot 10^{-4}$ holds up to $P_o = 1600$. Assuming that the same relation holds for cuprammonium solutions of cellulose and that it may be extrapolated, we can calculate P_o from the P_{sd}-values given by Gralén. It is then found that P_o so calculated is approximatively proportional to $[\eta]$ up to the highest molecular weights investigated and corresponds to a K_m constant of $3.6 \cdot 10^{-4}$!

TABLE VIII

Average Degrees of Polymerization of Cellulose in Various Products

Object	DP
Native Textile Fibres:	
Ramie fibre	4600[61]
Ramie fibre (treated with NaOH)	3500[62]
Egyptian cotton (native)	2000
Cotton (card sliver)	3000 — 4000
Cotton linters (raw)	3250[61]
Cotton linters (cleaned)	1400
Cotton linters (bleached)	1200 — 1300[63]
	700
Lignocellulose:	
Spruces (sulphite process) unbleached	1900[66]
Spruces („ „) bleached for artificial silk	700 — 900
Spruces („ „) purified (96 %)	800 — 1450
Woodpulp	600 — 1000[64]
Beechwood, unbleached	700 — 1450
Beechwood, bleached	700 — 1300
Straw (sulphate process)	800
Pinewood (sulphate process) bleached	1100
Hemicelluloses:	
Xylan from straw and beechwood	150[65]
Mannans from spruce	160[65]
β-Cellulose	10 — 50
γ-Cellulose	<15
Regenerated Cellulose:	
Artificial fibres and films from viscose	200 — 400
Artificial fibres and films from cuprammonium	400 — 550
Special staple fibres from viscose (Lanusa)	450 — 800[62]

[61] End-group determination; *K. Hess* and *E. Steurer*, Ber., 79, (1940) 669.
[62] *H. Dolmetsch* and *F. Reinecke*, Zellwolle und dtsch. Kunsts. Ztg., 5, (1939) 299.
[63] With ultracentrifuge in *Schweizer's* reagent; *E. O. Kraemer*, Ind. Eng. Chem., 30, (1938) 1200.
[64] Viscometrically; *E. O. Kraemer*, loc.cit.
[65] Osmotically; *E. Husemann*, J. f. prakt. Chem., 155, (1940) 13.
[66] Viscometrically; *G Jayme* and *J. Wellm*, Kolloid. Z., 108, (1944) 30.

TABLE IX

Average Degrees of Polymerization of some Cellulose Esters and Ethers

PREPARATION	DP
Cellulose nitrate:	
Explosives	3000 — 3500[67]
Plastics	400 — 600[67]
Lacquers	175
Various commercial products	70 — 750[68]
Cellulose ethers:	
Methyl cellulose (22—23% CH_3O) in water	200 — 500
Ethyl cellulose (2.0—2.5 C_2H_5O) in org. solvents	540[69]
Benzyl cellulose (2.1—2.3 $C_6H_5.CH_2O$) in org. solvents	55 — 200
Cellites (acetates soluble in acetone):	
Fractionated commercial products	80 — 380[70]
Fractionated commercial products	75 — 270[71]
Artificial fibres and films	200 — 300

[66] Viscometrically; *G. Jayme* and *J. Wellm*, Kolloid. Z., 108, (1944) 30.
[68] Osmotically; *E. H. Büchner* and *H. E. Steutel*, Proc. Akad. Sci., Amsterdam, 36, (1933) 671.
[69] With the ultracentrifuge in acetone; *E. O. Kraemer*, loc. cit.
[70] Osmotically; *E. Obogi* and *E. Broda*, Kolloid-Z., 69, (1934) 172.
[71] Osmotically; *F. O. Herzog* and *A. Deripasko*, Cellulosechemie, 13, (1932) 25.

Earlier investigations have led to values of 2000—3000 for the *DP* in native fibres. Purification and bleaching are apt to cause quite considerable breakdown of the chains. Native cellulose from wood is less readily isolated without breakdown, owing to the previous chemical treatments always necessary in this case to eliminate lignin and other substances. Its *DP* however, does not seem to be very much lower than that in native fibres like cotton and ramie. Technical wood pulp, however, certainly represents degraded products.

The *DP* of the substances regarded as "concomitant polysaccharides", such as xylans and mannans — to which as yet little attention has been given — appears to lie between 100 and 200. Smaller fragments yet, however, (β- and γ celluloses) occur in technically hydrolyzed wood cellulose.

In regenerated artificial fibres the *DP* is found to decline further still in comparison with the initial celluloses. It is mostly at its highest in cuprammonium silks prepared from cotton linters. Table X gives an extract of a determination of the *DP* of some commercial staple fibres made by *H. Staudinger* and *M. Sorkin* [72] in 1937.

TABLE X

*DP of some Commercial Staple Fibres after H. Staudinger, M. Sorkin and E. Franz**

Cuprama	560**
Lanusa	520**
Schwarza	370.435
Flox	325
Vistra	285
Courtaulds	265
Snia	265
Vistra	220
Celta	175

* Melliand Textilber., 18, (1937) 681.
** Produced from linters, after *K. Götze*, "Kunstseide und Zellwolle", Berlin, 1940, p. 36.

Of recent years it has been recognized more than formerly that the *DP*, and especially the chain length distribution (*DP* diagrams), have a great deal to do with the technical properties of artificial fibres and since then there has been an endeavour — very particularly in the staple fibre industry and for tyre cord yarn — to reach higher *DP* in the end product. Considerably higher values are found in special staple fibres and also in viscose products nowadays.

Except for the cellulose nitrates made for explosives, which are not much degraded, the cellulose esters and ethers used for technical purposes have an average DP ranging from about 100 to 500.

As interesting examples of satisfactory agreement between the results of various methods of molecular weight determination applied to polymer-

[72] *H. Staudinger* and *M. Sorkin*, Ber., 70, (1937) 1993.

homologous series of cellulose objects, we refer to recent observations made by *H. Staudinger* and *K. W. Eder*[73] and *E. Husemann* and *O. H. Weber*[74]. The former found good tallies for the *DP* of cellulose triacetates (admittedly of relatively low molecular weight) as determined by the osmotic, viscometric and end-group method devised by *M. Bergmann* and *H. Machemer*[75], the latter authors finding this also to apply to many hydrolytically broken down cotton celluloses between *DP* 250 and 1200 (see Table XI); the method of end-group determination employed in this case was discussed on page 83.

TABLE XI

Comparison between the DP of a Series of Celluloses Measured by the End-Group and Viscometric Methods with the DP of the Cellulose Nitrates Produced therefrom, Determined Osmotically, after E. Husemann and O. H. Weber

Viscometric Method (in Schweizer solution)	End-group method (carboxyl number)	Osmotic method (Nitrates in acetone)
266	269	250
366	366	363
506	538	470
817	820	770
1320	1230	1200

The length of a cellobiose residue is known (10.3 å) from X-ray data and with this knowledge the absolute chain length of straight stretched cellulose molecules can be calculated. These lengths, calculated for a few *DP*, are given in Table XII, together with the relation of the length to the "thickness", which may be denoted as the "elongation" of the straightened out particles (*d* being assumed to be 8 å).

TABLE XII

Absolute Lengths l (in μ) and Elongation l/d of Cellulose Molecules

	DP	l in μ	l/d
Native cotton cellulose	3000	1.55	1930
Cellulose from wood	1000	0.52	643
Viscose artificial silk	350	0.18	225

§ 6. SHAPE AND MOBILITY OF CHAIN MOLECULES

One of the most urgent, and also the most difficult, problems confronting the investigator into the structure of solutions of linear polymers is that of the shape of the molecules. Yet, without clarification on this point there can be no clear understanding of the processes of gelatination and the subsequent deformation of cellulose gels.

[73] *H. Staudinger* and *K. W. Eder*, Cellulosechemie, 19, (1941) 125; Naturwiss., 29, (1941) 221.
[74] *E. Husemann* and *O. H. Weber*, J. prakt. Chem., 161, (1942) 1.
[75] *M. Bergmann* and *H. Machemer*, Ber., 63, (1930) 316, 2304.

The task of the artificial fibre industry is to manufacture fibres with properties closely approximating to those of native fibres, and we know that in Nature the chain molecules are straightened out, almost parallel and well ordered. Were the molecules in the technical solutions to be crumpled and kinky, and even entangled to some extent, they could obviously not be brought into line afterwards by mere deformation of the gel; it must be assumed that loops (retrograding chain sections) and molecular entanglements would persist [76]. On the other hand, the shape and alignment of the molecules could conceivably be influenced by appropriate choice of the concentration or previous treatment of the solutions. There is good reason, therefore, briefly to consider the various possibilities and the results hitherto obtained as regards the shape of molecules in solution.

H. Staudinger [77] has always maintained that thread molecules in the solution behave rather like rigid rodlets, liable at most to vibrate slightly. For many reasons this idea is untenable from the point of view of physics and is also incompatible with the rules applying to the relationship between viscosity and chain length of dilute solutions found and stressed by *Staudinger* himself. It is also irreconcilable with the results of classical stereochemistry based on the "free rotation" around single C-C and C-O bonds. Admittedly, it is known that this so-called free rotation is limited by attractive and repulsive forces between the atoms or groups on both sides of the bond. Even in simple molecules like ethane, a certain amount of energy is required for rotation, and in 1.2 dichloro-ethane this hindrance to rotation is already quite considerable [78]. Yet the molecules can often absorb sufficient energy from the kinetic energy of heat motion to change their configuration [79].

What is more important is that the presence of large groups of atoms may inhibit rotation for purely steric reasons, as is demonstrated by the well-known example of the optical activity of certain o—o' substituted derivatives of diphenyl. An approximately correct estimation of the presence or otherwise of such steric hindrance may be made with the aid of the atomic models introduced by *H. A. Stuart* which were mentioned in Chapter I, § 2. As there stated, the examination of the model of cellulose has shown that the cellulose chain is to be considered as a relatively flexible organization which may assume a convoluted form [80]. A comparison with similar investigations carried out by *E. Jenckel* [81] upon other linear polymers supports the view that relatively considerable inner mobility actually can be ascribed to the cellulose molecule. *Jenckel* has compared the "freezing-in temperatures" (Einfriertemperaturen) of various high polymer glasses with the inner mobility of their molecular

[76] On the possibility of entanglements also see *K. Freudenberg, E. Plankenkorn* and *A. Boppel*, Ber., 71, (1938) 2435; Naturwiss., 26, (1938) 124.
[77] *H. Staudinger* "Organische Kolloidchemie", Braunschweig, 1940.
[78] *A. Eucken and K. Schäfer*, Naturwiss., 27, (1939) 122.
[79] *H. A. Stuart*, Naturwiss., 31, (1943) 123.
[80] *K. Freudenberg*, Papierfabrikant, Tech. Teil, 35, (1937) 52; *P. H. Hermans*, Kolloid-Z., 21, (1942) 52.
[81] *E. Jenckel*, Kolloid-Z., 100, (1942) 163.

chains as estimated from *Stuart* models, achieving remarkable results. As the low temperature transition point of cellulose and its derivatives is relatively low (40—70° as against, say, polystyrene with 120°), there is an inclination to assign an inner mobility to the cellulose chain which is, at first sight, unexpectedly high.

W. Kuhn [82] has considered the most probable configurations of dissolved chain molecules exhibiting free rotation of the monomeric residues in a statistical light. He states that the average distance between the two ends of the chain, which might be considered as the length of the convoluted molecule (cf. the diagram in Fig. 37) increases in proportion to $\sqrt{M}$, instead of in proportion to M, as would be the case with a straight chain.

During a discussion some years ago on the actual shape of thread molecules in solutions, *H. Mark* [83] concluded that, in reality, there must be an intermediate condition between the extremely convolute forms after *W. Kuhn* and the perfectly straight form favoured by *Staudinger*. Also compare the paper by *O. Kratky* and *H. Mark* [84].

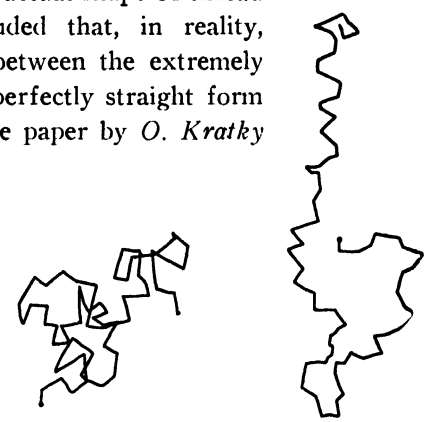


Fig. 37. Example of constellations of chain molecules suspended in solution, after *W. Kuhn*.

Earlier attempts to obtain information by experimental means as to the shape of the molecules in solutions had not at first produced a uniform picture. The properties of the monomolecular films of cellulose derivates spread on water which *N. K. Adam* [85] examined led him to assume that "the chains are flexible and may be vibrating vigorously in the plane of the surface". *W. D. Bridgman* [86] applied dielectric measurements to molecules carrying polar groups at both ends of a long paraffin chain, viz., with ω-hydroxy-carboxylic acids and their high-molecular polycondensates. He found that the molecules in the electric field were not orientated as rigid rodlets would be and that the two polar terminal groups were, rather, orientated independently of each other. From the fact that the polarity increased in proportion to $\sqrt{M}$ he concluded that *Kuhn's* hypotheses with regard to chain molecules were substantiated. On similar grounds *I. Sakurada* [87] infers from his experiments relating to the dielectric constants of cellulose derivatives in organic solvents that the molecules in the solution must be very apt to assume convoluted shapes.

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[82] *W. Kuhn*, Kolloid-Z., 68, (1934) 2; 101, (1942) 248; 76, (1936) 258; Z. angew. Chem., 49, (1936) 858; 51, (1938) 642.
[83] *H. Mark*, Der feste Körper, Leipzig 1938, p. 96.
[84] *O. Kratky* and *H. Mark*, Fortschritte d. Chemie organ. Naturstoffe, 1, (1938) 255.
[85] *N. K. Adam*, Trans. Faraday Soc., 29, (1933) 90.
[86] *W. D. Bridgman*, J. Amer. Chem. Soc., 60, (1938) 530.
[87] *I. Sakurada*, Kolloid-Z., 82, (1938) 67, 72, 194; J. Soc. chem. Ind. Japan, B., 43, (1940) 171, 190.

Since the experimental evidence produced by *R. Signer* and *H. Gross* [88], working with the ultracentrifuge on solutions of polystyrene, shows a substantially smaller dissymetrical factor for the particles deposited, the molecules cannot be straight. *E. O. Kraemer* and *W. D. Lansing* [89] obtained similar results upon subjecting solutions of a polyhydroxydecanoic acid to ultracentrifugal tests (cf. *W. D. Bridgman's* experiments, referred to above, with similar objects).

R. Signer and *P. v. Tavel* [90], on the other hand, found a much larger dissymmetrical factor for aqueous solutions of methyl celluloses, evidence, moreover, which was borne out by *A. Polson* [91] after diffusion tests applied to the same material. Experiments carried out by *A. Wissler* [92] and *H. Mosimann* [93] upon fractionated nitrocelluloses led to the same result. These results, again, come nearer to endorsing the theory of *H. Mark* as to moderate kinkiness of the chains (Fig. 38) [92a].

It should, however, not be forgotten that the inferences drawn both from sedimentation tests in the ultracentrifuge and from birefringence of flow experiments respecting molecular shape have as their foundation theoretical assumptions relating to the behaviour of rigid particles, and require revision (for which see page 103).



Fig. 38. Diagram of a cellulose chain in solution, free rotation being impeded.

W. Lotmar [94] concludes from experimental depolarisation of the *Tyndall* light that the "optically effective" length of the particles in nitrocellulose solutions is shorter than the chain length of the molecules and that the chains are not straight, but convoluted.

Though the question of the shape of chain molecules in solution still awaits a definite answer, the most recent results of *Kuhn's* theory of chain molecules kinked at random, obtained in the quantitatively correct treatment of very divergent physical properties of dilute solutions, appear to show that exceedingly convolute shapes in *Kuhn's* sense do at any rate occur in these dilute solutions. To this, cellulose certainly forms no exception, as is clearly evident from the work of *W.* and *H. Kuhn* [95].

A certain measure of the "flexibility" of the chains may also be derived from *Kuhn's* work. His theory deals with the length of the "statistical chain element", i.e., that section of the chain which is just long enough to permit statistically independent orientation of its two terminal monomeric residues,

[88] *R. Signer* and *H. Gross*, Helv. chim. acta, 17, (1934) 59, 335, 726.
[89] *E. O. Kraemer* and *W. D. Lansing*, J. Amer. Chem. Soc., 55, (1933) 4319.
[90] *R. Signer* and *P. Tavel*, Helv. chim. acta., 21, (1938) 535.
[91] *A. Polson*, Kolloid-Z., 83, (1938) 172.
[92] *A. Wissler*, Thesis, Bern., 1940.
[92a] This is also supported by the work of *A. Wissler*, Thesis, Bern, 1940.
[93] *H. Mosimann*, Helv. chim. acta, 26, (1943) 61.
[94] *W. Lotmar*, Helv. chim. acta, 21, (1938) 792, 813.
[95] *W.* and *H. Kuhn*, Helv. chim. acta, 26, (1943) 1394.

with due allowance for the free play of intramolecular mobility. The number of links comprised by the chain element to fulfil this condition is then a measure of the flexibility of the molecular chain. In paraffin hydrocarbons and in rubber the statistical chain element comprises about 12 successive carbon-to-carbon links, in cuprammonium solutions of cellulose, 48, and in nitrocellulose dissolved in acetone 185. Since, in the case of cellulose, the monomeric residue is five carbon atoms long, the length of the statistical chain element comprises 10 and 37 glucose groups respectively in the two cases. Therefore, in cellulose about four times, and in nitrocellulose roughly fifteen times as many carbon atoms come to the statistical chain element as in paraffin hydrocarbons and in rubber. The kinky molecules of cellulose must, therefore, represent far less dense clews thans those of rubber. This by no means implies a departure from *Kuhn's* theory of the randomly coiled molecule, as might be erroneously inferred from a recent discussion of *Gralén's* data by *W. Badgley, V. J. Frilette* and *H. Mark* [96]. It only means that the cellulose chains are rather stiff.

Quite recently arguments have been advanced from various quarters, as by *F. H. Müller* [97], *J. J. Hermans* [98], *A. Matthes* [99] and *E. O. Kraemer* [100], to the effect that the solvent may be a potent factor in the shaping of the molecule. The molecules are probably less convoluted in "good" solvents than in "bad" ones.

A very much more difficult problem, and one that has as yet received little consideration, is that of the c o n c e n t r a t i o n of the solution. Yet to us it is of the utmost importance. Quite conceivably, the tendency towards statistical convolution of the chains is no longer untrammelled in concentrated solutions and various modifying factors may come into play.

If, as the latest investigations tend to show, fairly extensive mutual orientation of neighbouring molecules takes place in low-molecular liquids, the like must certainly be reckoned with in concentrated solutions of high-molecular substances. *H. A. Stuart* [101] was recently able to demonstrate a parallelizing tendency of long chain molecules in small regions by his well-known model experiments. Apparently an u n coiling tendency is involved [102].

The marked interaction between the molecules in concentrated solutions, which is manifested by the formation of "solutions exhibiting a structure", might, as stressed elsewhere, give rise to a certain parallelization and stretching of the molecules, particularly as such an arrangement is favoured by the laws of the closest packing (p. 49, 52, 77, 375). Nor is the formation of associations, molecular swarms and similar structures, which are certainly

[96] *W. Badgley, V. J. Frilette* and *H. Mark*, Ind. Eng. Chem., 37, (1945) 227.
[97] *F. H. Müller*, 4. Forschungstagung Zellwolle und Kunstseidering, Weimar, Beihefte zu "Die Chemie", 47, (1943) 81.
[98] *J. J. Hermans*, Kolloid-Z., 106, (1944) 22.
[99] *A. Matthes*, J. prakt. Chem., 162, (1943) 245.
[100] *E. O. Kraemer*, J. Franklin Inst., 231, (1941) 1.
[101] *H. A. Stuart*, Naturwiss., 31 (1943) 123.
[102] For this also see *G. Centola*, X. Congr. Int. Chim. Roma, Vol. IV, (1938) 117.

likely to occur in concentrated solutions, conceivable without some straightening of the contributory molecules. *H. Mark* [103] states that the molecules in long paraffin chains in the melted state try to stretch, because free mobility is prevented by intermolecular forces.

The tendency towards the formation of crystalline regions upon gelatination of the solutions (which will be further dealt with in Part III, p. 374) provides another argument in favour of the assumption that numerous neighbouring chain sections locally take up parallel positions even b e f o r e gelatination. If there were a random agglomeration of fully kinked chains down to the smallest dimensions in the gel, the subsequent fairly advanced crystallization which is actually observed could scarcely take place [104].

We are therefore forced to conclude that, *with increasing concentration of the solution, there must be a growing tendency of the molecules in the smallest regions to straighten out and to parallelize statistically.* Such conformity as this to law would likewise find expression in the properties of the gels formed from solutions of different concentration. (We shall revert to this matter in the third part of this book).

[103] *H. Mark,* Hochpolymere Chemie, Vol. I, Leipzig 1940, p. 74.

[104] A certain low distance order of the chains, existing from the outset, must be assumed also in bodies such as amorphous isotropic rubber and gutta-percha, which crystallize readily and abundantly on cooling.

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CHAPTER IV

CHEMICAL REACTIONS AND BREAKDOWN OF THE CHAIN MOLECULES

§ 1. INTRODUCTION

Discussion of the chemistry of cellulose molecules does not fall within the framework of this book. The subject is dealt with by *H. Mark*[1], *K. Freudenberg*[2], *K. H. Meyer*[3] and, in particular, by the Englishmen *J. T. Marsh* and *F. C. Wood*[4]. We shall here only briefly touch on certain selected matters.

The course of chemical reactions in cellulose may depend largely on the supermolecular structure of the objects considered. Owing to their better accessibility to the reagent, chains in the amorphous parts of the fibres will, for instance, as a rule react sooner than chain sections belonging to the crystalline portion. Phenomena of this kind, however, will not be considered here. They are dealt with in Part II, Chapter VII (page 307). In the present Chapter we shall concern ourselves only with the reactions of the cellulose chain under conditions in which it is free to react, regardless of its position in a special structure.

Chemical reactions in long-chain molecules can be divided into those which take place without breakdown — i.e., with retention of the initial chain length — and those involving breakdown. The latter are always noticeable in a distinct change in certain physical properties, such as viscosity, for example.

§ 2. REACTIONS WITHOUT BREAKDOWN

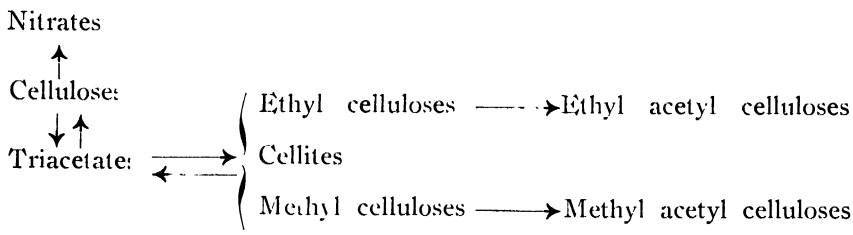
The reactions taking place without breakdown of the chain may have only a local effect, e.g., causing change in the terminal groups or individual members of the chain, or they may affect all, or the majority of, the members of the chain simultaneously. In the former case it is exceedingly difficult to detect them analytically in high-molecular products, for which reagents of the utmost sensitivity are required. Sometimes, however, these reactions are manifested indirectly. Changes in the cellulose molecule resulting from oxidation in an acid medium are known from examples yet to be given which affect only a few members of the chain and are scarcely to be detected by

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[1] *H. Mark*, Physik und Chemie der Cellulose, Berlin 1932.
[2] *K. Freudenberg*, Tannin, Cellulose, Lignin, Berlin 1933.
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direct means; yet later on they become clearly noticeable in that the chain splits up at the affected parts upon subsequent contact with alkaline liquids.

There are many chemical reactions — the esterification and etherification of the hydroxyl groups in particular — which are liable to take place over the entire chain more or less uniformly, with often little difference in reactivity of the OH groups in positions 2, 3 and 6[5], though occasionally probable distinctions have been made[6]. The reactions which take place in the whole chain with retention of its original length are described as polymeranalogous reactions. *H. Staudinger* and his associates applied many polymeranalogous conversions to cellulose objects and at the same time proved that the particle size in various solvents remains unchanged in the process. This not only provided an impressive substantiation of the chain theory, itself, but also strong support for the hypothesis of monomolecular dispersion in dilute solutions. The following scheme sets out the polymeranalogous conversions carried through by these investigators:



All particle weights were determined osmotically, except those of the cellulose itself, which could only be measured viscometrically.

Under circumstances in which a polymeranalogous reaction is to be expected, breakdown reactions would now and again be observed: Unlike the other esters, nitrates, for example, cannot be re-converted to cellulose by alkaline saponification without simultaneous considerable reduction of the DP. Contrarily, the reverse process, i.e., the nitration of cellulose, can be effected polymeranalogously. For this reason nitrocellulose can be used for the MW determination of cellulose objects and for their fractionation in the form of this ester, as now commonly practised. There are, however, certain complications which have to be taken into account and which we shall consider directly.

In heterogeneous esterification or etherification of cellulose objects in their fibrous form, the action will often not be uniform along the chains. In that case there will be selective reaction of those sections of the chain in the micellar structure which are particularly exposed. (See Part II, Chapt. VII).

[5] *H. M. Spurlin*, J. Amer. Chem. Soc., 61, (1939) 222.
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§. 3. BREAKDOWN REACTIONS

First in importance among the breakdown reactions are those brought about by hydrolysis of the glucosidic bonds and by oxidation. Hydrolytic breakdown takes place in the presence of acids, while oxidation may occur in either an alkaline, acid or neutral medium. The latter is most likely to occur in alkaline reaction and may often be instigated merely by atmospheric oxygen.

It should always be borne in mind that in objects constituted of long chains, minute actions scarcely detectable by analysis are liable to give rise to distinctly noticeable breakdown.

H. Staudinger and *I. Jurisch* [7] found that about 0.35 mg of oxygen in the form of permanganate was enough to break down 0.8 g. of a cellulose with approximately 1000 DP in a solution of phosphoric acid to half that value, which corresponds to roughly 4 oxygen atoms per mole of cellulose. *E. Scheller* [8] noted that, on the addition of no more than 0.007% of oxygen, as referred to the weight of dry cellulose, to a solution of ammoniacal copper oxide, the viscosity drops by about 10%. Measurements carried out by *W. Weltzien* and *G. Zum Tobel* [9] also show that the amount of oxygen absorbed during the breakdown of alkali-cellulose by oxidation in the technical process of preliminary ripening is likewise relatively small. Accordingly, since the strength of cellulose fibres is closely related to the length of the molecular chain, the action of relatively small amounts of acids or oxidants may cause serious damage to the fibre.

Detailed information and references to literature on the action of acids upon cellulose are to be found in *H. Mark's* textbook [10]. Its quantitative kinetic aspect has received the special attention of *W. Kuhn, K. Freudenberg, A. Alf Ekenstamm* and *G. V. Schulz* [11].

With acid hydrolysis, the reducing power of the sample, usually expressed in terms of its copper number as an empirical measure, increases owing to the formation of reducing (aldehydic) end groups. The copper number of carefully purified cotton is almost zero, while that for glucose amounts to roughly 300. If the copper number of a cotton sample rises to 5, breakdown will have advanced to such an extent that the sample will crumble to a powder. Treating cotton fibres under carefully controlled conditions, *C. Birtwell, D. A. Clibbens*, and *A. Geake* [12] found reproducible relationships between reducing power, viscosity and tensile strength. In accordance with an old-established custom, celluloses modified by acids are designated as "hydrocelluloses". Boiling with alkaline solutions again decreases the reducing

[7] *H. Staudinger* and *J. Jurisch*, Ber., 71, (1938) 2283.
[8] *E. Scheller*, Melliand Textilber., 16, (1935) 787.
[9] *W. Weltzien* and *G. zum Tobel*, Ber., 60, (1927) 2024.
[10] *H. Mark*, Physik und Chemie der Cellulose, Berlin 1932.
[11] Further details in the text-books of *H. Mark*, Physik und Chemie der Cellulose, Berlin 1932, and *K. Freudenberg*, Tannin, Cellulose, Lignin, Berlin 1933; also see the recent work of *G. V. Schulz* and *H. J. Lohmann*, J. prakt. Chem., 157, (1941) 238 and, in particular, *G. V. Schulz* and *E. Husemann*, Z. physik. Chem., B. 52, (1942) 23.
[12] *C. Birtwell, D. A. Clibbens* and *A. Geake*, J. Text. Inst., 17, (1926) T. 145.

power, when the aldehydic end groups are probably converted to carboxyl groups (along similar lines to the well-known Cannizzaro reaction). This is accompanied by increasing sorptive capacity for basic dyes (methylene blue test).

The far more complicated oxidation reactions of cellulose have been investigated and roughly explained, by English research workers in particular (cf. list of special references). These important investigations have been overlooked in the majority of German text-books, with the exception of that by *E. Valkó* [12]. They are comprehensively dealt with in the book published by *Marsh* and *Wood* [13], and the subject was also reviewed by *G. F. Davidson* [14]. We shall here deal only with some of the principal features of the subject.

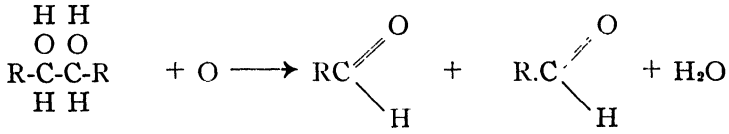
When cellulose oxidizes, the chains usually break down, probably as the result of opening and cleavage of the monomeric rings. Side by side with this, other reactions, not interfering with chain length may occur, such as oxidation of the primary hydroxyl groups in the 6 position to aldehyde or carboxyl groups, oxidation of the secondary hydroxyl groups 2 and 3 to ketone groups, oxidative opening of rings to form two aldehyde or carboxyl groups, etc. All according to the conditions, the resulting products actually have either a marked acid or equally pronounced reducing character. While the former exhibit intensified sorption towards methylene blue, the latter show an increased copper number; mixed types also occur. The modified celluloses designated in the older literature as "Oxycelluloses" do not as a rule represent any definite or uniform substances at all; the term was, rather, applied to a number of the most various products.

A great number of papers has dealt with the detection of the detoriation of yarns and tissues by acids or oxidants by means of colour reactions and with the discrimination of both kinds of attack from each other. These reactions are based on the specific functions of free aldehyde groups, aldehyde groups as semiacetals, keto- and carboxylgroups. For a survey and the explanation of a number of such reactions we refer to some recent papers by *F. Müller* and *E. Geiger* [14a]. Precise prescriptions for application are also given there.

Not long ago *E. C. Yackel* and *W. O. Kenyon* [15], treating cellulose with nitrogen tetroxide, obtained products of relatively high molecular weight, soluble in 2% NaOH and containing up to 25% carboxyl groups. They showed that the carboxyl groups were bound mainly to the C atom 5 and that they therefore originated from the oxidation of the primary hydroxyl groups in the 6 position. The same result was reported by *K. Maurer* and *G. Reiff* [16]

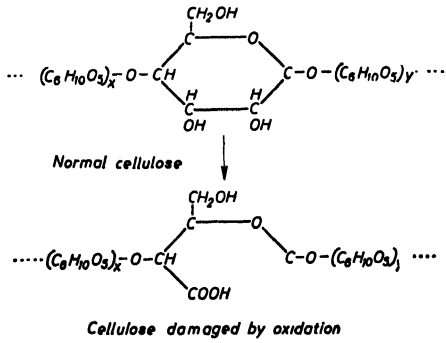
[12] *E. Valkó*, Kolloidchemische Grundlagen der Textilveredlung, Berlin 1937.
[13] *J. T. Marsh* and *F. C. Wood*, An Introduction to the Chemistry of Cellulose, London 1945.
[14] *G. F. Davidson*, J. Text. Inst., 27, (1936) P. 159.
[14a] *F. Müller*, Helv. chim. acta 22, 213, (1939); *E. Geiger*, ibid 28, (1945) 283, 1159; *E. Geiger* and *A. Wissler*, ibid *28*, (1945) 1638.
[15] *E. C. Yackel* and *W. O. Kenyon*, J. Amer. Chem. Soc., 64, (1942) 121-127.
[16] *K. Maurer* and *G. Reiff*, J. makrom. Chem., 1, (1943) 27.

Very interesting results have been obtained recently from investigations relating to the reaction of cellulose with periodic acid. This reagent is known to act on 1.2 diols in a specific way, giving rise to a fission of the molecule with formation of two aldehyde groups:



Cellulose undergoes this reaction at the C atoms 2 and 3 which correspond to this configuration [17].

Upon hydrolysis of the oxycellulose so obtained, glyoxal and d-erythrose were obtained, as was to be expected from the above formula. The yield of these products, however, remained far below that predicted by the theory. *E. Pacsu* [18] has suggested why this should be so. He thinks the hydrolysis is facilitated if the aldehyde groups are oxidized to carboxyl groups before hydrolysis is carried out and that up to 75% of the theoretical yield of glyoxylic acid could be obtained in this way. *G. Jayme* and co-workers [19] obtained a much better yield when using buffered solutions of periodic acid (at pH = 4) instead of the free acid.



Polymeric glyoxal was obtained in 97% of the theoretical yield. When the oxidized cellulose is treated with alkaline reagents, complicated reactions occur which have not yet been elucidated, but *Pacsu* (loc.cit.) was able to show that considerable amounts of low-molecular products are obtained in this way, from which it is evident that chain fissure takes place under the influence of the alkali. It seems probable that the oxidation reaction of the kind considered here is one of the reactions taking place in the formation of oxycelluloses in general. The breakdown of chains, which is often observed when oxycelluloses are treated with alkaline reagents (see below), might perhaps be understood in this way. According to *Pacsu* the breakdown observed when exposing cellulose in alkaline media to oxygen (e.g., in the "ageing" of alkali-cellulose) would be a reaction corresponding to a similar scheme.

Like the hydrocelluloses, oxycellulose, when acted upon by alkaline solutions,

[17] *E. L. Jackson* and *C. S. Hudson*, J. Amer. Chem. Soc., 59, (1937) 2049; 60 (1938) 989; cf. also *G. Davidson*, J. Textile Inst., 32, (1941) T. 109.
[18] *E. Pacsu*, Textile Research J., 15, (1945) 354; cf. also *Michell* and *Purves*, J. Amer. Chem. Soc., 64, (1942) 589.
[19] *G. Jayme, M. Sätre* and *S. Maris*, Naturwiss., 29, (1941) 768.

loses in reducing power to the benefit of its sorptive capacity for methylene blue, which increases. Contrary to hydrocelluloses, which show no change in DP after being subjected to the treatment, many oxycelluloses — those with reducing properties in particular — decrease in viscosity as a result of breakdown caused by the action of the alkali. This is what was observed by *G. F. Davidson*[20], for example, in celluloses oxidized by potassium bichromate, and by *G. L. Godman, W. N. Haworth* and *S. Peat*[21] after oxidation with acidified permanganate. Reduced tensile strength of fibrous samples may be another manifestation of subsequent breakdown caused by alkaline agents, for which reason it has become customary in practice, when testing for fibre deterioration through oxidation (as in the case of damage through bleaching), to determine the loss of tensile strength after previous treatment with boiling alkaline solutions. This test is more sensitive than the mere tensile strength test after oxidation.

The drop in viscosity which many oxycelluloses exhibit when tested in an ammoniacal solution of copper oxide may likewise be ascribed to subsequent breakdown upon solution, caused by the alkalinity of this solvent. There is impressive evidence of this when the unchanged samples and those modified by oxidation are carefully nitrated and the nitrates are tested in an organic solvent. There will be found relatively far less breakdown, or none at all. If, however, the samples undergo preliminary alkaline treatment prior to the nitration, the same drop in viscosity will be found as in the case of treatment in ammoniacal solutions of copper oxide.

Recently *H. Staudinger* and *A. W. Sohn*[22] have gone over this subject, which had already been thoroughly investigated by the English chemists. After conversion to nitrates, they found four to five times higher *DP* for cotton samples oxidized with bichromate solutions than by direct measurement in ammoniacal solution of copper oxide. If, however, they first precipitated the samples from *Schweizer's* reagent in an atmosphere free from oxygen, or pretreated them with dilute caustic soda, they obtained the same DP by both methods (Table XIII).

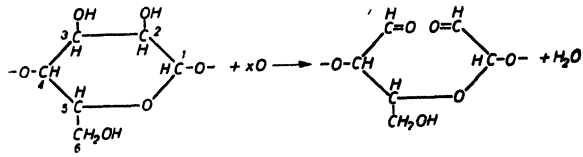
TABLE XIII

DP of Bichromate Oxycelluloses from Cotton and their Nitrates

		DP in Cuprammonia	DP of Nitrates in Acetone
Oxidized with bichromate	I	460	1530
	II	185	740
After precipitation from cuprammonia	I	400	430
	II	170	195
After treatment with dilute sodium hydroxide	I	420	480
	II	185	195

[20] *G. F. Davidson*, J. Text. Inst., 29, (1938) T. 195.
[21] *G. L. Godman, W. N. Haworth* and *S. Peat*, J. Chem. Soc., (1939) 1908.
[22] *H. Staudinger* and *A. W. Sohn*, Ber., 72, (1939) 1709; Naturwiss., 32, (1939) 548. Melliand Textilber., 21, Vol. 5, (1940); Cellulosechemie, 18, (1940) 25; J. prakt Chem., 155, (1940) 177.

H. Staudinger and *A. W. Sohn* assume that oxidation causes some glucose rings to open while bridges of an ester nature are formed:



In contact with alkaline reagents the ester bridge is saponified and the molecule is split up, but nitration leaves the ester bridge intact. *H. Staudinger* calls oxycelluloses with "faults" of this kind, "Ester-oxycelluloses". He then goes on to show that the tensile strength of an ester-cellulose sample is the same as that of an undamaged sample of equal *DP;* but, after alkaline treatment, the mechanical properties deteriorate in proportion to the resulting decrease in *DP. Staudinger's* "ester-oxycelluloses" are entirely hypothetical and the explanation offered by *Pacsu* (p. 137) would seem to be better founded.

In their papers cited above *Staudinger* and *Sohn* put some other rather complicated phenomena on record. In various specimens of native celluloses they found a higher DP for the nitrates in acetone than for the celluloses in cuprammonium solution, though they did not if the samples were reprecipitated from their cuprammonium solution (excluding air) before the nitration was carried out. For this reason they believe that saponifiable bonds may also occur in native cellulose which has not been pretreated with oxidizing agents [22a]. It is difficult to judge whether this interpretation is correct, as the same authors also find that the difference is liable to arise after partial acid hydrolysis of the samples. They explain this new phenomenon by assuming an occasional "condensation" (increased chain length due to an interlinking of neighbouring chain ends) in the process of nitration. If phenomena of this kind do really occur, the foundations of a great deal of previous work on the DP of cellulose would become very doubtful and verification of the reproducibility of *Staudinger's* results seems called for.

Anomalous intrinsic viscosities of cellulose nitrates prepared from wood celluloses were also recently reported by *H. Staudinger* and *E. Husemann* [23].

The breakdown reaction due to molecular oxygen in alkaline media, such as occurs in the ripening of alkali cellulose, is highly characteristic of cellulose and has important practical bearings. This reaction was quantitatively

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[22a] In this connexion also see a recent paper by *A. Banderet* and *E. Ranby,* Helv. chim. acta, 30, (1947) 1190, where bonds of this kind seem to have been shown to exist.

[23] *H. Staudinger* and *E. Husemann* ,Naturwiss., 29, (1941) 534.

investigated by *W. Weltzien* and *G. zum Tobel*[24] and later by *G. Saito*[25], *O. Eisenhuth*[26] and *A. Matthes*[27]. The mechanism of this reaction is not yet exactly known. The aforementioned authors were able to show that the velocity of the reaction depends on the partial pressure of the oxygen and that for every two molecules of oxygen absorbed one molecule of carbon dioxide is formed. Unlike *A. Matthes* (loc. cit.), *Eisenhuth* moreover found that oxidative breakdown is not affected by the chain length, but depends only on the total number of glucosidic residues present. *O. H. Weber* and *E. Husemann*[28] have recent evidence of the formation of one carboxyl group wherever chain cleavage occurs. Any aldehyde groups present from the outset in the cellulose are likewise, though slowly, oxidized. If oxidation is carried through beyond a certain limit (below P = 300), the molecules are probably subject to attack at other places as well, and more carboxyl is formed.

The presence of alkali sulphides considerably accelerates the reaction. According to unpublished results, the reaction then has the typical character of a coupled auto-oxidation, when the sulphide is oxidized to sulphite and the cellulose is oxidized in equivalent amounts.

The reaction of cellulose with bleaching agents, especially hypochlorites, is one with which practice is pre-eminently concerned and on which a great deal of work has been concentrated. Reference may be made to the thorough study of the subject made by *E. Elöd* and *F. Vogel*[29]. The effect of the alkalinity of the solution upon the course of the reaction and the breakdown involved is of paramount importance in bleaching with sodium hypochlorite. Here again *O. H. Weber* and *E. Husemann*[30] were able to account for the conditions to some extent by keeping a simultaneous record of the carboxyl number and the average degree of polymerization. Investigating the action of chlorine in the p_H range of 0.9 to 12.8, they found a considerable increase in the number of carboxyl groups, though little breakdown in the extreme alkaline region. Breakdown occurs at p_H 9, becoming particularly severe at the neutral point (p_H 7); it is then, moreover, accompanied by the formation of "faults" in the chains (i.e., places subject to cleavage by alkalis). The best conditions are obtained with p_H at 5, but in the extreme acid region, breakdown began again to increase.

Finally, it should be recalled that several cases have been reported indicating a considerable sensitivity of some oxidation reactions to minute amounts of heavy metals like copper and manganese, which act as a catalyst[31].

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[24] *W. Weltzien* and *G. zum Tobel*, Ber., 60, (1927) 2024.
[25] *G. Saito*, Monatsh., 67, (1936) 191.
[26] *O. Eisenhuth*, J. prakt. Chem., 157, (1941) 338.
[27] *A. Matthes*, Kolloid-Z., 98, (1942) 319. For further literature see special references in Part III, Chapt. II (p. 354).
[28] *O. H. Weber* and *E. Husemann*, J. prakt. Chem., 161, (1942) 20.
[29] *E. Elöd* and *F. Vogel*, Melliands Textilber., 18, (1937) 64.
[30] *O. H. Weber* and *E. Husemann*, J. prakt. Chem., 161, (1942) 20.
[31] E.g., *C. A. Seibert*, Am. Dyestuff Reptr., 29, (1940) P. 136.

Traces of heavy metals like copper and iron salts may have a detrimental effect in the hypochlorite bleach and should be rigorously excluded. Other, though more expensive, bleaching agents, less liable to attack cellulose fibres, are hydrogen peroxide[32] and sodium chlorite solutions[33], if the treatment is carried out under the correct conditions.

§ 4. BREAKDOWN DUE TO MECHANICAL CAUSES

Purely mechanical interference is also liable to break down cellulose chains. *K. Hess, E. Steurer,* and *H. Fromm*[34] state that, if cellulose fibres are ground in an oscillating ball mill, a drop in viscosity follows which, after prolonged grinding, reaches a final, uniform value for a variety of fibres. Investigation into the dependence or otherwise of this fact upon the temperature makes it clear that the breakdown resulting from milling is not due to secondary chemical reactions (such as are caused by oxidation, for example). The assumption must therefore be that mechanical causes are directly responsible for the rupture of the chain molecules.

[32] *H. Staudinger* and *J. Jurisch*, Papier Fabr., 35, (1937) 463.
M. L. Kolmann, Monatsh. Seide Kunstseide, 44, (1939) 142.
[33] *G. P. Vincent, A. L. Dubeau,* and *J. F. Synen*, Am. Dyestuff Reptr., 30, (1941) 358.
[34] *K. Hess, E. Steurer,* and *H. Fromm*, Kolloid-Z., 98 (1942) 148

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H. Ost and *Wilkening*, Chemiker Ztg., *34*, (1910) 461.
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P. H. Clifford, J Text. Inst., *14*, (1923) 69.
C. Birtwell, D. A. Clibbens and *B. P. Ridge*, J. Text. Inst., *14*, (1923) T.297; *16*, (1925) T.13.
C. Birtwell, D. A. Clibbens and *A. Geake*, J. Text. Inst., *17*, (1926) T.145; *19*, (1928) T.349; *21*, (1930) T.85.
D. A. Clibbens and *B. P. Ridge*, J. Text. Inst., *18*, (1927) T. 135; *19*, (1928) T.389.
B. P. Ridge and *H. Bowden*, J. Text. Inst., *23*, (1932) 319.
G. F. Davidson, J. Text. Inst., *23*, (1932) T.95; *25*, (1934) T.174; *27*, (1936) T.112; *29*, (1938) T.195; J. Shirley Inst., *16*, (1938) 29.
G. F. Davidson (Review), J. Text. Inst., *27*, (1936) P.159; J. Soc. Dyers and Colourists, *56*, (1940) 58.
J. Hanson, S. M. Neale and *W. A. Stringfellow*, Trans. Faraday Soc., *31*, (1935) 1718.
G. L. Godman, W. N. Haworth and *S. Peat*, J. chem. Soc., *1939*, 1908.
Fr. Müller, Helv. chim. acta, *22*, (1939) 208, 217, 376.
H. Staudinger and *A. W. Sohn*, Ber., *72*, (1939) 1709; J. prakt. Chem., *155*, (1940) 177.
H. Rath and *H. Rademacher*, Melliand Textilber., *20*, (1939) 749.
E. Geiger, Helv. chim. acta, *28*, (1945) 283, 1159, 1638.
E. Pacsu and *L. A. Hiller*, Textile Res. J., *15*, (1945) 354; *16*, (1946) 490, 564; *17*, (1947) 405.

OXIDATION BY PERIODIC ACID

E. C. Jackson and *C. S. Hudson*, J. Am. Chem. Soc., *58*, (1936) 378; *59*, (1937) 994, 2049; *60*, (1938) 989.
G. F. Davidson, J. Textile Inst., *31*, (1940) T.81; *32*, (1941) T.109.
G. Jayme, M. Sätre and *S. Maris*, Naturwiss., *29*, (1941) 768.
E. Pacsu, Textile Res. J., *15*, (1945) 354.

OXIDATION OF PRIMARY OH-GROUPS BY NITROGEN TETROXIDE

E. C. Yackel and *W. O. Kenyon*, J. Am. Chem. Soc., *64*, (1942) 121.
C. C. Unruh and *W. O. Kenyon*, J. Am. Chem. Soc., *64*, (1942) 127.
K. Maurer and *G Reiff*, J. makrom. chem., *1*, (1943) 27.

Review:

C. C. Unruh and *W. O. Kenyon*, Textile Res. J., *16*, (1946) 1.

CHAPTER V

RELATIONSHIP AND DIFFERENCES BETWEEN REGENERATED AND NATIVE CELLULOSE

§ 1. SOME FUNDAMENTAL DEFINITIONS

There are some rather dubious definitions which, having crept into the literature on cellulose, are apt to give rise to confusion. Before proceeding, therefore, we shall endeavour to clarify these doubtful expressions.

By *regenerated cellulose* we understand those preparations which by some means have been recovered in a solid form from a homogeneous solution and have suffered no extensive breakdown. The definition therefore embraces a variety of products from flocculent precipitates to artificial structures such as filaments and films.

Cultivated cellulose fibres, and those obtained from natural products (such as wood, straw, etc.) without excessive interference and with retention of the fibrous structure, are termed *native cellulose*.

There are some striking differences in many respects between native and regenerated cellulose with which we shall deal in this Chapter.

The evidence of X-ray spectrography is that the structure of the crystalline regions of native cellulose objects is different from that of regenerated cellulose. The most appropriate designations for the two modifications are "Cellulose I" and "Cellulose II", but they are often referred to as "native cellulose" and "cellulose hydrate" (or „hydrated cellulose").

When native cellulose products are mercerized, the X-ray diagram likewise changes into that of cellulose II (p. 18). This transformation may also be brought about by the action of concentrated acids, concentrated solutions of certain salts and cuprammonium solutions [1]. It is generally observed following reactions in which temporary intracrystalline swelling has taken place [2]. It may, however, also be brought about by strong mechanical action (see p. 145).

It need hardly be said that the X-ray diagram of a cellulose sample offers

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[1] *J. R. Katz* and *K. Hess*, Z. physik. Chem., 122, (1926) 126.
J. R. Katz and *H. Mark*, Z. physik. Chem., 115 (1925) 385;
T. Kubo, Kolloid-Z., 96, (1941) 41.

[2] According to *G. Centola*, Gazz. chim. ital., 65, (1935) 1015, the transformation of cellulose I to cellulose II after chemical reaction in the fibrous form only takes place if the reaction is accompanied by intramicellar infiltration of the solvent. Thus, he maintains, cellulose I nitrated in an anhydrous medium yields cellulose I upon denitration, whereas, if nitrated in an aqueous medium, it produces cellulose II.

no conclusive evidence whatever as to its other properties. Many important properties of well-orientated mercerized ramie fibres, for instance, are totally different from those of well-orientated artificial fibres. The former retain certain qualities peculiar only to natural fibres. Conversely, by certain operations the lattice of regenerated fibres can be converted to that of cellulose I, though it will acquire none of the hall-marks of native cellulose fibres.

Knowing what we do about the structure of cellulose samples, we shall not be surprised to learn that the structure of their crystalline regions has little bearing upon their physico-chemical and technological behaviour. The essential is, without doubt, the nature of the entire micellar system and the so-called "amorphous" regions in particular (which it is, admittedly, so much more difficult to investigate).

To avoid otherwise almost inevitable misconception, the following observances are recommended:

a. To adhere strictly to the designation "Cellulose I", "Cellulose II", etc. for the various lattice types of cellulose depending upon polymorphism.

b To apply the term "native cellulose" only to natural products, including those which, by mercerization (and kindred manipulations) have had their crystalline regions converted to cellulose II. Thus the wider application of the term "native cellulose" extends not only to preparations exhibiting the diagram of cellulose I. (Native cellulose preparations will, moreover, always be distinguishable from the regenerated products by their specific morphological microstructure).

c. To apply the term "cellulose hydrate" only to the lattice modification of cellulose II and, therefore, not to cellulosic products or fibres as such (otherwise there would be native and regenerated cellulose hydrates [3]).

Accordingly, we may expect to have both native and regenerated fibres in the form of cellulose I or of cellulose II

§ 2. FORMATION AND PROPERTIES OF CELLULOSE II IN NATIVE FORM

J. Mercer [4] at first believed that the products obtained by treating native fibres with concentrated caustic soda lye and washing out the alkali, contained chemically combined water, which accounts for their infelicitous classification as "Cellulose Hydrates". Later on, several critics attacked this theory [5], but it has recently transpired that hydrates actually are formed from Cellulose II, one of which can always be detected by X-rays, even at ordinary atmospheric humidity (Chapt. I, § 4). In a certain sense, therefore, *Mercer's* conception has been vindicated.

[3] Formerly, the author himself was prone to refer to regenerated fibres as "cellulose hydrate fibres", but subsequently admitted that the term was unsuitable and confusing.

[4] Cf. J. Chem. Soc., 20 (1867) 395; *E. A. Parnell*, The Life and Labours of *John Mercer*, London 1886.

[5] *Z. B. H. Ost* and *F. Westhoff*, Chem. Ztg., 33, (1907) 197

From the outset it has been noticed that marked changes in a variety of macroscopic properties never fail to result from the treatment of native objects — especially natural fibres — with reagents which transform Cellulose I into Cellulose II. They have frequently been attributed to dislocation, that is to say, enlargement, of the "inner surfaces". In their text-book, *J. T. Marsh* and *F. C. Wood* [6] describe (not very aptly) objects changed in this way as "dispersed cellulose".

Detection of the enhanced water-vapour sorptive capacity of the fibres goes as far back as *Mercer* himself. (We shall revert to this matter in greater detail in Part II, Chapter II, § 2). Furthermore, dyes were found to be absorbed in a marked degree and there was discovered to be easier penetration of other reagents, enhanced swelling power, etc., all showing that the "reactivity" of the fibres is increased.

It should be noted, however, that this enhanced reactivity does n o t in itself stand in direct relation to the changed X-ray spectrum. *J. R. Katz* [7] is at pains to point out that natural fibres may be nitrated and then again denitrated, when the final X-ray diagram will be that of the native modification (Cellulose I), though the fibres so treated will have retained the other properties of mercerized cellulose, such as sorptive power towards water, etc.

It would seem that the enhanced reactivity is due simply to an increased percentage of matter of a non-crystalline nature. Owing to the transient swelling occurring during the chemical reaction, the original fibre structure is disturbed to some extent. The crystalline regions may have become smaller, or have even partly broken up.

If the reagent has given rise to intramicellar swelling, it will depend upon the degree of such swelling whether the crystalline modification of the cellulose crystallites, regenerated after the washing out of the reagent, has or has not changed. Though, where lattice transformation to Cellulose II has taken place, the increased water absorption may in a minor degree be due to the formation of the cellulose hydrate I (Chapt. I, § 4), there is no doubt that most of the additional water absorbed by the transformed objects is bound i n t e r micellary, which indicates yet other changes in the structure of the fibre.

Mechanical treatment may also somewhat increase the waterbinding capacity of the cellulose, without necessarily involving any alteration of the lattice, a fact which has long been known in the paper industry [8]. Nevertheless, the lattice can be transformed by purely mechanical means, as is evident from interesting investigations recently published by *K. Hess, H. Kiessig* and *J. Gundermann* [9]. These authors report the total disappearance of the X-ray interferences of the cellulose lattice within a comparatively short interval

[6] *J. T. Marsh* and *F. C. Wood*, An Introduction to the Chemistry of Cellulose, London 1938; (3rd edition 1945).
[7] *J. R. Katz*, Die Röntgenspektrographie als Untersuchungsmethode. Berlin 1934. p. 92.
[8] Grinding in the beater, *C. G. Schwalbe* and *E. Becker*, Z. angew. Chem., 33, (1920) 58.
[9] *K. Hess, H. Kiessig*, and *J. Gundermann*, Z. physik. Chem., B. 49 (1941) 64.

on grinding (dry) native cellulose fibres in a vibrating ball mill. Instead, there appears only a wide interference similar to that known to occur with amorphous substances. When the ground material comes into contact with water, crystalline regions are again formed, notably in the form of Cellulose II (cellulose hydrate), and boiling with water further sharpens the X-ray diagrams. Mechanical treatment obviously disturbs the orderly arrangement of the molecular chains in the lattice. They have insufficient freedom of movement in the dry ground material to revert to order, but, when water is added, their mobility increases and recrystallization sets in [10]. The sorptive capacity and the heats of wetting of the amorphous products of grinding and the recrystallized ones were recently investigated by *P. H. Hermans* and *A. Weidinger* [11]. The deduction from these data and from a quantitative analysis of the X-ray diffraction pictures is that the percentage of crystalline substance in the recrystallized products is 30 to 40 (see also p. 190 and 316).

The conclusion to be drawn is that, when the lattice of Cellulose I is widened or disturbed and recrystallization takes place in the presence of water, the lattice of Cellulose II comes into being. This, however, invariably involves a change in the entire structure of the fibre which, while not visible in the X-ray diagram, is responsible for the characteristic enhanced reactivity of the material. The altered lattice structure is merely an indication, not the direct cause of the increased reactivity of the fibre. The latter is due to the previous intramicellar swelling, which was accompanied by powerful intermicellar swelling of the whole fibrous mass, traces of which are left behind [12].

The picture we had built up of micellar structure (for which compare Figures 15, 16, 17, 18 and 25) will help us now to represent to our minds the irreversible changes in structure with which we are at present dealing. In mercerization (or in other reactions producing the transformation), the swelling agent penetrates everywhere between the chain molecules, with consequent weakening of the cohesive forces which hold the system together. It is in the amorphous regions, above all, that the chains are torn asunder and, in a way, are "locally dissolved" (p. 63) by the powerful swelling. Quite conceivably this might go hand in hand with diminution of the lattice-ordered regions, that is to say deterioration in the orderly condition (multiplication of local points of distortion).

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[10] *K. Ueberreiter*, Z. physik. Chem., B. 48, (1941) 197, has clearly demonstrated that the mobility of cellulose chain molecules is increased in the presence of a sufficient quantity of water.

[11] *P. H. Hermans* and *A. Weidinger*, J. Amer. Chem. Soc. 68, (1946) 1138, 2547.

[12] For further particulars on the "activation" of native cellulose by preliminary swelling and on methods of quantitative measurement we refer to an article by *S. M. Neale*, Trans. Faraday Soc., 29, (1933) 228 and to descriptions in the books by *E. Valkó*, Kolloidchemische Grundlagen der Textilveredlung. Berlin 1937, p. 210, and by *J. T. Marsh* and *F. C. Wood*, An Introduction to the Chemistry of Cellulose, London 1938. Furthermore, we wish specially to draw attention to *J. R. Katz*' still excellent and often cited contribution, entitled Micellartheorie und Quellung der Zellulose, to *K. Hess's* now otherwise rather out-of-date book, Die Chemie der Zellulose, Leipzig 1928, p. 605 ff. The said contribution is a rich mine of interesting information and of theoretical arguments still of great value.

In the very swollen amorphous regions, the now independent and mobile chains will tend to change their shape (convolution), which, in turn, will tend to shorten the fibre and, indeed, fibre shrinkage of the kind is actually observed when swelling takes place in strong bases. It is significant that, according to *J. R. Katz* [13], such shrinking does not result from swelling in water. The same author states that, the longer and the more intense the reaction with alkali hydroxide in mercerization, the more indistinct do the X-ray interferences become, while the orientation of the crystalline regions changes with respect to the fibre axis; in fact, considerable disorientation takes place. The mercerized fibres acquire rubber-like qualities to some extent, owing to the increased flexibility of the molecular chains, a fact already pointed out by *J. R. Katz* in particular.

If the fibre is prevented from shortening during mercerization (under tension), the micellar system remains forcibly stretched; but there is then less swelling of the fibre and experience has shown that mercerization under these conditions never produces complete, but only partial transformation to Cellulose II. The resulting objects have less enhanced sorptive power than those mercerized without tension.

Nevertheless, disorientated fibres mercerized without tension can be quite well re-orientated by subsequent stretching [13a]. Our own evidence shows that the enhanced sorptive power of the fibres with respect to water vapour which is produced by mercerization, decreases in this operation by 10 to 15%.

It is abundantly clear that the changes taking place in native cellulose objects after pronounced swelling are the result of a reduced percentage of crystalline substance. The greater free energy of the less densely packed substance in itself accounts for the increased reactivity of the objects towards water, swelling agents and so forth. This conception we shall retain as a working hypothesis, but only further research can show whether there are other factors as well that have to be taken into account (cf. § 3).

In the next section we shall compare these with regenerated objects, when we shall see that natural cellulose fibres "activated" by mercerization (or similar pretreatment) and converted to Cellulose II, often resemble the unchanged material far more closely in their behaviour — especially towards solvents and swelling agents than do the regenerated objects.

§ 3. DIFFERENCES BETWEEN NATIVE AND REGENERATED CELLULOSE

The behaviour of regenerated cellulose might at first sight be roughly described as representing an intensification of those changes which mercerized native cellulose undergoes, as compared with the unchanged product found in Nature. There is nothing surprising in the fact that, owing to the complete

[13] *J. R. Katz*, In *K. Hess'* book: Chemie der Zellulose, Leipzig 1928, pp. 657—768.
[13a] *T. Kubo*, Z. physik. Chem., A. 187 (1940) 297, to which we shall also revert in Part II.

destruction of the original fibrous structure during solution, a system of even looser structure and more deranged order comes into existence after precipitation than that exhibited by the mercerized fibres which have merely been preliminarily swollen. This matter is really the main theme of the third part of this book and some of its many aspects will be dealt with later.

The increased power to absorb water and dyes and the more marked swelling of the artificial fibres in water are not unconnected with conceptions of structure which are readily evolved from those dealt with in the preceding section. The main thing is that the regenerated objects contain an even smaller percentage of crystalline substance. As we shall see in the second part of this book, this hypothesis goes a long way towards explaining many physical properties of the fibres. But it may be as well to point out at once that the hypothesis is by no means able to explain, apart from the morphological structure, all the other striking differences in the physical and chemical behaviour of native and regenerated cellulose. In this section we wish to put forward, in addition to some phenomena which may be understood within the terms of so general and simple a statement, certain other facts of which it does not offer an adequate explanation and which therefore deserve our attention.

W. Schramek and *O. Succolowsky*[13b] have attributed the somewhat different reaction of regenerated cellulose to conc. sodium hydroxide solutions to the presence of an augmented constituent of non-crystalline ("amorphous") cellulose. There is readier formation of the various sodium celluloses and, compared with native cellulose, there is appreciably greater swelling power in caustic soda solutions.

The close relationship between solubility and swelling capacity has been emphasized repeatedly in this book (see the references given above) and is also manifested in the behaviour of regenerated cellulose.

The solubility of regenerated cellulose in alkali hydroxide solutions of varying concentrations is substantially greater than that of the native product, though it depends upon the conditions under which regeneration takes place. We would recall the observation made by *C. F. Cross* and *E. J. Bevan*[14] some time ago, to the effect that, in its flocculated form, freshly precipitated cellulose is soluble in 2 n sodium hydroxide solution, a property which it loses rapidly as time progresses (recrystallization?)

We have several older papers dealing with the solubility of artificial filaments and films in caustic soda lyes but, for reasons which will be mentioned directly, they are only of limited qualitative value. *A. Marschall*[15] found recently that mixtures of concentrated formic acid and certain salts provide solvents which completely dissolve regenerated cellulose and leave native

[13b] *W. Schramek* and *O. Succolowsky*, Die Kunstseide, 18, (1936) 235.
[14] See in *K. Hess's* Chemie der Zellulose, Berlin 1928.
[15] *A. Marschall*, Kunstseide u. Zellwolle, 22, (1940) 215; 23, (1941) 160.

cellulose almost unchanged. On this fact he based a practical method of separation for the analysis of fabrics [16].

Since the solubility of high-molecular substances is also a function of their molecular size (p. 114), distinctions of this kind are, of course, only characteristic if the comparison is between samples of the same distribution of chain length, or at any rate of the same average degree of polymerization *(DP)*. Investigations were actually carried out by *H. Staudinger* and *J. Jurisch* [17], *A. Marschall* (loc.cit.) and *O. Eisenhuth* [18] *Staudinger* and *Jurisch* established the fact that the solubility of degraded cotton samples in alkali is different from that of regenerated cellulose fibres of the same *(DP)*. *Marschall* had degraded cotton and sulphite cellulose by various chemical reactions and compared the properties of the resulting samples with artificial fibres of approximately the same average degree of polymerization. Some of his results are collected in Table XIV.

TABLE XIV

Swelling and Solubility of degraded Celluloses after Marschall

	DP	SWELLING IN %		SOLUBILITY IN %			
		Water*	NaOH*	NaOH*	Ca (CNS)$_2$ solution	Na Zincate solution	Formic acid sol. + $CaCl_2$
Not degraded	897	60	187	11	16	19	6
Degraded with:-							
H_2O_2	222	54	254	43	100	51	14
$K_2Cr_2O_7$ (acid)	375	53	>330	62	100	79	6
Alkali ripening	180	74	224	8	29	100	16
" " + H_2O_2	227	77	249	5	19	77	1
Regenerated fibres	280	92	420	23	100	100	100

* According to *H.Dillenius*, Kunstseide und Zellwolle, 22, (1940) 314.

It will be seen that the samples decomposed by H_2O_2 and acidified bichromate have greatly increased solubility in caustic soda solution, calcium thiocyanate and sodium zincate solutions, approximating that of the regenerated cellulose, or even surpassing it (in NaOH). Yet samples decomposed by alkaline oxidation (alkali ripening with or without the addition of hydrogen peroxide) remain far less soluble in this respect than the regenerated sample (produced from viscose and, therefore, likewise with alkali ripening [19]). The greater stability of all "native" samples in the presence of formic acid-calcium chloride, as compared with the regenerated fibre, is particularly striking.

[16] Separation methods of the kind were critically reviewed by *O. Kirret*, Klepzigs Textilzeitschr., 43, (1940) 739, since when *E. Schwartz* and *W. Zimmermann*, Melliands Textilber., 22, (1941) 525, have published another method of separation, which relies on the complete solubility of regenerated cellulose in sodium hydroxide solution of 10% at —5° (up to about DP 600).

[17] *H. Staudinger* and *J. Jurisch*, Kunstseide und Zellwolle, 21, (1939) 6.

[18] *O. Eisenhuth*, Cellulosechemie, 19 ,(1941) 45; Z. angew. Chem., 54, (1941) 135.

[19] The samples degraded by alkali ripening only appear to be less soluble in lyes than those not degraded. The seeming difference is due to the elimination of a small percentage of lye-soluble substance during the preceding steeping process.

O. Eisenhuth (loc.cit.) obtained similar results. He examined cotton linters and wood pulp from spruce in different stages of decomposition, degradation being brought about by alkali ripening or by heating with dilute hydrochloric acid. The samples were compared with artificial fibres of roughly the same average degree of polymerization manufactured by the viscose process. Some of the results obtained by Eisenhuth from linters are given in Table XV.

TABLE XV

Solubility in 10% NaOH at 5°C. of Cotton Linters Decomposed in different Ways, after O. Eisenhuth [20]

STAGE OF DECOMPOSITION	TREATMENT	DP	SWELLING IN WATER IN %	% SOLUBLE IN 10 % NaOH AT 5° C.
—	Untreated starting material	~ 1000	45	2.5
I	Ripening of alkali cellulose	750	75	2.5
	Hydrochloric acid		44	4.0
	Viscose process		80	56
II	Ripening of alkali cellulose	550	75	3.0
	Hydrochloric acid		45	11.0
	Viscose process		85	63
III	Ripening of alkali cellulose	325	75	7.0
	Hydrochloric acid		45	26
	Viscose process		85	82

It will be seen that, as far as their solubility in caustic soda solution is concerned, the regenerated samples — even those but little degraded — are clearly distinguishable from those objects decomposed to the same degree but without any intermediate dissolving process. By thermal degradation (dry heating), *Eisenhuth,* it is true, obtained preparations exhibiting the same solubility in alkali hydroxide as that of the regenerated object.

It is evident from the foregoing experimental material that the distinctive difference in solubility and swelling capacity of native and regenerated objects cannot be accounted for by any difference in degree of polymerization. *S. M. Neale* [21] had already pointed out that "Degradation" and "Activation" were due to entirely different changes in the original material. He demonstrated how, though the tensile strength, viscosity of the solution and absorption of methylene blue (see p. 83) were connected with the degree of breakdown, they were not affected by "activation", whereas in sorptive power towards water, absorption of alkalis and dyes, such as Chicago Blue, for instance, it was just the reverse.

[20] *O. Eisenhuth*, Cellulosechemie, 19, (1941) 45; Z. angew. Chem., 54, (1941) 135.
[21] *S. M. Neale*, Trans. Faraday Soc., 29, (1933) 288.

Nor does the assumption of a different constituent percentage of crystalline substance help us to explain the reported differences in solubility. We shall see later (Part II, Chapter II) that the percentage of crystalline substance may be assumed to decrease very substantially in the mercerization of native fibres, yet, judging by the preceding tables, the solubility of mercerized fibres (alkali ripening) does not correspondingly increase in all cases.

The following possibilities remain to be discussed:

a. Difference in morphological structure (biostructure of the native objects).
b. Other physical differences in polymolecular structure.
c. Possible chemical differences.

It is difficult to estimate the influence of the specific histological structure of grown fibres upon the properties we have been considering. *W. Schramek* and *O. Succolowsky*[22] state that it is responsible for the only partial transformation to sodium cellulose I in sodium hydroxide solutions of approximately 10 per cent. concentration. But, once the fibre has reacted fully, as it had in the preliminary "alkali ripening" of the experiments under consideration, this factor can no longer be operative. *K. Schwertassek*[23] states in an article that the limited swelling of native fibres is due to the presence of a non-swelling outer layer.

Interesting observations have also been made following the publications already mentioned on p. 145 by *K. Hess* and co-workers regarding the reaction of native cellulose by intensive, purely mechanical means, such as grinding. These were recently reported by *J. Löbering*[24] and *K. Ph. Jung*[25], who investigated the effect of sodium hydroxide and carbon disulphide upon fibres pulverized to fragments of about 20 μ. Although X-ray data showed that the lattice of the native cellulose had not been broken down by the preliminary mechanical treatment, the behaviour of the pulverized native fibres in this reaction, unlike that of the native fibres not so treated, was almost identical to that of regenerated cellulose hydrates. The authors conclude that the phenomenon is obviously due to a disruption of the morphological structure of the native fibres and point out to what interesting technical uses their results may be put.

This, we think, is an appropriate moment to draw attention to investigations recently published by *W. A. Sisson* and *W. R. Saner*[26] on the mercerization of raw and variously pretreated cotton fibres, which likewise shed some light on hitherto unexplained structural details of native fibres. These investigators examined the effect of sodium hydroxide over a wide range of temperature and concentration (-20° to 100° and 0 to 50%). After the alkali had been washed out, the samples were dried and X-rayed. Fig. 39, illustrates the result for raw cotton and for cotton bucked and bleached in

[22] *W. Schramek* and *O. Succolowsky*, Die Kunstseide, 18, (1936) 235.
[23] *K. Schwertassek*, Klepzigs Textilz., 44, (1941) 101.
[24] *J. Löbering*, Kolloid-Z., 98, (1942) 186.
[25] *K. Ph. Jung*, Kolloid-Z., 98, (1942) 193.
[26] *W. A. Sisson* and *W. R. Saner*, J. phys. Chem., 44, (1940) 717.

the customary way. Next to the region of unchanged native cellulose and that of complete conversion to cellulose hydrate, the diagram shows a large region of only partial transformation (enclosed by dotted patches in Fig. 39).

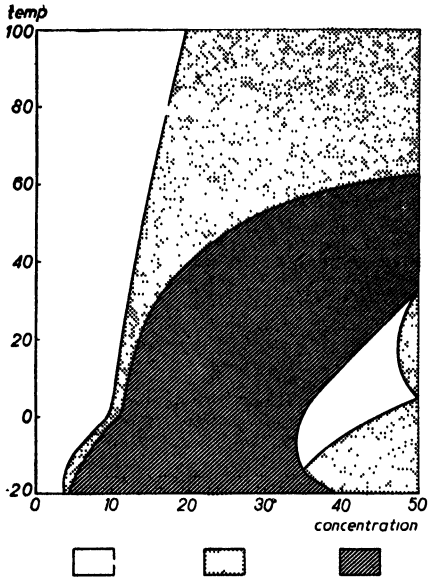


Fig. 39. Result of the action of sodium hydroxide of different temperatures and concentrations upon cotton fibres, after *W. A. Sisson* and *W. R. Saner*. White patches native cellulose; hatched patches partial transformation; shadowed patches completely mercerized.

If the fibres were preliminarily treated for 5 minutes with 1 n hydrochloric acid at 75°, the native cellulose region remained almost unchanged, but the region of partial conversion disappeared almost completely and was occupied by that of the pure cellulose hydrate. The result was the same when, after the alkali treatment under conditions which in Fig. 39 produced partial conversion, the fibres were heated for some considerable time with the alkali, provided, however, air was not excluded during the operation. If oxygen was not admitted during heating, the diagram of Fig. 39 remained unchanged. Once again, however, evidence is forthcoming that not only the molecular breakdown resulting from the acid treatment and heating with alkali is responsible for the change, inasmuch as the pulverized fibres, or those cut up into pieces no longer than 0.3 mm., whose viscosity remains unchanged, likewise produced a diagram similar to that of the chemically pretreated samples. Moreover, the solubility in caustic soda solutions of the mechanically triturated fibres had also remained unchanged, whereas that of the chemically pretreated fibres had increased. These remarkable observations undoubtedly go to show that the peculiarities of the structure of native fibres are not open to a simple, straightforward explanation.

The following views have some bearing on the second possibility (b). It may be that, apart from the percentage of crystalline substance, the dimensions of the crystalline regions and their perfect orderliness (number and size of the lattice distortions) may also affect solubility (cf. pages 22, 28, 32). We would also recall the suggestion made on page 20 that the order in the "crystalline" regions of regenerated cellulose must needs remain imperfect, since the regular alternation in the polarity of the chains, essential to the formation of a perfect lattice, cannot be attained. It is merely statistically probable, according to the law of averages, that, in the spinning and drawing of artificial filaments, the molecules will fall into an alternating head-to-tail arrangement.

There is another point of view to be considered. If regenerated cellulose is conceived to be a molecular felt structure or network formed during primary gelatination, which is orientated by subsequent stretching (a conception which we shall come across again and for which there is much to be said), it is necessary to allow for the possible occurrence of twisted chains, i.e., recurrent loops in the finished fibre [27] (cf. p. 80). This would likewise effectively prevent any such perfect and orderly parallel juxtaposition of the molecules as obviously exists in natural fibres.

The experimental verification of these possibilities will certainly be no easy matter and has yet to be attempted. The increased swelling and solubility brought about by purely mechanical preliminary treatment, with X-ray proof in some cases of disruption of the lattice order, may possibly be accepted as indication of the tenability of such views.

We have thirdly to consider the possibility of certain finer chemical distinctions (c).

In this connection not much weight should be attached to the presence of a larger number of carboxyl groups as end groups in regenerated cellulose.

Reference may be made to pages 85, 139 and 154 regarding the possible presence of chemical bridges in native cellulose [28].

Consequent upon their discovery of alien groups at regular intervals of about 510 glucose residues in the molecule of native cellulose (cf. p. 84), *G. V. Schulz* and *E. Husemann* [29] have recently propounded an interesting hypothesis, by which fresh light may possibly be thrown upon the distinctive solubilities of native and regenerated cellulose objects.

It may be inferred from the regular, superperiodic structure of the native cellulose molecule that its lattice order may assume one of two alternative forms, which might be differentiated as the fundamental lattice (ordinary lattice) and the superperiod lattice (with lattice distances in the *c*-axis of 10.3 å or 2600 å). In the superperiodic lattice, the alien groups lie side by side in certain network planes. In the regenerated cellulose, the superperiodic order is disrupted by solution and reprecipitation.

A clearer difference might now appear with respect to solvents, since the cohesive forces operating in the superperiodic lattice in the marked-out lattice planes are different from those obtaining in the other regions. There will be solvents which, though able to overcome the cohesive forces of the fundamental lattice, cannot break up the cohesion in the superperiodic lattice planes. This difference will be particularly liable to occur in cases where the main mass of the substance produces little heat of solution, that is with the "bad" solvents, such as sodium hydroxide.

H. Staudinger and co-workers have carried out some new investigations which should be mentioned. They have brought to light some curious

[27] See *F. Horst Müller*, Kolloid-Z., 95, (1941) 138, 306.
[28] See also the recent survey by *E. Heuser*, Paper Trade J., 122, (1946) 43.
[29] *G. V. Schulz* and *E. Husemann*, Z. physik. Chem., B. 52, (1942) 23.

differences in the chemical behaviour of native and regenerated fibres, the theoretical explanation of which is not yet clear. After esterification in their fibrous form, *H. Staudinger* and *R. Mohr* [30] found striking differences between native and regenerated cellulose. These authors state that fibre acetates produced from native cellulose by reaction with acetic anhydride and pyridine are insoluble and do not swell in organic solvents as from a *DP* exceeding 400, whereas the acetates with *DP* from 500 to 2000 manufactured under the same conditions from regenerated cellulose dissolve in organic solvents after first swelling. The acetates of mercerized native fibres behave like those produced from the unchanged fibres (see Table XVI).

Something has already been said (p. 139) about the remarkable behaviour of native and degraded native fibres upon nitration. *H. Staudinger* and *R. Mohr* [30] found that native fibres (with the X-ray diagram of Cellulose I) can be esterified in nitration in mixtures of nitric acid and sulphuric acid without noticeable breakdown, whereas re-precipitated celluloses (even those of high *DP*) were degraded by these nitration mixtures. Only by nitration in mixtures of nitric acid and phosphoric acid does reprecipitated cellulose yield polymeranalogous nitrates. In this respect the behaviour of native fibres decomposed with acid is the same as that of the non-degraded fibres, but the mercerized native fibres behave like the re-precipitated celluloses.

Some of the differences observed are recapitulated in Table XVI after Staudinger and Mohr.

TABLE XVI

Behaviour of Different Kinds of Cotton Cellulose after H. Staudinger and R. Mohr [30]

	X-RAY DIAGRAM	SOLUBILITY IN 10 % NaOH	SOLUBILITY OF THE TRI-ACETATES IN m-CRESOL	NITRATION NUMBER*
Native fibre cellulose DP = 200—3000	Cellulose I	Soluble up to DP = 400	Soluble up to DP = 500	1
Mercerized cellulose DP = 200—3000	Cellulose II	Soluble up to DP = 400	Soluble up to DP = 500	0.5
Reprecipitated cellulose DP = 50—2000	Cellulose II	Soluble up to DP 1200	Soluble up to DP 1200	0.5

* The Nitration Number represents the ratio of the DP of the sulphuric acid nitrates to that of the phosphoric acid nitrates.

Finally, we should remember *P. Karrer's* observation [31] to the effect that a portion of the substance (roughly 8%) in native cellulose resists all attempts to methylate it.

[30] *H. Staudinger* and *R. Mohr*, J. prakt. Chem., 158, (1941) 237
[31] *P. Karrer*, Helv. chim. acta, 19, (1936) 1192.

In many respects, then, the differences in the physical behaviour of various fibres can be traced back to differences in the degree of crystallinity. Obviously, these will again run parallel to the differences in "density of packing" to which *H. Staudinger* and *J. Jurisch* [32] and *H. Dolmetsch* and *F. Reinecke* [33] have alluded. At the same time we thus have a more rational representation of what was formerly described as the "innere Auflockerung" of the fibrous structure, a point to which we shall revert in greater detail in Part II, Chapter II, § 5.

It is of especial importance to the artificial fibre industry that the differences between native and regenerated cellulose should be fully understood, as several of the disadvantages attaching to artificial fibres as compared with native fibres are often due to these differences. The staple fibre industry is prominent among those which have latterly displayed growing interest in this problem. Though far more systematic experimental work will be needed for the solution of these difficult problems, it is a promising sign of notable progress that many of the latest commercial staple fibres possess some of the erstwhile troublesome properties, such as swelling and solubility in caustic soda solutions, in a diminishing degree.

§ 4. RECONVERSION OF CELLULOSE II (CELLULOSE HYDRATE) INTO CELLULOSE I (NATIVE CELLULOSE)

It appears that Cellulose II can be reconverted to Cellulose I by nitration and denitration under given conditions. Some relevant statements made by *J. R. Katz* [34] and *G. Centola* [35] were mentioned in the preceding sections (pages 143 and 145). The writer has found that this also occurs upon saponification of cellulose acetates in 2N ammonia solutions at 100° C. (and not below 40°).

The important question is, of course, whether also the fibre properties of a regenerated object are somehow transformed into those of native fibres after the conversion of the lattice of Cellulose II into that of Cellulose I. Experiments to discover this were to be taken in hand, but as yet no reports have been published. *Katz,* however, states that n a t i v e fibres reconverted to Cellulose I after nitration and denitration, retained the properties of mercerized fibres.

After what has been said hereabove in § 1 and § 2, a recovery of the "native" properties by mere conversion of the lattice is scarcely to be expected.

K. Hess and *J. Gundermann* [36] also report that the lattice of Cellulose I was recovered after the decomposition of a certain modification of alkali cellulose (alkali cellulose III) with hot water.

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[32] *H. Staudinger* and *J. Jurisch*, Kunstseide u. Zellwolle, 21, (1936) 6; Melliand Textilber., 20, (1939) 693.
[33] *H. Dolmetsch* and *F. Reinecke*, Zellwolle, Kunstseide, Seide 5, (1939) 219, 299.
[34] *J. R. Katz*, "Die Röntgenspektrographie als Untersuchungsmethode", Berlin 1934, p. 92.
[35] *G. Centola*, Gazz. chim. ital., 65, (1935) 1015.
[36] *K. Hess* and *J. Gundermann*, Ber. 70, (1937) 527, 1788.

In 1937 *K. H. Meyer* and *N. P. Badenhuizen*[37] and, shortly afterwards, *T. Kubo* and *K. Kanamaru*[38] stated that they had succeeded in reconverting Cellulose II to Cellulose I by heating the objects to approximately 200° in polar liquids such as formamide or glycerol. The conversion was successful when the starting material was regenerated fibres and also mercerized native fibres. For example, a specimen of Lilienfeld-viscose silk was heated in glycerol to 250°; at the end of half an hour its lattice had changed into that of Cellulose I.

K. Hess, H. Kiessig, and *J. Gundermann*[39], however, maintain that it is not Cellulose I which is obtained in these thermal experiments, but another modification, viz., Cellulose IV (HT cellulose), the lattice of which closely resembles that of Cellulose I (cf. Chapter I, §4). *T. Kubo* studied the conversion fully (see separate list of references at the end of this Chapter).

[37] *K. H. Meyer* and *N. P. Badenhuizen:* Nature 140, (1937) 281.
[38] *T. Kubo* and *K. Kanamaru:* J. Soc. Chem. Ind. Japan, 41, (1930) 301.
[39] *K. Hess, H. Kiessig,* and *J. Gundermann,* Z. physik. Chem. B. 49, (1941) 64.

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K. H. Meyer, L. Misch, and *N. P. Badenhuizen,* Helv. chim. acta, *22,* (1939) 59.
T. Kubo, Cellulose Ind. (Japan), *15,* (1939) 13.
T. Kubo, Kolloid. Z., *88,* (1939) 62; J. Soc. chem. Ind. Japan, *42,* (1939) 282 B; *43,* (1940) 85 B.
K. Hess, H. Kiessig, and *J. Gundermann,* Z. physik. Chem., B *49,* (1941) 64.
P. H. Hermans and *A. Weidinger,* J. Colloid Sci., *1* (1946) 495.

SECOND PART

GENERAL PROPERTIES OF CELLULOSE IN THE FORM OF FIBRES
MORPHOLOGY AND MICRO STRUCTURE
PHYSICAL AND CHEMICAL BEHAVIOUR OF CELLULOSE FIBRES

INTRODUCTION

The object of manufacturing artificial fibres is not merely to imitate natural fibres to the utmost. It is, indeed, a matter rather of emulation than imitation, inasmuch as it has its own peculiar problems in meeting the vast variety of technical demands and prospective uses of textiles. Nevertheless, in many respects native fibres continue to serve as the pre-eminent example and model.

In this part of the book, therefore, which is designed to provide a general survey of the physical and chemical properties of both native and regenerated fibres, we shall devote the first chapter to the morphology of native fibres. Chapters II to V will deal for the greater part with recent investigations carried out by the author and his co-workers, which were published a short time ago under the title: "Contributions to the Physics of Cellulose Fibres" (A Study in Sorption, Density, Refractive Power and Orientation), Elsevier, Amsterdam—New York (1946). For general convenience, citations from this publication are referred to in the body of the book as (Contrib.); for instance, (Contrib. p. 77) means that reference is made to page 77 of the booklet. Where the investigations have also been published elsewhere, the reader will be referred to the relevant publication.

CHAPTER I

MORPHOLOGY OF CELLULOSE FIBRES

§ 1. GENERAL PICTURE OF THE MORPHOLOGY AND THE MICROSTRUCTURE OF NATIVE FIBRES[1]

The cell walls of higher plants are formed initially as thin membranes, termed primary wall, which envelop the cells during the period of their growth and grow by intussusception[2].

The main valence chains in the primary wall are orientated differently from those in the thicker secondary wall, which is deposited mainly by apposition at a later period, when cell growth has ceased. This secondary wall is particularly developed in the fibres needed for technical purposes and represents the bulk of the cellulose substance proper.

With cotton — no doubt the most thoroughly investigated fibre — it was found that a network of cellulose chain molecules in crosswise arrangement probably makes up the primary wall; at any rate, the chains are orientated with a large angle of inclination relative to the fibre axis, instead of more or less parallel to it, as in the secondary wall. *E. E. Berkley*[3] established this by X-ray spectrography. In young, unripe cottons hairs, however, the cellulose chains in the primary wall are not yet in the order of a crystalline lattice, but seem to be individually embedded in an unknown watersoluble substance containing nitrogen and phosphorus; the X-ray diagram shows that "crystallization" takes place[4] when this substances has been extracted by water. For the deposition of single chains in the primary wall, they must be able to slide past each other during the growth of the wall. It is not known to what extent the primary wall is responsible for the mechanico-technological properties of the fibres[5].

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[1] When writing this Chapter, the author often had recourse to the articles by *G. van Iterson* in Chem. Weekbl., 30, (1933) 1 and by *A. Frey-Wyssling* in Naturwiss., 28, (1943) 385, to which he gratefully refers for further reading on the subject.

[2] *A. Frey-Wyssling*, Submikroskopische Morphologie des Protoplasmas und seiner Derivate, Berlin 1938, p. 214; Naturwiss., 28, (1940) 385.

[3] *E. E. Berkley*, Textile Research, 9, (1939) 355. Cf. also Amer. J. Botany 29, (1942) 416.

[4] *W. A. Sisson*, Contrib. Boyce Thompson Inst., 8, (1937) 389.
K. Hess, W. Wergin, H. Kiessig, W. Engel and *W. Philippoff*, Naturwiss., 27, (1939) 622; *E. E. Berkley* and *T. Kerr*, Ind. Eng. Chem., 38, (1946) 104.
K. Hess, W. Wergin, and *H. Kiessig*, Planta, 33, (1942) 151.

[5] By swelling nitrated cotton fibres in organic liquids in stages, *G. Mangenot* and *M. Raison*, Compt. Rend., 210, (1940) 674, were able to detect the primary wall and its annular cleavage perpendicular to the fibre axis under the microscope. Accordingly, ramie fibres, which, botanically, are bark fibres and have no primary wall, produced a different picture. For a recent account on the structure of the outer wall of the cotton fibre and its influence on fibre properties, see *T. Kerr*, Textile Res. J., 16 (1946) 249.

The secondary wall, which is of much greater technical importance and exhibits a crystalline character directly after being deposited, is lamellar in build-up, as can be seen under the microscope after the fibre has been allowed to swell. This structure, which is a result of the periodic character of the processes of deposition during growth, has no outstanding bearing upon the general picture of fibre structure. Cotton fibres formed in plants grown under controlled conditions of light exposure and temperature produce a homogeneous cross-section under the microscope [6].

We have a similar state of affairs with fibrillation. By previous swelling and crushing, or by mechanical means, the secondary walls of fibres can be split up into minute fibrillæ. Good micrographs of these have been published more than once, e.g., by *M. Staudinger* [7], *O. Eisenhuth,* and *E. Kuhn* [8].

According to *A. Frey-Wyssling,* however, these fibrillæ do not represent structural units of definite length and thickness, but are fragments of a coherent submicroscopical micellar frame in the sense of structures as discussed in Part I (Chapter I, § 5). Owing to imperfect crystallization and the occurrence of capillary voids, the density of the cellulose varies from place to place, the fibrillæ representing fragments of better regional crystallization.

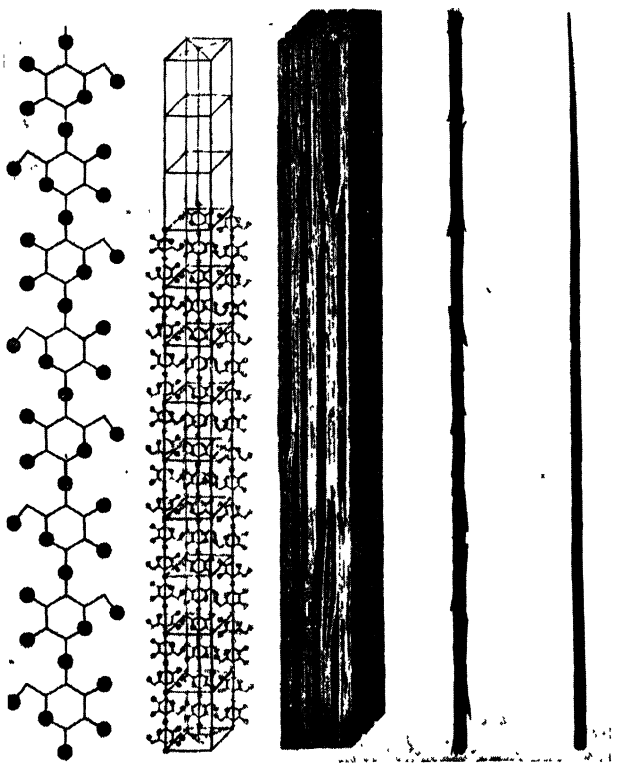


Fig. 40. Diagram of microstructure of fibre with indication of scale after *A. Frey-Wyssling.*

[6] D. *B. Anderson* and *T. Kerr,* Ind. Eng. Chem., 30, (1938) 48.
[7] *M. Staudinger,* J. prakt. Chem., 160, (1942) 203.
[8] *O. Eisenhuth* and *E. Kuhn,* Die Chemie, 55, (1942) 198.

The fact that the fibrillæ in cotton appear to have an almost definite diameter of approximately 0.25 micron may be due to the corresponding thickness of the lamellæ which, on swelling, tend to fall into fragments with an isodiametric cross-section. Fig. 40 reproduces a diagram of fibre structure after *A. Frey-Wyssling*. Noncellulose membranic substances (incrusting pectins, lignin, etc.) may have penetrated into the capillary fissures between the cellulose bundles.

The electron microscope has recently revealed a further cleavage of the fibrillæ beyond the range of ordinary microscopic visibility. To *D. Beischer* falls the credit of being the first to make a discovery of this kind; he detected fibrillæ of 50-100 å diameter in photographs taken with the electron microscope of thin, wedge-like sections.

On milling dry cellulose fibres from wood, *K. Hess, H. Kiessig* and *J. Gundermann* [9] found distribution into elementary fibrillæ ("Grundfibrillen") of 100–750 å diameter. Unlike *Frey-Wyssling*, they believe these infinitesimal fibrillæ to be preformed structures, a view shared by *W. Wergin* [5], who is of opinion that a number of elementary fibrillæ of 150 å diameter are assembled within an as yet unkown enveloping substance to form the next largest structural unit, the fibrillar bundle.

The evidence of recent investigations by a number of other workers, however, tends to call the existence of morphologically pre-formed fibrillæ in native fibres very much into question [10].

G. R. Sears and *E. A. Kregel* [11], who examined beaten pulp and rag stock under the electron microscope, also note the splitting of natural fibres into fine fibrillæ of irregular thickness, an observation which is borne out by the electron micrographs of mechanically disintegrated fibres published by *O. Eisenhuth* and *E. Kuhn* [12], *R. B. Barnes* and *C. J. Burton* [13], *E. Husemann* [14], *P. H. Hermans* [15]. The two last-mentioned authors were unable to reproduce the results of *Hess, Kiessig* and *Gundermann*, either upon dry or upon wet grinding of cellulose fibres. They observed no elementary fibrillæ with a definite lower limit of thickness in their experiments. On wet grinding, the fibres disintegrate into fibrillæ of all sizes down to the limit set by the resolving power of the instrument used. This would seem to confirm *Frey-Wyssling's* views respecting the coherent micellar structure of the cell wall.

E. Husemann came to the same conclusion in the light of her enquiry, with the aid of the electron microscope, into the disintegration of fibres previously treated with acids [16].

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[9] *K. Hess, H. Kiessig* and *J. Gundermann*, Z. physik. Chem. B. 49, (1941) 64.
[10] See also the discussion between *A. Frey-Wyssling* Kolloid Z. 100 (1942) 304 and *W. Wergin*, ibid 100, (1942) 436.
[11] *G. R. Sears* and *E. A. Kregel*, Paper Trade J. 114, (1942) 43.
[12] *O. Eisenhuth* and *E. Kuhn*, Die Chemie 55, (1942) 198.
[13] *R. B. Barnes* and *C. J. Burton*, Ind. Eng. Chem. 35, (1943) 120.
[14] *E. Husemann*, J. makrom. Chem. 1, (1943) 16, 158.
[15] *P. H. Hermans*, Text. Res. J. 16, (1946) 545.
[16] *E. Husemann*, J. makromol. Chem. 1, (1943) 158. According to *Husemann, Hess* and *Gundermann's* micrograph showing elementary fibrillae must be due to some unknown impurity in their preparation.

Fig. 41 reproduces a photograph of wet ground wood pulp (taken by the gold shadow technique), borrowed from H e r m a n s.

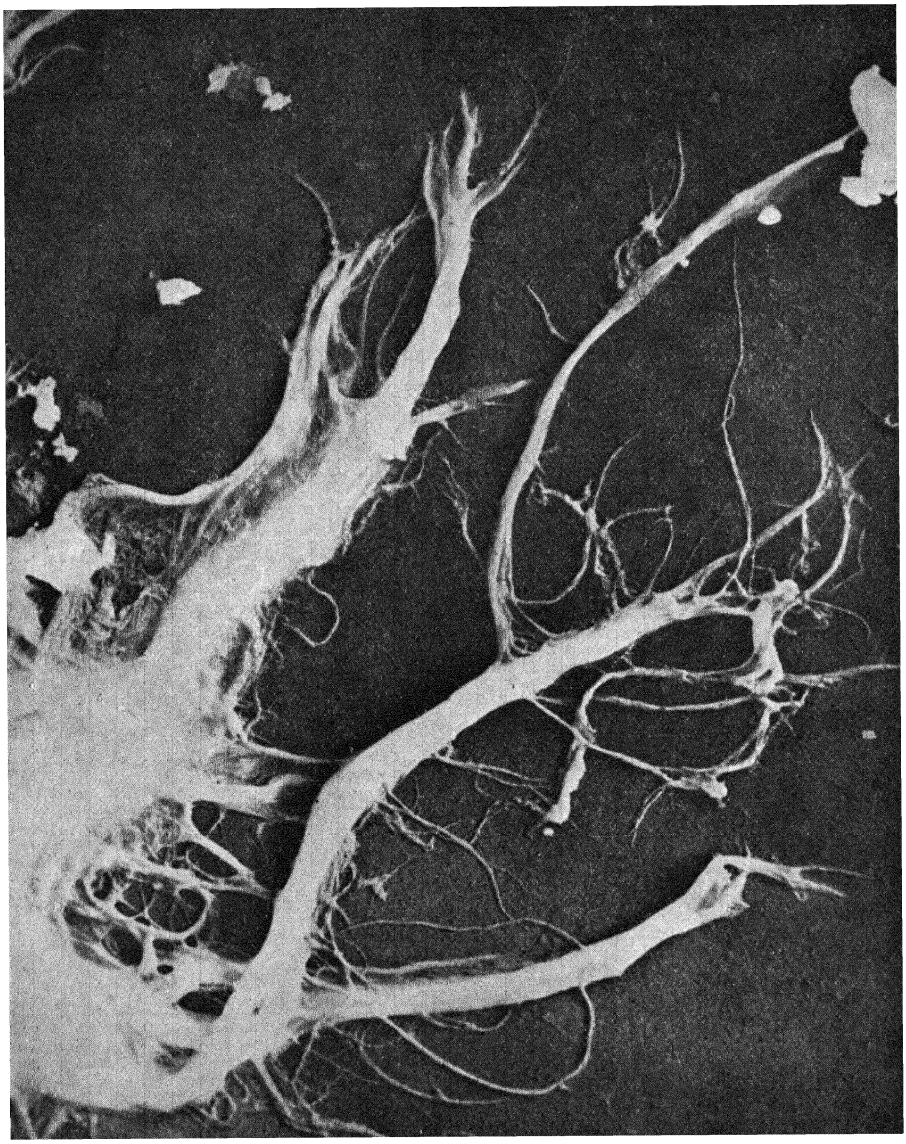


Fig. 41. Electron micrograph (gold shadow technique) of a particle of wet ground sulphite pulp (magnified 12000 times).

If properly orientated, artificially produced cellulose fibres also exhibit the phenomenon of fibrillation when mechanically disintegrated in the wet state, as shown in the pictures published by *Eisenhuth* and *Kuhn, Husemann* and *Hermans* (loc.cit.). The better the orientation of the fibres, the more

pronounced is the fibrillation. The fibrillæ, however, tend to be shorter and thicker than those obtained from natural fibres and particles of a more irregular shape are also sometimes observed.

Fig. 42 represents Lilienfeld rayon ground wet for 3 hours.

The marked fibrillation observed also in artificial fibres, in which there can certainly be no pre-formed fibrillæ, would seem further to endorse *Frey-Wyssling's* doctrine of the coherent micellar structure of native fibres.

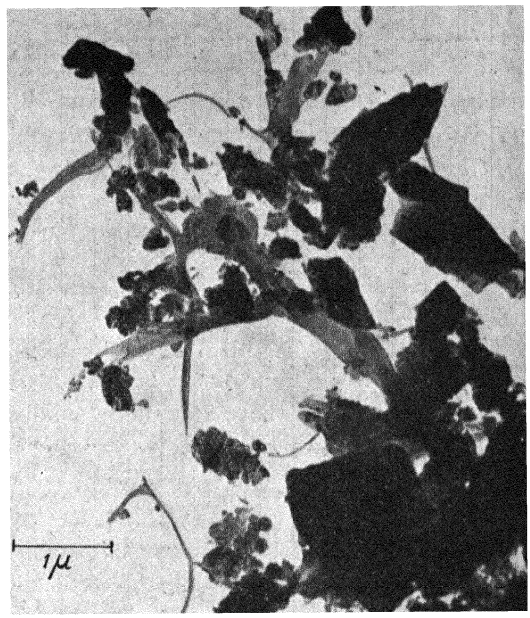


Fig. 42. Electron micrograph of Lilienfeld rayon ground wet for 3 hours. (The irregular black particles are porcelain powder from mill abrasion).

Lateral structure. There are means of splitting up fibres at right angles to the fibre axis into fragments which so resemble pre-formed lateral structures that they often gave rise to the assumption of transverse membranes intersecting the fibres. There are, for example, the "chemical" cross-sections which *H. A. el Kelaney* and *G. O. Searle* [17] say are obtained if, after being heated for a short time with acid, fibres are placed in sodium hydroxide of 10 to 15% (a phenomenon which is also observed occasionally on dissolving xanthated wood fibres [18]). In the reaction of hydrophobic esterification reagents [19] conversion sometimes proceeds in transversal patches, owing to the fact that the heterogeneous reaction obviously proceeds with greater ease laterally to, than in the direction of, the fibre (Fig. 43). Lateral structures of the most diverse orders of magnitude may be found, dependent upon the preliminary treatment applied.



Fig. 43. Heterogeneous esterification of a ramie fibre, in the polarization microscope after *A. Frey-Wyssling*. White: unesterefied cellulose; grey: cellulose acetate.

K. Hess and co-workers [20] worked out the hypothesis of the "alien membrane system" in an endeavour

[17] *H. A. el Kelaney* and *G. O. Searle*, Proc. Roy. Soc. London, 106, (1930) 357.
[18] *E. Kühnel*, Kunstseide und Zellwolle, 21, (1940) 369.
[19] *A. Frey-Wyssling*, Protoplasma, 26, (1936) 45.
[20] *K. Hess, C. Trogus, N. Ljubitsch*, and *L. Akim*, Kolloid-Z., 51, (1930) 89.

to explain the shortening of the fibre and other phenomena during swelling, but the bottom was knocked out of this theory by evidence of *M. A. Calvert* [21].

K. W. Farr and co-workers [22] reported that, after chemical reactions, there was an even finer subdivision. They observed that the fibres disintegrated to particles of about 1.1 μ in length and 1 μ in width, upon which fact they based a comprehensive theory respecting the microstructure of fibres, the principles of which have since been called into question [23] by experiments carried out by *M. Harris* and co-workers [24]. The "dermatosomes" postulated by *Wiesner* may also be likened to *Farr's* "cellulose particles"; after reaction with cuprammonium, *W. Wergin* [25] found even smaller particles of 0.2—0.25 μ, confirmed by electron micrographs [26]. Both *Farr* and *Wergin* assumed that their particles are cemented in the fibre by an "alien substance".

It was no easy matter to reconcile such theories with the facts, many of which seemed to contradict them; nor were they able to explain the almost exclusive lateral swelling of the fibres and the anisotropy of tensile strength. It seems probable that all such subdivisions hitherto obtained yield artificially produced particles resulting from breakdown by chemical reactions, and not systems preformed in the fibre. This would appear to be endorsed by the fact that, as evidenced by convincing illustrations in a publication by *H. Staudinger, M. Staudinger* and *E. Sauter* [27], artificially produced polyoxymethylene fibres can likewise be split up into fibrillæ or into cross sections by chemical pretreatment. This was later verified by *M. von Ardenne* and *D. Beischer* [28] by means of both the ordinary and the electron microscope. Recently published investigations by *W. Schramek* [29] on the disintegration of fibres of wood cellulose and of cotton during the viscose reaction are especially revealing on this point. He was able to obtain longitudinal and lateral splits, all according to the experimental conditions, and went a long way towards explaining the morphological microstructure of these fibres.

Nor does the explanation of a beaded appearance on swelling (paternoster structure), which is to be observed in many native fibres, call for the assumption of lateral structures, or lateral membranes; it is due rather to the cuticles so difficult to dissolve. *A. Frey-Wyssling* [30] states that superficially

[21] *M. A. Calvert*, J. Text. Inst., 21, (1930) T. 293.
[22] *K. W. Farr*. Contrib. Boyce Thompson Inst., 6. (1934) 309; *K. W. Farr* and *S. H. Eckerson*, J. phys. Chem., 42, (1938) 1113.
[23] For this compare also the arguments advanced by *D. B. Anderson* and *T. Kerr*, Ind. Eng. Chem., 30, (1938) 48 and the article by *E. B. Barnes* and *C. J. Burton*, Ind. Eng. Chem., 35, (1943) 120.
[24] *M. Harris, C. W. Hock, A. E. Martin*, and *R. L. Whistler*, J. of Research Nat. Bur. of Standards, 24, (1940) 13, 555, 743.
[25] *W. Wergin*, Naturwiss., 26, (1938) 613.
[26] *W. Wergin*, Kolloid-Z., 98, (1942) 131; 100, (1942) 436.
[27] *H. Staudinger, M. Staudinger*, and *E. Sauter*, Z. physik. Chem., B. 37, (1937) 403; Melliand Textilber. 18, (1937) 849.
[28] *M. von Ardenne* and *D. Beischer*, Z. physik. Chem., B. 45, (1940) 465.
[29] *W. Schramek*, Z. physik. Chem., B. 50, (1941) 298; Cellulosechem., 19, (1941) 93, 20, (1942) 38.
[30] *A. Frey-Wyssling*, Protoplasma, 25, (1936) 261.

acetylated artificial fibres, which are, therefore, protected by an insoluble film, are also subject to ball swelling and *R. Haller*[31] produced ball swelling in artificial fibres by similar expedients[32].

Interesting investigations recently published by *H. Dolmetsch, E. Franz,* and *E. Correns*[33] may serve to bridge the gap to some extent between the theory propounded by *Frey-Wyssling*, according to which the fibres constitute a coherent micellar system, and the views upheld by *Wergin, Farr, Lüdtke*, etc. *Dolmetsch* and his associates examined very thoroughly and systematically the phenomena brought about by swelling. These investigators suppose that the fibrillæ of the secondary wall contain consecutive strings of crystalline regions, all of the same size and made up of molecules of the same length. In some way, not yet clearly explained, they are connected with each other by non-crystalline intermediate regions (possibly by fringe-like or brush-like interweaving). These intermediate regions are spaced out on gradual transverse spirals permeating the secondary wall and, under certain treatment, prove to be cleavage surfaces. The secondary wall then disintegrates into spiral bands, across which the bundles of fibrillæ lie. In this view, the crystalline regions are identical with the *Farr* particles.

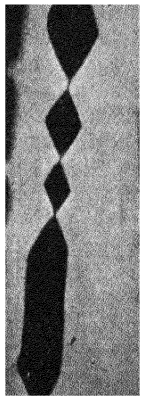


Fig. 44. Corrosion patterns in the fibre wall caused by fungi.

If fibre structure is interpretated in the sense of the microfibrillar micellar system dealt with earlier (Part I, Chapter 1, § 5), then the products of lateral disintegration must be regarded as chemically conditioned lateral fragments of a chain lattice. *A. Frey-Wyssling*[34] has suggested an acceptable explanation which at the same time covers the peculiar, uniformly shaped manifestations of corrosion which are seen in fibres attacked by fungus[35]. (Fig. 44).

If, following *A. Frey-Wyssling*, cellulose is considered as a chain lattice (Fig. 45), and if the lateral divisions and corrosion figures are regarded as pictures of hydrolysis, the following suggests itself. If the invading "agressor" begins its attack at the point in the top left-hand corner of the figure and if the hydrolysis progresses laterally in the chain lattice, the attack must follow the level, zigzag, dotted line. But if the attack follows a straight course, inclined planes of hydrolysis must be formed (dash-and-dot lines in Fig. 45). The angles computed from Fig. 45 agree with the acute angles of

[31] *R. Haller*, Melliand Textilber., 22, (1941) 153.
[32] See also *T. Kerr*, Textile Res. J., 16, (1946) 249.
[33] *H. Dolmetsch, E. Franz*, and *E. Correns*, Kolloid-Z., 106, (1944) 174; J. makromol. Chem., 1, (1943) 167.
[34] *A. Frey-Wyssling*, Papierfabrikant, 36, (1938) 212.
[35] *Bailey* and *Vestal*, J. Arnold Arboretum, 18 (1937) 196; *Bailey*, Ind. Eng. Chem., 30, (1938) 40.

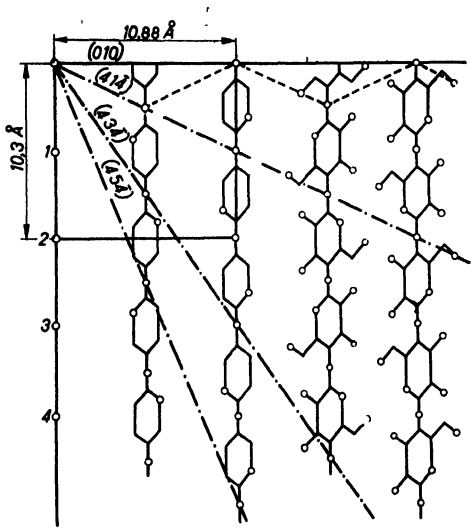


Fig. 45. Hydrolysis planes in the chain lattice of cellulose. At right angles to the fibre axis the hydrolysis proceeds along a light, dotted zig-zag line (.....), but inclined towards the fibre axis it follows straight lines (—.—.—.—).

the corrosion figures. These angles are not modified by the loose structure of the micellar system, but, as has actually been observed [34], by reactions due to swelling.

The ready splitting up of the fibrillæ into short sections of regular length as the result of chemical reactions in certain circumstances has also been accounted for in a different way, thanks to newly reported investigations by *G. V. Schulz* and *E. Husemann* [36], inasmuch as these authors discovered that alien groups are built into the molecule of native cellulose fibres at regular intervals of about 2000 å, the bond of which is attacked in hydrolysis about 1500 times more rapidly than is the normal glucosidic bond. For, if it be assumed that these groups in the native fibrillæ occur from time to time in certain lateral lamellæ (long-period lattice, cf. p. 20), then the fibrillæ would easily disintegrate into sections of 0.26 μ during decomposition. This is precisely the size of the particles discovered by *W. Wergin* (see above) with the aid of the ordinary and the electron microscope. If this really proves to be the case, "chemically pre-formed" lateral splits may come into the picture.

Recently this hypothesis obtained considerable support from a paper by *E. Husemann* and *I. Carnap* [37]. They investigated the length distribution of fibril fragments obtained from acid-disintegrated ramie and cotton fibres with the aid of electron-micrographs and always found a marked maximum of particle length at 2250 ± 250 å which is only 15% short of the expected length of 500 glucose units.

A. Frey-Wyssling [38] is also able to reconcile with the chain lattice structure those commonly occurring so-called "displacement lines" which are produced by mechanical action — especially upon bark fibres — and which always incline towards the fibre axis. Displacement marks of the kind can also be obtained with asbestos fibres, which undoubtedly have a purely chain lattice structure.

[36] *G. V. Schulz* and *E. Husemann*, Z. physik. Chem., B. 52, (1942) 23.
[37] *E. Husemann* and *A. Carnap*, Naturwiss. 32, (1944) 79.
[38] *A. Frey-Wyssling*, Z.f. wiss. Mikrosk., 56, (1939) 309.

Porosity. A characteristic feature of native fibres, and probably a telling one for their technological properties, is the micellar structure permeated with coarser and finer, tapering, anastomotic capillaries. The finer "pores" are of colloidal dimensions; they moreover constitute the passage along which colloidal dyes and other substances enter the fibres. It may be that the heterocapillary void system, developed longitudinally, is largely responsible for the excellent transverse strength (resistance to bending) of certain native fibres, and it does, of course, play a part in the swelling of fibres.

Spiral structure. In native fibres the submicroscopical fibrillar skeins (the secondary wall) do not ordinarily run exactly parallel to the fibre axis, but are somewhat spiral in their course. The pitch (deviation of the screw tangent from the axial direction) is roughly 30° for cotton, being much smaller in ramie and linen fibres (0–6°) [39]. The spiral structure is detected in the polarization microscope by the fact that the fibres do not become entirely extinguished, and it is manifested in X-ray diagrams by the curved widening of the punctuated interferences to form crescents. The screwing is either uniform in the whole secondary wall, or else varies in the different radial layers in accordance with the pitch, or helical twist. Yet a characteristic feature of the helical texture is that, as in ideal fibre texture, the micellar clews, themselves, are parallelised. Thus, fibres of a distinctly spiral character, like cotton hair, possess all the corresponding peculiarities of bark fibres, such as divisibility into fibrillæ, lateral splitting, displacement lines, etc. These characteristics are part and parcel of the parallel texture; cell walls whose fibre textures were found to interlace in layers [40] could not be made to split up into fibrillæ.

The theory that the microstructure of fibres is based on a coherent micellar frame with parallel texture provides a satisfactory explanation of all the properties of fibres.

There is as yet no answer to the question as to which of the morphological and chemical elements of the structure of native fibres are responsible for those technological properties which have proved to be useful. This is one of the problems which artificial fibre research has to investigate and it cannot, therefore, be indifferent to the microstructure of native fibres.

We shall revert later (p. 280; 302) to the interesting relationship, recently discovered, which exists between spiral texture and the strength of cotton hair. The possible significance of the intermicellar spaces detected in native fibres, as "spare space" in bending and compression, has been pointed out

[39] The pitch of the spiral in cotton fibres is variable in a single fibre as well as in different fibre specimens. Studies of this subject have been published by, inter alia, *W. L. Balls*, Proc. Roy Soc. London, 95, (1923) 72; *D. B. Anderson* and *T. Kerr*, Ind. Eng. Chem., 30, (1938) 48; E. *E. Berkley*, Textile Research, 9, (1939) 355; Chronica Botanica, 6, (1941) 364; Amer. J. Botany, 29, (1942) 416.

[40] *A. Frey-Wyssling* and *E. Nicolai*, Protoplasma, 30. (1938) 401.

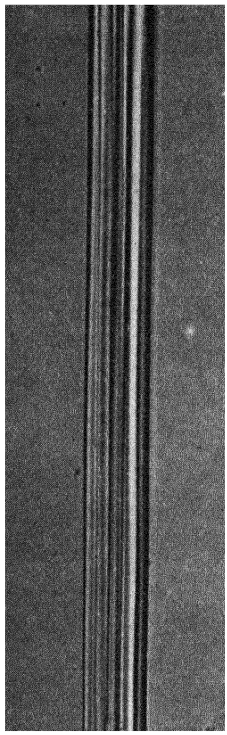


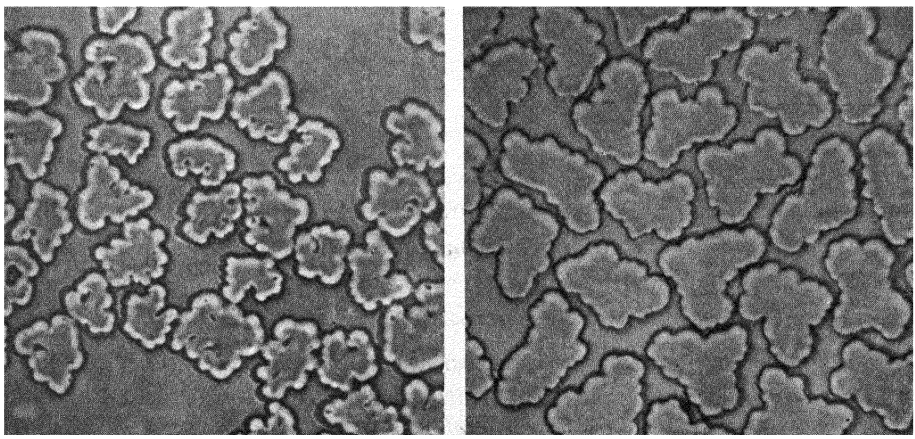
Fig. 46. Microscopic plan of a viscose rayon.

by *O. Kratky, K. Kainz* and *R. Treer*[41]. Finally, we recommend an article by *C. Steinbrinck*[42] on the relation between the morphological microstructure of bark fibres and their ecologically important mechanical functions in plants.

§ 2. MORPHOLOGY OF ARTIFICIAL CELLULOSE FIBRES

At this place we shall deal only very briefly with the most salient features of the morphology of rayon fibres, as any more comprehensive treatment would be outside the scope of this book.

New commercial rayons consist of cylindrical filaments; rather do they commonly comprise cross sections of the most various shapes. Fig. 46 represents a typical micrograph of a viscose filament, where may be seen the longitudinal striations corresponding to the serrated cross section. Two random examples of cross sections are reproduced in Fig. 47. As the conditions of manufacture vary, so does the shape of the cross sections, which also depends upon the composition of the spinning bath and other factors[43]. Circular, non-serrated cross sections may result from spinning in a bath of



A B

Fig. 47. Two specimens of cross-sections in viscose rayon.

[41] *O. Kratky, K. Kainz*, and *E. Treer*, Holz, 2, (1939) 409.
[42] *C. Steinbrinck*, Naturwiss., 15, (1927) 987.
[43] See, for example, *K. Götze's* book, Kunstseide und Zellwolle nach dem Viskoseverfahren (1940) and *J. M. Preston*, Modern Textile Microscopy, London, 1933.

ammonium sulphate solution. The cross sections of cuprammonium and viscose rayons spun by the funnel process (Part III, Chapter III. § 2) and *Lilienfeld* rayons, are likewise apt to be more circular (compare Part III, Chapter III, § 3). There are also what are known as „hollow filaments" which, owing to the evolution of gases during spinning, are inflated to tubular fibres. When dry, these filaments are usually flattened out to ribbon-like objects [44].

Faults in manufacture, such as small or large gas pockets, "milkiness" [45], enclosed foreign particles, etc., are liable to give rise to all manner of anomalies from the normal microscopic picture of the fibres. It would, however, lead us too far afield to enter into the "pathology" of rayon fibres, a subject which might easily fill a whole chapter.

It has been found that ordinary viscose rayons (except those spun by the funnel process) contain a skin and a core differing in swelling capacity, solubility, dye absoption and orientation and that there is a fairly sharply defined boundary between the two, as *J. M. Preston* [46] was the first to report.

The differentiation between skin and core is easily demonstrated by making use of their different behaviour in the absorption of dyestuffs. Either the core or the skin can be preferentially stained all according to the procedure of dyeing employed.

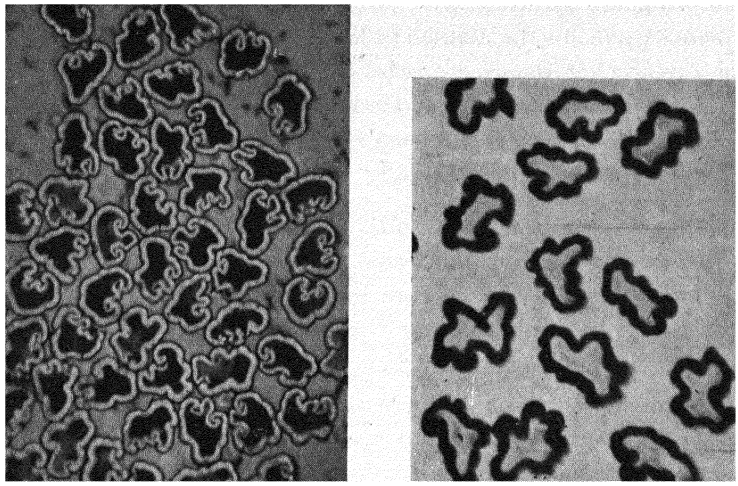
W. Schramek and *J. Helm* [47] and later also *P. H. Hermans* [48] have published indications as to how such selective staining effects can be obtained. By a number of substantive (and other) dyes the core is more quickly stained than the skin and, at room temperature, effects like that shown in Fig. 48A can be obtained. On prolonged dyeing, particularly at higher temperatures, both skin and core become stained. Subsequent washing of the dyed sections with water then first removes the dye from the core, while the skin remains stained.

The procedure of selective skin dyeing with the basic dyestuff Victoria-blue recommended by *F. F. Morehead* and *W. A. Sisson* [49], as later simplified by the author [48], is essentially a modification of this principle.

Fig. 48A shows cross-sections of a modern tyre cord type of viscose yarn treated for 5 minutes with a dilute solution of Solophenyl-blue-green BA (Geigy). The core is stained dark blue, whereas the skin, which is exceptionally thick in yarns of this type, has scarcely absorbed any dyestuff at all.

Fig. 48B shows sections of a similar yarn stained with Victoria-blue after removal of the dye from the core by washing with alcohol of 89% (by vol.). Both the thickness of the skin and the degree of differentiation between skin

[44] For this cf. *R. Stoll*, Zellwolle und Kunstseide, 2, (1944) 51.
[45] Particularly fine work on "milkiness" has recently been published by *W. Kling* and *H. Schwerdtner*, Melliands Textilber. 23, (1942) 233.
[46] *J. M. Preston*, J. Soc. Chem. Ind., 50, (1931) 199.
[47] *W. Schramek* and *J. Helm*, Kolloid-Z. 85, (1938) 291.
[48] *P. H. Hermans*, Text. Res. J., 18, (1948) 9.
[49] *F. F. Morehead* and *W. A. Sisson*, Text. Res. J. 15, (1945) 443.



A B

Fig. 48. Cross-sections of viscose rayon (tyre cord yarn type); A. core selectively stained with solophenylblue-green; B. skin selectively stained with Victoria-blue.

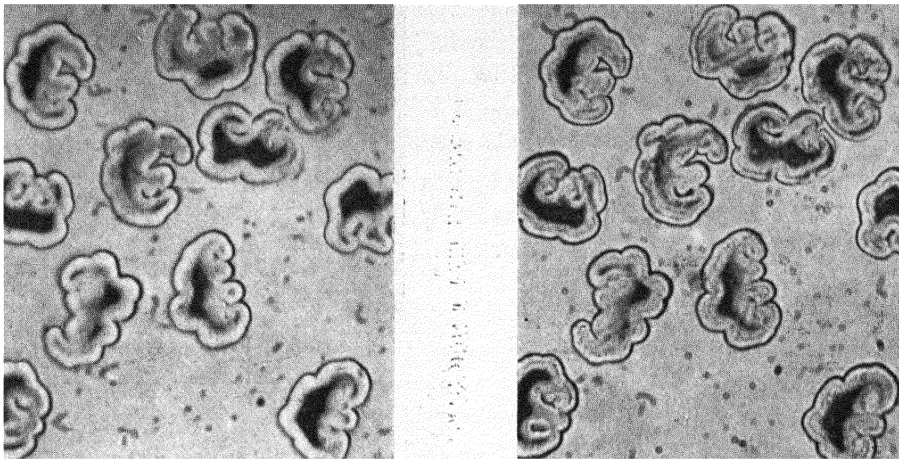
and core towards dyestuffs and other reagents depend upon a number of factors in the manufacturing process of the fibres, which at the time of writing are neither fully known nor understood. Though various theories as to the cause and nature of the skin-core effect have been advanced, none seems to be entirely satisfactory and to account for all the facts so far observed.

According to *Preston*, the skin has a higher degree of orientation than the core and this is apparently confirmed by the work of *Wuhrmann*. But there is a great deal more to it than that and we shall revert to the matter in Part III (Chapter III, § 3).

The Japanese author *K. Ohara*[50] claims to have observed that the skin is further differentiated and that there is, moreover, a very thin outer skin of yet another nature. *Ohara* states that this thin outer skin is also observed in cuprammonium rayon and in viscose rayon spun by the funnel process (cf. Part III, Chapter III, § 2), in which the skin-core differentiation referred to above does not occur.

Nothing is known of the nature of this thin outer skin and it is even open to doubt whether it actually exists and whether it is not rather some optical effect which is responsible for its appearance in the microscopic image. Two micrographs are shown in Fig. 49 of the same cross-sections selectively stained in the core, a) taken with an illumination aperture equal to about half the aperture of the objective and, b) taken with the condensor diaphragm almost entirely closed. The thin outer skin can be seen only in the latter

[50] *K. Ohara*, Sci. Papers Inst. Phys. Chem. Res. Tokyo, 25, (1934) 152.



A B

Fig. 49. Cross section of viscose rayon with selectively stained core, photographed with A moderate and B very low illumination aperture.

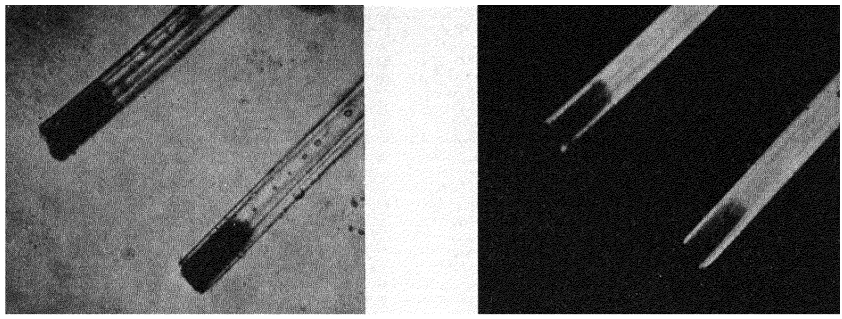
photograph, which is exactly like the sketch given by Ohara. In this case the cross-sections, the refractive index of which is about 1.52, were embedded in a liquid of lower refractivity (n = 1.44). If the sections are observed in a liquid of equal refractivity (n = 1.520), the Ohara skin cannot be observed under any forms of illumination, including dark-field illumination.

Calculation showed that, in the case of Fig. 49B, the skin appearing in the image is too thin to be resolvable with the aperture of the optical arrangement used.

In practice a distinction is made between "mantle fibres" and "non-mantle fibres", referring to the presence, not of the thin outer skin described by Ohara, but to the differently orientated cortical layer. Therefore, the funnel-processed rayons and, as usually stated, also Lilienfeld makes, in which no such cortical layers have been found, are not counted among the mantle fibres[51].

The selective staining of the filament core by a number of substantive dyes is due to a more rapid diffusion of the dyestuff into the core than into the skin and not, as Preston believed, to dichroitic effects connected with the difference in degree of orientation of skin and core. This is demonstrated by Fig. 50 showing cut ends of the same rayon fibres of which the sections in Fig. 48A were made, treated for some time with the same dyestuff solution, now viewed from the side, a) in ordinary light and, b) in polarized light between crossed nicols.

[51] Recently, however, indications have been obtained that also Lilienfeldrayons exhibit a differentiation between skin and core of, at least, a similar nature (see ref. 48).



A B

Fig. 50. Cut ends of the rayon fibres of which the sections in Fig. 48 were made, treated with solophenyl-blue-green, A in ordinary light; B between crossed nicols. The dye has penetrated from the end into the core of the filament; the skin has remained practically unstained.

It will be seen that the dye has selectively penetrated the core from the cut end, whereas the skin has remained transparent and has taken little, if any, dye. The dye diffuses so much slower into the skin than into the core, that the former acts as a protective coating inhibiting lateral penetration of the dye into the fibre.

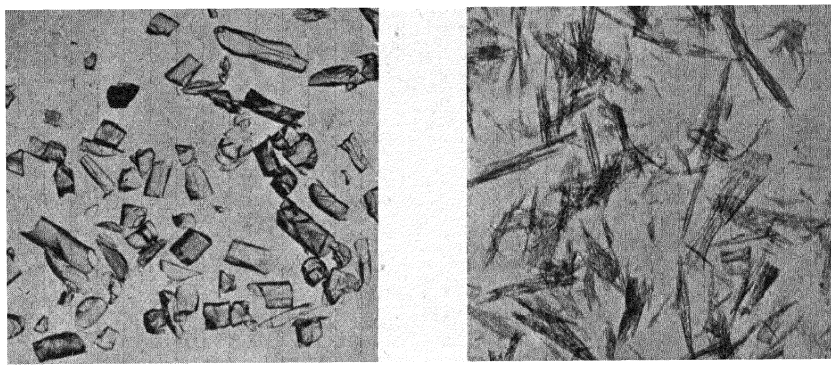
This phenomenon can be readily reproduced with almost any commercial viscose rayon, but, as the author has shown [52], the velocity of diffusion of the dye Solophenyl-blue-green into the core may vary several orders of magnitude from one brand of rayon to the other. Longitudinal penetration of the dye into the core at room temperature over a distance of 100 micron may be a matter of less than one hour in one sample and of 2500 hours, or even more, in another. Diffusion is usually slowest in the common types of viscose rayon with a relatively thin skin, and faster in the so called tyre cord brands which exhibit a much thicker skin. These facts seem to indicate that there must exist a corresponding variety in microstructure which remains to be elucidated.

All we would further say here on cross-sections is that fibres of purely longitudinal (uniaxial) orientation should appear isotropic with respect to the cross-section. The occurrence of a regular black cross in parallel polarized light would point to a "higher orientation" [53]. As an actual fact, both freshly spun and finished viscose rayon fibres display quite different phenomena in cross-section in polarized light, phenomena to which we shall revert later (Part III, Chapter III, § 3).

The electron-microscopic picture of wet rayon fibres ground in the vibrating ball mill was examined by *E. Husemann* [53a] and by *P. H. Hermans* [54], who

[52] See ref. 48.
[53] For this, see Part II Chapt. IV § 5.1 and Chapt. V § 1.3
[53a] *E. Husemann*, J. makromol. Chem., 1, (1943) 158.
[54] *P. H. Hermans*, Textile Res. J., 16, (1946) 545.

found nothing particularly characteristic. Splitting tends to take place in the fibre direction owing to the anisotropic structure; therefore, though fibrillar organizations are formed, they are so in a far less marked degree than in native fibres. Fully dry model filaments from viscose also show this preference for longitudinal splitting when crushed, and in that state they are of a glassy hardness. Whereas isotropic filaments produce irregular splinters having the appearance of crushed glass, the splintering of orientated filaments is distinctly fibrillar. Micrographs are reproduced in Fig. 51.



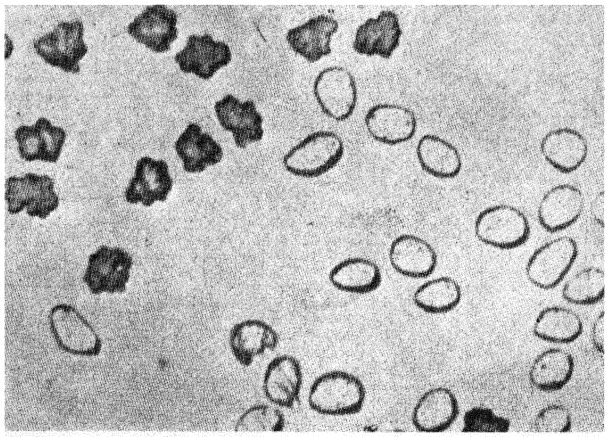
a b

Fig. 51. (a) Isotropic and (b) well-orientated model fibres of viscose, crushed in a mortar when completely dry. (Magnification about 20).

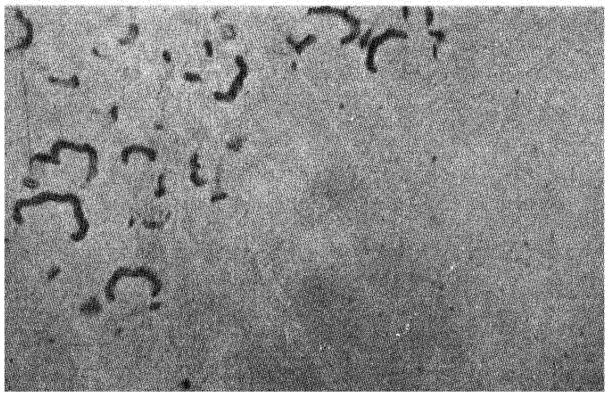
Fibres previously decomposed by acid to less than 200 DP are easily shattered, when wet, if knocked. Investigations on these objects with the aid of the ordinary and of the electron microscope have been published by *M. Staudinger*[55] and *E. Husemann*[56]. Whereas native fibres splinter extensively into fibrillar fragments, while at the same time abundant lateral splitting takes place, rayon fibres, though splitting to some extent into fibrillar systems, produce thicker ones; they do not split up into the thinnest of fibrous fragments, but are occasionally inclined to pass over, at the edge, into a homogeneous layer. Prolonged decomposition results in masses of material without structure. This is where the far less orderly structure of rayon fibres is manifested. A great number of micrographs of fibres which had first been made to swell and were then crushed, have been published by *O. Eisenhuth*[57] and also by *E. Franz, F. H. Müller* and *L. Wallner*[58]. They can scarcely be said to open up any new aspects. Fibrillar splitting becomes more distinct as the average degree of polymerization increases and as orientation improves.

[55] *M. Staudinger*, J. prakt. Chem. 160, (1942) 203.
[56] *E. Husemann*, J. makromol. Chem., 1, (1943) 16.
[57] *O. Eisenhuth*, Kolloid-Z., 98, (1942) 141.
[58] *E. Franz, F. H. Müller*, and *L. Wallner*, Zellwolle, Kunstseide, Seide, 47, (1942) 407.

H. Siebourg [59], placing cross sections of fibres in an acetylation mixture which has a solvent effect [60], detected interesting differences between mantle fibres and non-mantle fibres. In the former, the filament core dissolves sooner than the skin (Fig. 52). This does not occur in funnel-spun lanusa fibre; moreover, the fibre dissolves more quickly (although the degree of polymerization is sometimes higher).



a



b

Fig. 52. Cross sections of a viscose fibre (left) and of a "Cuprama" fibre (right) (a) before and (b) 6 min. after a dissolving acetylation reagent has been allowed to act (after *H. Siebourg*). Remains of the more slowly dissolving skin are to be seen in the viscose fibre in the second picture.

A variant of these experiments has been provided by the work of *A. Marschall* and *M. Stauch* [61], in which longitudinal fragments of fibre were examined

[59] *H. Siebourg*, Zellwolle, Kunstseide, Seide, 46, (1941), 215.
[60] 50% acetic acid, 50% acetic anhydride with 0.125% sulphuric acid as a catalyst.
[61] *A. Marschall* and *M. Stauch*, Kunstseide u. Zellwolle, 25, (1943) 112.

in the same way. It was found that, with ordinary viscose fibres, the core dissolves first and swells up, whereas the outer skin divides into long fibrillæ before dissolving (Fig. 53). Funnel-spun filaments present a totally different picture, there being a more uniform swelling followed by gradual solution. The picture is again somewhat different with Lilienfeld rayon. *Marschall* and *Stauch* state that it is as though the filament consisted entirely of the mantle substance of the viscose fibres.

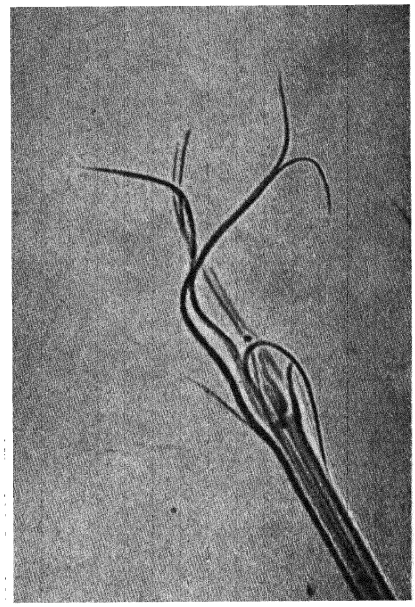


Fig. 53. Lengthwise view of a viscose fibre during solution in the acetylation reagent. The skin detaches itself in stripes similar to fibrillae, while the fibre core swells and dissolves (after *A. Marschall* and *M. Stauch*).

A. Hamann[62] chafed some wet rayon filaments on a rotating serrated godet, following the customary procedure for testing chafing resistance, finding that the filaments split up into thin and extremely thin fibrillæ of a diameter well below 1 μ. A micrograph is reproduced in Fig. 54. His publication includes electron-microscopic photographs of the same objects. Investigation of the kind described in this Chapter may go far towards solving a number of problems connected with the finer details of the structure of artificial fibres, a domain which is being strenuously explored, but from which barely the first fruits have yet been gleaned[63].

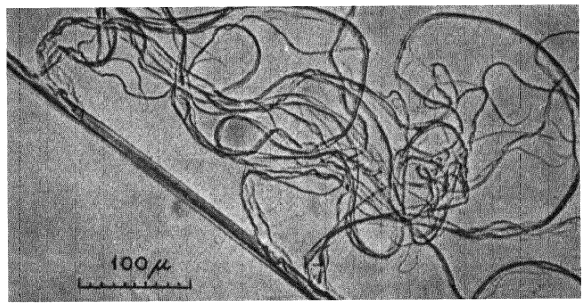


Fig. 54. Viscose fibres chafed down to the zone of the pith. (Enlarged 180 times). (After *A. Hamann*).

[62] *A. Hamann*, Kolloid-Z., 100, (1942) 248.
[63] cf. also the recent publication of *E. L. Lovell* and *O. Goldschmid*, Ind. Eng. Chem., 38, (1946) 811.

CHAPTER II

SORPTION AND SWELLING

§ 1. GENERAL REMARKS

Dry cellulose is an exceedingly hygroscopic substance, withdrawing water even from phosphorus pentoxide. The usual drying in air at 105 to 110° does not suffice to extract all its water content, as, let us say, in the conventional water content determination, for the cellulose then still contains a quantity of water varying with the prevailing humidity of the air (under ordinary conditions about 0.5%). *H. Ost* and *W. Westhoff* [1] dry the cellulose in a dry current of hydrogen at 120—125°; according to *J. R. Katz* [2], the material is dried at 100° in vacuo over phosphorus pentoxide. *Nelson* and *Hullet* [3] state that the dry weight in vacuo depends to some extent upon the temperature at which the substance is dried. It is our own experience (Contrib. p. 201) [4] that the weight variations between 100 and 120° are negligible and that good results are obtained by heating in a dry nitrogen current at 110—115° [5].

The literature on the absorption of water vapour by cellulose fibres and their swelling in water is extensive. Both properties and their correlated phenomena are of paramount importance in the processing and use of cellulose for textiles. They are, however, also closely dependent upon the microstructure of the fibre and are specially interesting because they are far more highly developed in artificial filaments than in native fibres. From the outset, this has been felt to weigh heavily against artificial fibres and the industry has studiously endeavoured to find a remedy.

Though we can only deal with the fundamental points of view here, reference may be made to the separate list of selected publications given at the end of this Chapter, respecting the relation between cellulose and water.

The sorption of water by cellulose was at first generally supposed to be a process of adsorption to the highly developed "inner surface" of the material. This explanation was closely associated with classical colloid-chemical points of view and with the conception of cellulose fibres as a "colloidal" system with "multimolecular" elementary particles.

We now realize, however, that this idea of the "inner surface" does not help us much [6]. Sorptive capacity should be regarded as a function of the

[1] *H. Ost* and *W. Westhoff*, Chem. Ztg., 33, (1909) 197.
[2] *J. R. Katz*, Kolloid chem. Beih., 9, (1916) 47.
[3] *Nelson* and *Hullet*, Ind. Eng. Chem., 12, (1920) 40.
[4] This reference to "Contrib." refers to *P. H. Hermans*, Contribution to the Physics of Cellulose Fibres, Amsterdam—New York, 1946.
[5] Also compare *G. F. Davidson* and *S. A. Shorter*, J. Text. Inst. 21, (1930) T. 165.
[6] Contrib., p. 11.

amorphous regions[7] (also cf. Part I, Chapter V, § 3). The inner surface is a molecular surface and there can therefore be no question of a "surface" at all. It is more to the point to consider sorption in exactly the same way as swelling, i.e., as a process of solution, a view advanced many years ago by *J. R. Katz.*

In the ensuing pages we shall encounter many arguments in favour of this view. When water is absorbed by sulphuric acid or by calcium chloride, it is eventually bound to the "inner surface" of these substances, but it is quite obvious that no useful purpose would be served by applying this argument.

After what has been said, water-absorptive power can confidently be expected to stand in close relation to the percentage of the amorphous matter in the object.

§ 2. SORPTION ISOTHERMS

The quantity of water absorbed by a cellulose object in a humid atmosphere depends upon the water vapour pressure, the temperature, the nature of the object and its past history. The atmospheric humidity may most conveniently be expressed as the percentage of relative humidity (r.h.).

If fresh, ripe cotton linters, freshly mercerized, undried fibres or newly manufactured artificial filaments (i.e., objects produced direct from a highly swollen state) are placed at constant temperature in air of r.h. diminishing in stages, with a pause at each stage until equilibrium is reached, the humidity of the fibre follows the course represented by the S-shaped curve 1 in the diagram of Figure 55.

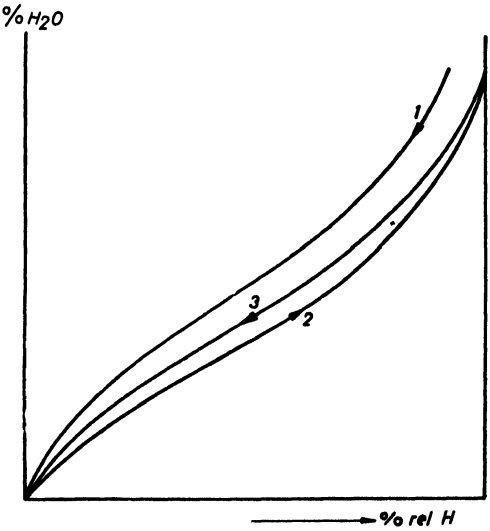


Fig. 55. Sorption isotherms of cellulose objects (diagrammatic). 1. Fresh fibres (desorption); 2 and 3: absorption and desorption after first drying.

If, after the object has become quite dry at 0% r.h., the atmospheric r.h. is again allowed to increase, curve 2 will result, this being called the absorption isotherm. With equilibrium reached at 100% r.h. and the humidity diminished, the result is curve 3, which is termed the desorption isotherm. Repetition of the operation reproduces curves 2 and 3. The theory that the sorption isotherms depend upon the preliminary history of the object, i.e., its initial condition, is exemplified by the fact that in the first desorption it everywhere

[7] In the case of Cellulose II it also depends to a certain extent upon the formation of cellulose hydrate I in the crystalline regions (cf. Part I, Chapt, I, § 4).

exhibits a higher regain than in subsequent desorption tests. Let us follow desorption curve 3 with a sample which has been swollen at 100% r.h. (hence in water) up to point A (see Fig. 56, where curves 2 and 3 again appear in diagram) and let the humidity of the air again increase; it will be seen that our path is along the broken curve AA'. Following the absorption curve to point B and once more placing the sample in air of decreasing humidity, we pass along the broken curve BB', etc. These

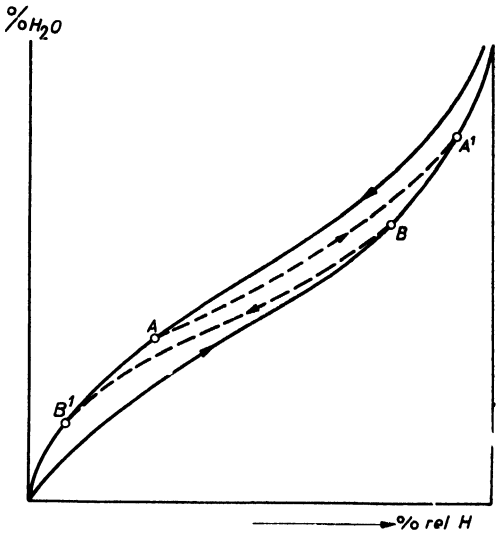


Fig. 56. All points of condition within the domain of hysteresis can be attained by suitable operations

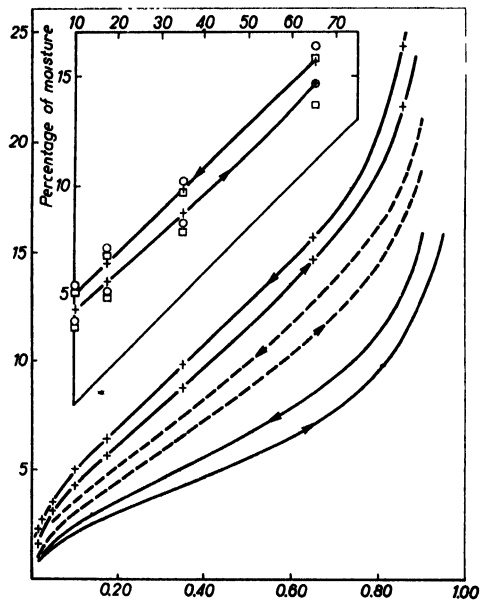


Fig. 57. Absorption and desorption isotherms of various fibres at 20°. ——— cotton; ····· mercerized cotton (25°). + isotropic model filaments. O viscose rayon with very little orientation. □ Viscose rayon well orientated. (Both the latter in the top, left-hand corner together with isotropic model filaments).

phenomena are called *hysteresis*. It has been known since *J. M van Bemmelen's* work[8] that many gel-like systems exhibit similar hysteresis effects.

The determination of absorption and desorption curves 2 and 3, representing the sorption isotherms of objects previously dried or moistened completely, is generally considered adequate to denote their moisture -absorptive power[9]. It will be clear from Fig. 56, however, that all the points of condition within the region bordered by the two curves (i.e., the hysteresis loop) are attainable by suitable operations. Thus the two principal curves

[8] *J. M. van Bemmelen*, Z. anorg. allgem. Chem., 13, (1896) 233.

[9] As a rule this matter is somewhat over-simplified. For exact measurements it is necessary to take many points into account. For example, to determine the absorption isotherm at 20°, an object should be used which has been made absolutely dry at 20°. Yet in practice cellulose cannot be dried completely at this temperature. If the samples are dried at higher temperatures, the subsequent isotherm slightly depends upon the drying temperature. Moreover, it is often very difficult to reproduce the extreme right-hand part of the isotherms where the moisture contents are high.

serve merely as demarcation lines of the entire range of sorption of the fibre. As to the sorptive power of various kinds of cellulose, it is known that native fibres absorb less water at the same r.h. than artificial fibres. The lower part of Fig. 57 reproduces the sorption isotherms for native bleached cotton fibres (at 20°), for mercerized cotton (at 25°) and for isotropic rayon filaments regenerated from viscose (at 20°). The first two have been borrowed from *A. R. Urquhart* and *A. M. Williams* [10] and the last-mentioned are from our own observations. The isotherms of native cotton practically coincide with those of native ramie fibres [11]. The position of the isotherms for mercerized cotton is subject to some extent to the conditions of mercerization [12], they differ little from those reported for ramie fibres mercerized under the same conditions [13].

It will be seen that, at a given r.h., native fibres absorb the least amount of water, mercerized native fibres absorbing more and the regenerated specimens more still. The curves for sulphite and sulphate cellulose produced from wood, which may also be classified as native fibres, come a little above those for native cotton. The isotropic regenerated filaments represent model filaments approximately 0.5 mm. thick manufactured in accordance with directions issued by *P. H. Hermans* and *A. J. de Leeuw* [14]. The examination of a number of artificial filaments, each the product of a distinctive manufacturing process, has shown that all the isotherms are within a narrow compass and that the sorptive power of all regenerated fibres is therefore subject to but little fluctuation [15], to which those highly orientated rayons manufactured by the *Lilienfeld* process form no exception [16]. Examples are given in the upper part of Fig. 57, where sections are represented of the sorption isotherms of a slightly and of a highly stretched viscose rayon, side by side with the isotropic model filaments.

It would seem to be the rule that the sorptive power of artificial filaments produced by the same spinning process decreases slightly as orientation increases [17] (also see Table XVII).

Urquhart and *Williams* were the first to point out that if, at a given r.h., the regain absorbed by a fibre is divided by the regain of the native cotton at the same r.h., the result is an almost constant number over the whole isotherm, which those authors termed the sorption ratio. By means of this number, therefore, it is possible to denote the regain of a fibre with fair accuracy, provided the isotherms of the cotton be known. It means that the S-shaped sorption isotherms are altogether similar, differing only

[10] *A. R. Urquhart* and *A. M. Williams*, J. Text. Inst., 15, (1924) T. 138; 16, (1925) T. 135, 155.
[11] Contrib., p. 15.
[12] *A. R. Urquhart* and *A. M. Williams*, J. Text. Inst., 16, (1925) T. 135, 155.
[13] Contrib. p. 14.
[14] *P. H. Hermans* and *A. J. de Leeuw*, Kolloid-Z., 81, (1937) 322.
[15] Contrib. p. 15.
[16] Also cf. *A. R. Urquhart* and *N. Eckersall*, J. Text. Inst., 21, (1930) T. 449.
[17] Cf. *C. Matano* and *T. Ozawa*, J. Soc. Chem. Ind. Japan, 40, (1937) 174. (Contrib. p. 20)

in the scale of ordinates. Thus the differences in the sorptive power of various samples are merely of a quantitative, and not of a qualitative nature; in other words, the nature of the sorbing substance is the same everywhere and it is only the amount of it which varies.

If, as has been assumed, the sorptive power really is a quality proper to the amorphous regions of the fibre and if it is of practically the same nature in all fibres, then precisely those conditions would exist which have actually been observed.

A constant sorption ratio, however, is found only where the r.h. is neither very high nor very low. The measurements become difficult to reproduce in the higher ranges of r.h. (above roughly 85% r.h.), where several factors come into play which are not readily explained[18]. At very low regains (below roughly 10% r.h.), the sorption ratios of all fibres containing Cellulose II show a tendency to increase, probably due to the absorption of a small quantity of water in the lattice of Cellulose II (see § 5).

If we ignore these complications and if our hypotheses are correct, the mean sorption ratio between about 10 and 70% r.h. should provide us with an approximate relative yardstick for the percentage of amorphous fibrous substance. Table XVII gives the sorption ratios of a few fibres[19].

TABLE XVII

Sorption Ratios of some Fibres for Absorption and Desorption at 20°, and their Mean Value (native cotton = 1).

	Absorp.	Desorp.	Mean
Wood pulp	—	—	1.2—1.3
Mercerized cotton	1.46	1.50	1.48
Mercerized ramie fibre	1.53	1.64	1.59
Isotropic model filaments	2.02	1.98	2.00
Orientated model filaments	1.94	1.90	1.92
Viscose rayon not stretched	1.84	2.13	1.99
Viscose rayon 70% stretched	1.79	2.03	1.91
Lilienfeld rayon I*	1.95	2.08	2.02
Lilienfeld rayon II*	1.89	2.01	1.95
Mean value for artificial fibres	1.91	2.02	1.97

* *Lilienfeld* rayon II is more thoroughly orientated than I.

[18] Fibres kept for a prolonged period above water swell up further when immersed in fluid water. *L. K. Wolff* and *E. H. Büchner* have suggested an explanation of this phenomenon, known as the "*Schroeder* Paradox" (Report Kon. Akad. Wetensch. Amsterdam, 17, (1915) 92). The seeming paradox — for it is only that — is due to the fact that it is exceedingly difficult in experiments to keep the atmosphere in a vessel really and completely saturated all over with water vapour, while, owing to the steep ascent of the sorption isotherms in the neighbourhood of the saturation pressure, the slightest fluctuations in vapour pressure bring about enormous differences in swelling. These difficulties can be minimised by proper precautions (*P. H. Hermans*, Kolloid-Z., 97, (1941) 233).

[19] Contrib. p. 18.

If we take the mean value as the standard, it would mean that the quantities of amorphous substance in native, mercerized and regenerated fibres would be in the approximate proportion of 1 : 1.5 : 2.

The absorption ratio for almost entirely amorphous cellulose, as obtained by subjecting fibres to a rigorous mechanical disintegration in a vibrating ball mill, was found to be as high as 2.12 [20].

§ 3. THE HEAT OF SORPTION

Water absorption by cellulose is accompanied by positive heat effect. Accordingly, the temperature coefficient of the sorption is negative; less water is absorbed at higher temperature and constant r.h. [21]. *Urquhart* and *Williams* (loc.cit.) have already measured the sorption isotherms of cotton within a fairly wide range of temperature, and *J. G. Wiegerink* [22] has recently published extensive data respecting the sorption isotherms of various kinds of fibres in a range of temperature extending to upwards of 100°.

The evolution of heat when 1 gram of dry cellulose is fully moistened is called the integral heat of sorption. For native cotton and ramie fibres it amounts to roughly 10—11 cal/g, for wood cellulose 12-14 cal/g and for artificial fibres 22-24 cal/g. These figures, being practically proportional to the sorption ratios, may likewise be used as a measure of the relative amount of the amorphous portions.

Another interesting datum is the differential heat of sorption, i.e., the heat effect brought about when 1 gram of water is combined with, or extracted from a very large quantity of dry or moist cellulose. The differential heat of sorption can, alternatively, be deduced thermodynamically from the dependence upon the temperature of the vapour pressure isotherms. Its value shows that the first quantities of water are combined with very pronounced heat effect. The damper the cellulose becomes, the more rapidly does the heat effect diminish and it approaches zero asymptotically [23]. According to calculations made by *A. J. Stamm* and *W. K. Loughborough* [24], there is, initially, less reduction in free energy during the process of absorption than corresponds to the heat effect, so that a reduction in entropy takes place (cf. Part I, Chap. II, §6). This means that the water molecules are bound to the cellulose in a more or less orientated order.

It is obvious from direct measurements taken by *G. H. Argue* and *O. Maas* [25] from cotton and our own measurements from rayon [26] that the heat effect

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[20] *P. H. Hermans* and *A. Weidinger*, J. Amer. Chem. Soc. 68, (1946) 2547.
[21] With cotton, an anomaly was discovered above roughly 80° and in the domain of very high r.h., in that the temperature coefficient of the sorption became positive.
[22] *J. G. Wiegerink*, Textil Research, 10, (1940) 357.
[23] This statement is based on the assumption that the water is absorbed in its liquid state. With absorption from the vapour phase the final value corresponds, of course, to the latent heat of the water.
[24] *A. J. Stamm* and *W. K. Loughborough*, J. physic. chem., 39, (1935) 121.
[25] *G. H. Argue* and *O. Maass*, Canad. J. of Research, 12, (1935) 564.
[26] Contrib., p. 37.

which takes place upon the absorption of 1 gram of water by an infinite quantity of dry material is practically the same in the two cases (230-240 cal/g H_2O). Thus it seems to have a constant value for all cellulose fibres. The differential heat of sorption of the moist material as a function of regain, on the other hand, dies away far more rapidly in cotton than in rayon.

These observations substantiate the proposition that, in point of sorption, the differences between the various fibres are quantitative and not qualitative and that the mechanism of sorption is, therefore, everywhere essentially the same. They also bring to the fore a fact already emphasized, viz., that the first quantities of water are so firmly bound that this is a case of a chemical combination of the water in the form of real hydrates. The decrease in entropy during sorption is another significant pointer, as is also the fact noted by *Stamm* and *Loughborough* (loc. cit.) that, in the case of low water contents, both the heat of sorption and the entropy of sorption represent values independent of the temperature. It is not until the higher regains are reached that these values noticeably change with the temperature; this points to other weaker bonds of the nature of *Van der Waal's* forces.

If, as previously suggested, we consider the process of sorption to be a homogeneous solution of water in the amorphous regions of the fibre, then the physico-chemical aspects should be analogous to those which prevail in homogeneous binary systems of a volatile and a non-volatile component when, with evolution of heat, these are able to enter into additive reaction. And this is exactly how things actually are. *J. R. Katz*[27] and also *Stamm* and *Loughborough* (loc. cit.) have drawn attention to the striking similarity to the behaviour of systems such as sulphuric acid/water and phosphoric acid/water. These also display S-shaped vapour pressure isotherms and here too hydrates are formed with evolution of heat. When sulphuric acid absorbs water there is likewise a reduction in entropy initially and, at the higher concentrations of the non-volatile component, the heat effect and the change in entropy are independent of temperature.

§ 4. VELOCITY OF DIFFUSION OF WATER THROUGH CELLULOSE

Before entering more fully into the mechanism of sorption, we shall briefly consider a few more phenomena. *P. H. Hermans* and *D. Vermaas*[28] have pointed out that the velocity of diffusion of water through cellulose is an exceedingly sensitive function of the percentage of water already present in the material. The water diffuses very slowly indeed through very dry cellulose, and up to a water content of above 10% the velocity of diffusion has the high coefficient of temperature of a chemical reaction, from which an energy of activation of roughly 13 kcal/mole can be computed. Hence in this range the water molecules are still very firmly bound; they cannot move

[27] *J. R. Katz*, Ergebn.d. Exakten Naturwiss., 3, (1924) 316.
[28] *P. H. Hermans* and *D. Vermaas*, J. Polymer Sci. 1, (1946) 149.

from one place to another without each time being pulled out of a considerable potential trough.

These observations will make it clear why the last traces of water are so difficult to eliminate from cellulose objects; also why, in the low regain ranges, equilibrium is always slow to set in during the conditioning of cellulose fibres.

All this will also explain the fact discovered by these authors, viz., that the conditioning of cellulose fibres is a decidedly heterogeneous process; for, if dry fibres, or fibres conditioned at 10% r.h., are placed in an atmosphere of 65% r.h., a sharply defined moistened mantle is first formed at the periphery of the fibre, which gradually thickens, whereas the core of the filament retains its initial moisture, a fact which can be seen under the microscope. A sharp line of demarcation becomes visible between the dry core and the already moistened mantle, which gradually moves inwards.

Similar phenomena have been observed by *A. Tiselius* [29] in the absorption of water by certain zeolites.

§ 5. THE MECHANISM OF SORPTION IN RELATION TO THE PERCENTAGE OF AMORPHOUS SUBSTANCE

It was long ago recognised that water must be combined in at least two ways. The particularly strong retention of the first quantities of water was attributed to a "surface adsorption", which leads to a vapour pressure isotherm of the nature of *Langmuir's* adsorption isotherms, i.e., a concave curve against the vapour pressure axis. The S shape of the sorption isotherms would result from superposition of two mechanisms [30].

Now that the existence of real hydrates and the character of sorption as a homogeneous mixture of two components have been recognized, another interpretation may usefully be suggested.

As to the formation — established by X-rays — of a hydrate in cellulose II (page 25), it is well to remember that, contrary to the formation of hydrates in low-molecular substances, the formation of a crystalline hydrate in a macromolecular lattice does n o t, theoretically, lead to a step-ladder curve for vapour pressure isotherms as does the former, but to a curve similar to the *Langmuir* adsorption isotherm [31].

Moreover, the hydrates are also formed in those parts of the fibre which have no lattice order, where they are no more detectable by X-rays than are the hydrates of sulphuric acid mixed with liquid water. Yet these sulphuric acid hydrates (known also in their crystalline form) do, of course, exist in dilute sulphuric acid, where they are dissolved in the water.

It may equally be assumed that the cellulose molecules in the amorphous

[29] *A. Tiselius*, Z. physik. Chem., A. 169, (1934) 425.
[30] Cf. *F. T. Peirce*, J. Text. Inst. 20, (1929) T 133; *S. E. Sheppard* and *P. T. Newsome*, Ind. Eng. Chem., 26, (1934) 285.
[31] Contrib., p. 188.

regions are capable of forming those hydrates which are known in the crystalline state. According to page 25, these are cellulose hydrates I and II with 3.7% (1/3 mole) and 14.8% ($1\frac{1}{3}$ mole) of water respectively. The heat of formation of the former hydrate will be greater per mole of H_2O than the latter, as is shown by the fact that the first hydrate is formed spontaneously in Cellulose II, whereas the second hydrate is unstable.

In the amorphous regions, where the disturbed order will to a large extent neutralize the competition of the strong cellulose-to-cellulose bonds, the conditions for the formation of the first hydrate will in all probability be favourable everywhere, and in most places also for that of hydrate II. Greater heat of formation will be released when a water molecule is bound to cellulose hydrate I at a place in the amorphous regions than when bound in the lattice of cellulose II, as no energy is needed to widen the lattice. Let us now consider what happens when dry cellulose gradually absorbs water.

If the crystalline regions consist of cellulose I, it is hydrate I that will first be formed in the amorphous portions; if they consist of cellulose II, the water will likewise be bound as hydrate I, while equilibrium of distribution develops between the crystalline and the amorphous portions, the water binding predominating in the latter. As more water is absorbed, hydrate II will eventually begin to form in the amorphous portions. Once hydrate II has been formed at all the available places, more water will be bound — though assuredly with even less heat effect — by the *Van der Waal* forces.

No more hydrate II will be formed at places where there is still considerable cohesion of cellulose to cellulose (so-called junction points; see below).

As there is more amorphous substance in regenerated fibres more water is bound in them than in native fibres. An exact analysis [32] shows the balance of the chemically combined water to be as follows (upon the assumption, the probability of which is supported by other evidence, that there is 40% of amorphous substance in native fibres and 75% in regenerated ones). See Table XVIII.

TABLE XVIII

Balance of chemically combined water

Nature of bond as	Native Fibre	Regenerated Fibre
Hydrate I in crystalline portion	—	0.25 × 3.7 = 0.9%
Hydrate I in amorphous portion	0.4 × 3.7 = 1.5%	0.75 × 3.7 = 2.8%
Hydrate II in amorphous portion	0.4 × 11.1 = 4.4%	0.75 × 11.1 = 8.4%
Total chemically combined	5.9%	12.1%

It is also to be inferred from this balance that the ratio of the fractions of amorphous substance in rayon and native cellulose is about 10% lower than the sorption ratio (1.9 instead of 2.0). Since the native fibre absorbs roughly

[32] Cf. Contrib. page 44.

7% and the regenerated fibre about 14% of water at 65% rh., most of the water is then present as true water of hydration. Comparison with the sorption isotherms (Fig. 57) shows that the first concave section of the isotherm approximately coincides with the formation of the first hydrate, while the next, practically straight section, corresponds to the formation of hydrate II. In conformity with the theory, the third, rapidly rising section begins with the binding of the water by weaker bonds. Exactly the same sections are found when studying the phenomena of contraction in water binding (page 208). The deduction from them is that, as from 10—12% of water in the native fibres and from 20—25% of water in regenerated cellulose, the monomolecular covering of the chain with water in the amorphous portions ceases and thence forward films of water, more than one molecule thick, begin to form. This, on the above assumptions, corresponds to approximately 2.5 mol. of water per glucosidic group.

Recently a very interesting contribution to the theory of sorption has been published by *A. J. Hailwood* and *S. Horrobin* [33]. Assuming the formation of a monohydrate (one water molecule bound by every glucose residue taking part in absorption) followed by a simple dissolution of more water in the amorphous regions (with no evolution of heat) they derived a formula for the sorption isotherm which very well fits the experimental data over the entire range of vapour pressures. From it the fraction of monomeric residues taking part in hydrate formation can be derived and is then found to be 0.32 for native cotton and 0.65 for regenerated cellulose. In other words the quantities of crystalline substance would be 68% and 35% respectively, figures which are well in line with those arrived at independently from other data as we shall see later. (see p. 316). The corresponding figures for wool and natural silk were 44% and 80% respectively.

So we see that the phenomena arising from the absorption of water are intimately related with many of the problems inherent in the microstructure of fibres with which we are concerned. Having connected water absorption with the amorphous regions, we have now to consider the following.

There are probably many places in the fibre structure where relatively short chain sections of a few molecules are so parallelized and arranged as to bring almost into full play those attractive forces which prevail in the lattice order. Such regions may be too small to provoke sharp X-ray interferences and cannot, therefore, in this sense lay claim to the appellation "crystalline". Yet, in regard to water absorption, they may exercise the same function as the regions of lattice order. They may therefore conveniently be described as permanent "junction points" (with respect to the water).

Thus, where water absorption is concerned, we may differentiate between "swellable" and "non-swellable" substance, rather than between

[33] *A. J. Hailwood* and *S. Horrobin*, Commun. at Gen. Discussion on Swelling and Shrinking, Trans. Faraday Soc., 42 B, (1946) 84; cf. discussion remarks by *D. Vermaas*.

"crystalline" and "amorphous" substance; the choice of terms is merely a matter of taste. The distinction is of some practical use only if it is thereby made clear that small changes may take place in the sorptive capacity of a fibre without entailing intensification of the X-ray interferences. To take an example: cellulose fibres dried for a long time in heat absorb somewhat less water than before this treatment [34], though no noticeable differences are visible in the X-ray diagram. This may be ascribed to an increased number of permanent junction points.

The higher level of the sorption isotherms of fresh fibres which have not been previously dried (Fig. 55) may be accounted for in a similar way; the number of junction points in the amorphous portions has increased after the first drying operation.

P. H. Hermans and *A. Weidinger* have investigated the sorptive power and the heats of wetting of the products obtained from ramie fibres and viscose rayon after vigorous mechanical disintegration in a vibrating ball mill. These products may be considered as being almost entirely amorphous, since the X-ray diffraction picture shows no more crystalline interferences, but merely a broad diffuse band [35]. When treated with water, these products crystallized and the recrystallized products were also examined. The figures found are shown in Table XIX.

TABLE XIX

Sorption Ratio and Integral Heats of Wetting of Ground and Recrystallized Cellulose

	Sorption ratio	Integr.heat of wetting cal/g.
Wood Pulp		
Original fibre	1.25	14.3
Ground product	2.12	29.0
Recrystallized product	1.65	18.8
Viscose Rayon		
Original product	1.88	21.7
Ground product	1.98	30.0
Recrystallized product	1.70	20.0

Taking the average figure of 1.68 for the recrystallized powders and assuming 40% amorphous substance in native cotton and ramie as estimated from density determinations in previous work [36], the quantity of amorphous substance in the recrystallized powders is found to be $1.68 \times 40 = 67\%$.

The difference between the heat of wetting of the amorphous powder and that of the recrystallized one (10 cal/g or 1.62 kcal/mole, in both cases

[34] Contrib. p. 99.
[35] *P. H. Hermans* and *A. Weidinger*, J. Amer. Chem. Soc., 68, (1946) 2547.
[36] Contrib. p. 71.

investigated) may be presumed to be equal to the heat of crystallization of the percentage x of the crystalline portion in the wetted samples. Assuming that the heat of crystallization of cellulose II will be almost equal to that of β-glucose ($\sim$ 5.5 kcal/mol), x would be 1.62 : 5.5 = 28% corresponding to 72% amorphous substance.

The percentage of amorphous substance in the recrystallized samples was also computed from the X-ray photographs, the figure being 62%, which is in the same order of magnitude.

In later, more accurate investigations (see appendix on p. 517) it was found from X-ray work that the amorphous powder still contains about 10% ordered substance and that this figure becomes about 40% after recrystallization. The difference of 30% is in conformity with the difference of 28% following from the heats of wetting.

We have now to consider hysteresis. The explanation suggested by *A. R. Urquhart*[37] needs only slight modification to fit in with our present views. Briefly, it is that "inner surfaces" are added during the swelling which is a concomitant of adsorption. *S. E. Sheppard* and *P. T. Newsome*[38] speak of "a relief of local strains, consequent on the uncoupling of polarized hydroxyl groups". Junction points are loosened which do not close again during desorption altogether reversibly, owing to inner resistances within the gel structure. *W. B. Campbell*[39] likewise speaks of "internal stresses" in this connection. Evidently the changes in volume which are inherent both in swelling and de-swelling, necessitate certain movements and, possibly, mutual shifting or configurational changes of the chains[40] giving rise to internal stresses.

The idea of internal stresses of opposite sign involved in the contraction and dilation of the gel as the cause of hysteresis has recently been put forward more explicitly by *W. W. Barkas*[41] and applied to wool by *A. B. D. Cassie*[42]. The authors have shown that the effect may be formally represented by an additional hydrostatic pressure of the absorbed water giving rise to a change in vapour pressure.

The fact that, owing to a process of esterification such as acetylation (or nitration), water absorption decreases along with the degree of esterification and with increasing length of the fatty acid residue (where esterification is with fatty acids), goes to prove that sorption is intimately connected with the chemical nature of the cellulose molecule. Interesting investigations on this subject have been published by *S. E. Sheppard* and *F. T. Newsome*[43].

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[37] *A. R. Urquhart*, J. Text. Inst., 20, (1929) T 125.
[38] *S. E. Sheppard* and *P. T. Newsome*, Ind. Eng. Chem., 26, (1934) 285.
[39] *W. B. Campbell*, Ind. Eng. Chem., 26, (1934) 218.
[40] cf. *P. H. Hermans*, Kolloid-Z., 97, (1941) 213.
[41] *W. W. Barkas*, Swelling Stresses in Gels, Forest Prod. Res. Special Report No. 6 London, 1945; Trans. Faraday Soc., 28, (1943) 205.
[42] *A. B. D. Cassie*, Trans. Faraday Soc., 41, (1945) 450.
[43] *S. E. Sheppard and P. T. Newsome*, J. Phys. Chem., 33, (1929) 1817; 37, (1933) 389; 39, (1935) 143.

§ 6. SWELLING IN WATER

As soon as water absorption begins, the fibres start to swell (cf. Chapter III). Absorption, accompanied by the formation of hydrates, is the first stage of swelling, this being followed by further monomolecular covering of the chains in the amorphous regions with water; finally, swelling continues while thicker layers of water are being formed. This last phase is often called "capillary condensation", but, as the "capillaries" are not formed until the swelling takes place, the term is not very felicitous. (Remember the analogy with the sulphuric acid/water system).

The end state reached in liquid water is the hall-mark of the fibre specimen under consideration. The factors governing this end state (which is interesting for many practical reasons) are far more difficult of apprehension than those which determine the first phases of sorption.

Let it be said at once that the end value of swelling should by no means be connected directly with the percentage of amorphous substance. In the cases of cotton and ramie the water content of the fibres is then about 35 to 40% and in that of regenerated fibres it varies considerably with the nature of the sample, but it is, roughly, 2½ to 3 times greater.

The final swelling value is probably determined primarily by the geometrical structure of the micellar system of the fibre, i.e., by the extent to which the network frame can expand while absorbing water without provoking resistance to further expansion by excessive strain.

There is other evidence to show that the effect of the slightest changes in the gel structure is liable to be enormous. The swelling of rubber, for instance, is influenced very strongly by the degree of vulcanization, i.e., by the number of cross linkages between the chains. It is likewise known that the addition of minute quantities of divinyl benzene during the polymerization of styrene has an amazing effect upon the swelling capacity of the polystyrene in benzene.

It will be obvious that the structure and, therefore, the swelling capacity of the network frame — especially of artificial fibres — will depend upon the conditions of manufacture. If only comparatively few new junction points are formed during the first drying, this would already enable us to account for the substantial difference in degree of swelling between freshly made artificial filaments and those re-swollen after the first drying [44].

The swelling capacity of cellulose can also be restrained by introducing bridges between the chains (stenosage or formalization). But the swelling power of a cellulosic material after the first drying by no means constitutes a stable end state which is reproducible under all circumstances; it is rather, moreover, dependent upon the conditions under which drying takes place.

For a long time, an interesting observation made by *K. Risch* [45] received little

[44] E.g., see *P. H. Hermans* and *A. J. de Leeuw*, Kolloid-Z., 81, (1937) 322.
[45] *K. Risch*, Thesis, Zürich 1930.

attention; it was that the water absorption of rayon filaments while swelling drops to approximately half the initial value after treatment for three hours with water vapour under pressure at 103 to 115° (without any fundamental change in their dry and wet strength). Recently, *E. Hubert, A. Matthes* and *K. Weisbrod* [46] have published more extensive, important evidence of the considerable influence which the drying conditions (temperature and humidity and, therefore, rate of water extraction) have upon the swelling power of regenerated cellulose. These investigations, to which we shall revert in the third part of this book, show that, upon the linking of the, at first, loose fibrous structure of freshly regenerated objects during the first drying process, no final state is as a rule reached; this can only be attained by repeated drying under properly adapted conditions. *K. Risch* states, however, that the final state can be accelerated by heating in vapour under pressure. In this way the regain of the swollen fibres can be reduced to roughly 55% (against roughly 100% prior to the operation).

That once more the reduction in swelling power is brought about by the addition of comparatively few new junction points is clear from the fact that artificial fibres thus treated show only insignificantly reduced sorption at low and average r.h. Hence the amount of "amorphous substance" (in the sense previously described) has scarcely changed at all. Here again we see how different are the factors which determine the sorption proper from those which govern swelling in liquid water. Without chemical aids, (cf. concluding passages of previous section) [47], there is little prospect of diminishing the strongly bound water in artificial filaments which is part of their constitution. Yet, in actual practice, the effect of the strongly bound water should be favourable rather than detrimental. In cotton, too, the textile properties of the dry fibres are very unfavourable [48] and processing includes certain operations to ensure a given water content. With artificial fibres the conditions should be no different. We may put it this way: to be suitable as textile fibres, cellulose fibres must be wetted at least to saturation of the two hydrate stages in the amorphous regions. When the water content is approximately that at which a complete monomolecular covering of water is obtained, the fibres acquire maximum flexibility i.e., native fibres with about 12, artificial fibres with roughly 25% water content [49].

In their completely dry state, cellulose fibres have the consistency of a brittle resin and are altogether inflexible. The cohesive forces in the micellar system are then so powerful at all points that the whole becomes rigid and immovable. Water is a typical and indispensable softener to cellulose, no other substance having this property in as marked a degree as water.

[46] *E. Hubert, A. Matthes* and *K. Weisbrod*, Kolloid-Z., 98, (1942) 193.
[47] *K. Kanamaru*, Kolloid-Z., 71, (1936) 351; *K. Kanamaru and co-workers*, J. Soc. Chim. Ind. Japan, 34, (1931) 119, states that the sorptive power could be appreciably diminished by the absorption of small amounts of Al or Th ions.
[48] *J. Meritt Mathews*, Die Textilfaser, Berlin 1928.
[49] Cf. *P. H. Hermans*, Die Kunstseide 16, (1934) 173, where an important instance of technical application is dealt with.

There is an apparent duality in the effect of the hydroxyl groups in cellulose, to which attention should be drawn before we conclude. The firm cohesion of the molecules in a cellulose gel and its insolubility in water can be traced to the powerful cohesive forces between OH groups; yet, at the same time, they determine the hydrophilic character and the swelling capacity in water. This duality becomes comprehensible if we ascribe the first function to those hydroxyl groups which are reciprocally bound by "hydrogen bonds" and the second function to the "free" hydroxyl groups present in other places. Hydrogen bonds can be formed only where the chains are in very close proximity and where a maximum degree of order prevails (as, for instance, in the crystalline regions). Wherever the hydroxyls of neighbouring chains are unable to approach each other to within the requisite minimum distance, they remain "free".

The striking fact that slightly methylated cellulose is soluble in water, whereas completely methylated cellulose is insoluble, might be explained in this sense, viz., that in the former case the formation of a sufficient number of hydrogen bonds is impeded, while in the latter case the affinity to water is too slight.

The striking point about the changes in dimension which the fibres undergo during sorption and swelling is the anisotropy that is revealed. Almost all the changes are in width only, with but very few in length. The mere orientation of the molecular chains in the direction of the fibre axis is sufficient to explain this phenomenon, to which we shall revert in greater detail in Part III, Chapter VI, § 2. For the water can only penetrate laterally between the chains, or between the crystalline regions. Therefore, with ideal orientation, there could only be swelling in width. *A. R. Urquhart* [50] reports that the swelling in volume of cotton in water amounts to roughly 45%, lengthwise swelling being less than 1%. Artificial fibres from cellulose swell by 70 to 100 per cent., 2 to 5% of which falls to longitudinal swelling. Regenerated fibres can also be processed in a completely isotropic state, when their swelling is, of course, likewise isotropic.

Quantitative data respecting volumetric proportions of swelling will be dealt with in Chapter III, § 3.

For the phenomena observed in the swelling of fibres in sodium hydroxide we refer to *E. Valko's* description in his book[50a] and to extensive investigations reported by *G. Saito* [51].

[50] *A. R. Urquhart*, J. Text. Inst., 20, (1920) T 125.
[50a] *E. Valkó*, Kolloidchemische Grundlagen der Textilveredlung, Berlin, 1937.
[51] *G. Saito*, Kolloid-Beih., 49, (1939) 365.

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CHAPTER III

DENSITY

§ 1. GENERAL ASPECTS OF DENSITY DETERMINATIONS AND THE CONCEPT OF DENSITY IN CELLULOSE FIBRES

Although a fair body of work has been devoted to the density of fibrous material, the theoretical inferences drawn from it have, more often than not, ignored the crux of the matter, owing to a failure of vision in grappling with such concepts as density and porosity [1]. For this reason, many of the early hypotheses can now be summarily dealt with, as, indeed, will be the case in this Chapter.

The conception of cellulose as a "colloidal" system with large "inner surfaces" in the classical sense, has involuntarily led to a representation of the fibres as a system consisting of fine and minute internal voids; that is to say, as a p o r o u s b o d y.

The object of a density determination is to find the volume of the sample, which is estimated with the aid of some liquid or gaseous buoyancy medium. The "true volume" of a porous body is understood to be its external volume after deduction of the volume of the voids, while the true density is derived from this volume and the weight of the body [2].

The result of a density determination of a porous body depends upon the extent to which the buoyancy medium is capable of penetrating into all the pores, for if these are not filled completely, the density found will be too low. Alternatively, the buoyancy medium may become compressed within the pores of the body, in which case the resulting density will be too high. This has often been found to happen with gaseous buoyancy media; e.g., gases such as air, and even hydrogen, will be compressed in porous carbon.

Such conditions have actually been met with frequently in density tests applied to porous bodies. Thus *A. M. Williams* [3] reported that, with ceramics, and *H. E. Cude* and *G. A. Hullet* [4] that, with charcoal, the density found depends upon the buoyancy medium used. With several organic liquids varying values were obtained with carbon, all considerably lower than the density of the

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[1] Contrib. 32.

[2] The specific gravity of a substance at t° is known to be a nondimensional number indicating how much heavier 1 ml. of the substance is at t° than 1 ml. of water of 4°. To within a correction of — 0.003%, the sp. gr. is also equal to the d e n s i t y of the body in g. per ml.

[3] *A. M. Williams*, Proc. Roy. Soc. London, 98A, (1920) 223.

[4] *H. E. Cude* and *G. A. Hullet*, J. Amer. Chem. Soc., 42, (1920) 391.

graphite crystal derived from X-ray data. But in gases such as air the values obtained exceeded the density of graphite and it was demonstrable that these gases were adsorbed by the carbon and so „compressed". *H. C. Howard* and *G. A. Hullet*[5], using helium as the buoyancy medium, which is not adsorbed by carbon, reported a value very nearly approximating the density of graphite.

These findings were now adapted to cellulose fibres. Density estimations in helium gas were first carried out by *G. F. Davidson*[6] and later by *P. M. Heertjes*[7], these having since been regarded as the nearest to the "true" densities. Some of the more reliable of the older cellulose fibre density determinations performed by *Davidson*, *W. Biltz*[8] and *H. L. Bredee*[9] are collected in Table XX.

TABLE XX

Densities of Cellulose Fibres in Various Buoyancy Agents

AUTHOR AND OBJECT	BUOYANCY MEDIUM USED		
G. F. Davidson	*Helium*	*Toluene*	*Water*
Native cotton			
American Upland	1.567	1.550	1.6095
Sea Island	1.558	1.548	1.6038
Sakel	1.563	1.550	1.6061
Mercerized cotton			
American Upland	1.550	1.536	1.6066
Sea Island	1.546	1.531	1.6017
Sakel	1.550	1.536	1.6041
Viscose rayon	1.548	1.534 [10]	1.6081
Cuprammonium rayon	1.531	1.522	1.6005
Nitrocellulose rayon	1.543	1.529	1.6149
W. Biltz		*Heptane*	
Native cotton	——	1.540	——
Viscose rayon	——	1.516	——
H. L. Bredée		*Benzene*	
Viscose rayon, little orientated	——	1.513	1.604
better orientated	——	1.519	1.608
greatly stretched	——	1.522	——
Lilienfeld rayon	——	1.534	1.594

[10] This value of *Davidson's* is undeniably far too high. In all later investigations lower figures were found for rayon.

It will be noted that the densities determined in organic liquids are throughout lower, and those determined in water higher than the densities determined in helium. In view of what is to follow, we wish to stress the fact that *Davidson* moreover discovered that equal values are found in benzene, toluene, chloroform, carbon tetrachloride and nitrobenzene.

The usual explanation of these established facts[11] was that the organic

[5] *H. C. Howard* and *G. A. Hullet:* J. Phys. Chem., 28, (1924) 1082.
[6] *G. F. Davidson*, J. Text. Inst., 18, (1927) T. 175.
[7] *P. M. Heertjes*, Dichtheidsmetingen aan vezels en enkele toepassingen hiervan (Density Determinations of Fibres and some of their Uses) Diss., Delft, 1938; Rec. trav. chim. 60, (1941) 689.
[8] *W. Biltz*, Z. physik. Chem., A. 151, (1930) 13.
[9] Unpublished determinations made in 1932, quoted with *Dr. Bredée's* kind permission.
[11] For this also cf. *E. Valkó*, Kolloidchem. Grundlagen der Textilveredlung, Berlin, 1937, p. 93 ff

liquids produced too low a density because they were unable to penetrate into all the "pores" of the material, whereas water, though penetrating fully, produced too high a density because it became compressed in the pores owing to strong surface forces. The small, adsorptively indifferent helium atoms, on the other hand, were said to penetrate unhindered and to fill up the volume of the pores entirely.

An attempt was then made to calculate the density of the bound water from the difference between the density in helium and in water, as also the "pressure" under which the water was supposed to be compressed. The result was an exceedingly high, but, from the point of view of physics, meaningless value.

P. H. Hermans, J. J. Hermans and *D. Vermaas*[12] have recently pointed out that, in these investigations, it should be borne in mind that density and porosity are typically macroscopic concepts which are of practical value only if applied to bodies, or voids, which, compared to molecular dimensions, are very large indeed.

In a certain sense every solid body is "porous", as there are always minute voids between the molecules; yet this "porosity" cannot be estimated by means of buoyancy tests, for the dimensions of the molecules of the available buoyancy media are of the same order of magnitude. The macroscopic density concept likewise loses its meaning with very small particles which consist of only a few molecules.

These authors put the matter like this: A small particle, consisting of only a few molecules, might be pictured as an agglomeration of molecules packed together like a heap of globules. If we wish to determine its density by means of buoyancy tests, the experiment must aim at determining its volume with the aid of a buoyancy medium likewise consisting of molecules of a certain size and shape. Neither the volume, nor the density can be defined in the usual sense without taking the relative dimensions and the shape of both kinds of molecules into account.

The problem may be compared to that which would arise if one wished to estimate the density of a pile of spheres by means of a medium consisting of smaller spheres, knowing only the weight of the smaller spheres included in the unit of volume.

The result depends upon the relative dimensions of the two kinds of spheres and is governed by the rules of spherical packing. If the spheres constituting the medium are small enough to penetrate even into the voids between the larger spheres, it wil moreover be found that the density of the pile of spheres is suddenly far greater than when such penetration cannot take place. It is necessary to bear these facts in mind when determining the density of very small particles. The same applies, of course, to porous bodies, the pores of

[12] *P. H. Hermans, J. J. Hermans* and *D. Vermaas*, J. makromol. Chem., 1, (1944) 247. J. Polymer Sci., I, (1946) 149, 156, 162. Cf. Contrib. p. 32.

which are accessible to the buoyancy medium and which are of molecular dimensions. Nor should the molecular coarseness of the "pore walls" be neglected.

There is yet another possibility. Extraneous spheres may be built into the pile of spheres. If the spheres of the medium are too large to penetrate of themselves in the voids within the pile representing the object, but are nevertheless drawn and fitted in by some force or other, the total volume of the pile of spheres will increase ("swelling"). Yet the volumetric increase will be less than equal to the volume of the spheres thus incorporated, since the latter will in part already have occupied the available voids. Therefore, if the two kinds of spheres are mixed, contraction may result.

If only for purely geometrical reasons such as these, it will be clear that contraction is liable to occur when two liquids are mixed, or when one liquid, such as water, infiltrates into the lattice of some other substance. There is no reason whatever to assume that this entails compression of the water absorbed. Molecular forces are needed to bring about penetration, or mixing, but we do not have to invoke them to explain contraction, since this can be understood on purely geometrical grounds.

According to *Hermans* and co-workers, cellulose fibres and like macromolecular systems liable to swell, such as gelatin, keratin, etc., are not entitled to be considered as porous bodies in the macroscopical sense.

With few exceptions (of which water is one), the macroscopic density of a substance in its crystallized state is greater than that of the same substance in its vitreous amorphous state. The latter state being a less orderly one, the molecules are less compact and on an average, therefore, the intermolecular "pores" are slightly larger. The additional empty space within the amorphous substance can be calculated from density determinations performed upon macroscopical fragments of the substance in both conditions, yet it would scarcely occur to anyone to estimate this additional "volume of pores" in the amorphous substance when endeavouring to establish the extent to which some other liquid or gaseous substance, like helium, is able to penetrate into it. Even if, say, helium were to penetrate into the objects — as it actually does into hot glass and many other materials —, it would be the solubility of helium in the substance that would be ascertained, rather than the volume of the pores in that substance in the above sense.

Now, since cellulose fibres consist of a mixture of crystalline and amorphous substance, it will be evident that their density is a function of the quantitative distribution between these two components. The relevant density here should be determined as the macroscopic density in a suitable liquid which, not penetrating into the fibrous substance at all, merely envelops it. There is a wide choice of suitable organic liquids and these, as *Davidson* had already found (see above), produce the same values.

The authors cited were able to show that these liquids which are "indifferent"

to cellulose do not in fact penetrate into regenerated fibres in anything but a negligible degree. Under proper experimental conditions, however, these liquids do fill up the true pores (see § 4) occurring in dry native fibres, as a result of the peculiar histological structure of the latter. (Judged by the standard of molecular dimensions, they are l a r g e). Thus in this case the density of the actual cell-wall substance of the fibre can be determined (cf. page 210). However, microscopically visible gas-locks, which often occur in regenerated fibres, are apt to be troublesome, as the buoyancy liquid does not fill them; for which reason regenerated fibres should be viewed under the microscope before density measurements are taken.

In this way density determinations in organic liquids, such as benzene, nitrobenzene and carbon tetrachloride, provide us with values most closely approximating that measure which interests us, viz., the compactness, or density of packing, of the fibrous substance, which is closely related to the condition of order. From the fact that helium gas diffuses [13] (though slowly) through dry cellophane membranes, it should be inferred that helium is to some extent soluble in cellulose. (These membranes are impermeable to oxygen and nitrogen.) It is therefore doubtful whether any favoured value can be assigned to the densities determined in helium.

The high density values in water are not attributed to any compression of the water (in itself very improbable), but are regarded as a perfectly normal result of the homogeneous mixing of cellulose and water in the amorphous portions. As with other mixtures, the volume relations in the mixture are considered to be similar to those obtaining in the packing of spheres of different sizes (cf. above). In this case the "spheres" of different sizes and shape are the glucosidic groups and the water molecules.

P. M. Heertjes [14] had already rejected the hypothesis propounding the compression of the water, yet his explanation of the contraction resulting from water absorption was still strongly coloured by the conception of cellulose fibres as porous bodies in the macroscopical sense.

All further references in this book to the density of cellulose fibres will be to their macroscopic density in the above sense.

§ 2. DENSITY OF PACKING OF DRY CELLULOSE FIBRES

Model filaments produced, after *P. H. Hermans* and *A. J. de Leeuw* [15], from regenerated cellulose, being crystalclear, homogeneous, cylindrical objects, lend themselves particularly well to exact density measurements. Column 1 of Table XXI reproduces accurate densities, as measured by *P. H. Hermans, J. J. Hermans* and *D. Vermaas* [16] by the suspension method, of objects dried in vacuo over P_2O_5, in mixtures of carbon tetrachloride and nitrobenzene.

[13] *F. H. Müller*, Kolloid-Z., 100, (1942) 355.
[14] Thesis, Delft, 1938. Rec. trav. Chim., 60, (1941) 689; 61, (1942) 751.
[15] *P. H. Hermans* and *A. J. de Leeuw*, Kolloid-Z., 81, (1937) 300.
[16] *P. H. Hermans, J. J. Hermans* and *D. Vermaas*, J. Polymer. Sci, 1, 156 (1946); Contrib. p. 112.

The "steamed" filaments were objects (likewise isotropic) treated in accordance with the suggestions of *Risch, Hubert, Matthes* and *Weisbrod* (cf. page 441) and thereby reduced in swelling value.

TABLE XXI

Density, Refractive Index n_{iso} and Refraction after Gladstone and Dale of Model Filaments as per Hermans and Co-workers

	d	niso	$\frac{niso-1}{d}$	$M\frac{niso-1}{d}$
Isotropic	1.512[9]	1.544[4]	0.3600	58.31
Isotropic (steamed)	1.515[5]	1.545[7]	0.3590	58.15
Orientated	1.518[5]	1.545[0]	0.3600	58.31
		Mean	0.3597	58.26

Column 2 of the table gives the refractive index n_{ISO} of these objects for sodium light[17], being likewise measured in organic liquids (mixtures of butyl stearate and tricresyl phosphate) which do not penetrate into the fibres.

The density and refractivity of every substance are known to be correlated. According to an empirical rule formulated by *Gladstone* and *Dale*, the refraction $(n-1)/d$ represents a constant value, from which, by multiplication by the molecular weight M (162 for $C_6H_{10}O_5$), one obtains the molecular refraction of the substance. Both these values are given in the last two columns of the table. The authors state that the mean value 58.26 found for the molecular refraction (MR) may be considered exact to within about 1.5 per thousand.

Independently of this, the MR can alternatively be computed from the tables of atomic and group refractions, which have been derived from measurements applied to many organic compounds. Calculating in this way, one finds 58.46, which tallies with the figure obtained by the direct method to within 3 per thousand[18].

The important inference from this is that, within this margin of accuracy, it may safely be stated that the liquids used both for the density and for the optical measurements have merely enveloped the filament, and have not, as liquids of so different a nature and molecular weight might have been expected to do, penetrated into it in a varying degree. There are other experimental arguments as well which could be advanced to show that the liquids do not penetrate into the filaments.

On this basis the authors then tried to determine the density of other fibres on the same principles. As we shall see directly, they succeeded but for a systematical error, whose magnitude is known. They were obliged to adopt a

[17] For orientated fibres the refractive index niso for the isotropic state can be calculated from the two main refractive indices in a manner which will be explained later (see Ch. IV, § 2).

[18] The MR calculated from the tables is, itself, subject to an error of this order of magnitude.

somewhat different experimental technique owing to the peculiar nature of technical fibres. (Ejection of the air by heating the samples at 100° in a current of carbon tetrachloride vapour and determination of the density by the suspension method in carbon tetrachloride in a closed chamber from which air and water were excluded [19]). Table XXII gives some selected results.

TABLE XXII

Density, Refractive Index n_{iso} and Refraction, as Determined by Gladstone and Dale, of some Cellulose Fibres after Hermans and Co-workers

	d	n_{iso}	$\frac{n_{iso}-1}{d}$
Natural fibres			
Native ramie	1.553	1.554[3]	0.3568
Ramie mercerized without tension	1.526	1.545[6]	0.3576
Viscose rayon			
Slightly orientated	1.518	1.541[1]	0.3565
Highly orientated	1.525	1.543[8]	0.3566
Orientated to maximum	1.523	1.543[0]	0.3566
Lilienfeld rayon			
Moderately orientated	1.520	1.542[9]	0.3572
Highly orientated	1.525	1.544[1]	0.3568
Model filaments			
Isotropic	1.519	1.544[4]	0.3588
Orientated	1.522	1.544[9]	0.3592

Working on extensive material such as that given here, the authors find 0.3570 to be the mean value for the refraction of technical fibres, with a probable error of ± 0.0006 (which is approximately 1.5 per thousand). From the fact that this value is lower by 7.5 per thousand than that produced by the exceedingly accurate measurements performed on model filaments, as recapitulated in Table XXI, they come to the conclusion that some slight penetration of the carbon tetrachloride into the fibres did in the long run take place when the finally adopted method of determination (using higher temperatures) was employed; and this agrees with an observation made by *K. Lauer* [20], who says that cellulose fibres absorb a quantity of carbon tetrachloride precisely of this order from the saturated vapour.

With model filaments the second method (by which the filaments are heated to 100° in carbon tetrachloride vapour) likewise produces somewhat lower refractions than the first (cf. Table XXI with Table XXII), but penetration into these far thicker objects is naturally much slower. (The densities found increased slightly when the filaments were let longer in contact with the liquid; Contrib. p. 71).

It is evident from the consistency of the refractions that the degree of penetration is practically the same for all technical fibres. The authors decided

[19] The temperature at which the fibres were suspended in CCl_4 was ascertained and their density was then derived from the density of the CCl_4 at that temperature.

[20] *K. Lauer*, Kolloid-Z., 107, (1944) 86.

that the densities of technical fibres measured by their method are higher by about 0.7% than the actual macroscopic densities of the objects. Table XXIII gives some further density measurements obtained by this method.

TABLE XXIII

Densities of Cellulose Fibres after P. H. Hermans and Co-workers
(Suspension Method in CCl_4.)

Native Fibres		*Viscose rayon* d	
Cotton A a	1.547	LA 0% stretch	1.518
Cotton B a	1.545	„ 30% „	1.523
Ramie fibres	1.553	„ 50% „	1.524
Mercerized ramie b		„ 70% „	1.525
I	1.543	HA 10% stretch	1.521
II	1.526	„ 50% „	1.521
III	1.546	„ 80% „	1.520
Sulphite Wood Pulp (alpha fibre)	1.537[5]	„ 120% „	1.523
Staple Fibre		*Lilienfeld rayon* e	
Plox	1.519c	Sodura A	1.520
Phrix BR	1.518c	„ B	1.524
Duraflox	1.518c	„ C	1.525
Lanusa	1.525	Bemberg rayon	1.524
Model filaments isotropic	1.519		
„ „ orientated	1.521		

a A. Cotton standardized to prescriptions of the Amer. Chem. Soc.
B. A bleached cotton yarn.
b I. Mercerized under tension (approx. 50% cellulose II).
II. Mercerized without tension (100% cellulose II).
III. The same subsequently stretched (highly orientated).
c Filaments not entirely free from gas-locks.
d LA and HA signifies spun from viscose of low and high alkali content respectively. The figures represent the stretch applied in spinning.
e A, B and C are specimens with increasing orientation.

There is little variation in the numerical values found for regenerated fibres, which range from 1.518 to 1.525 [21]. The density of wood pulp is a degree higher, and one degree higher still come the densities of native cotton and ramie. The density of mercerized ramie varies with the mode of treatment, coming near to that of regenerated fibres when mercerization is effected without tension. If, as was presumed to be likely:

1. the density of packing of the fibrous substance provides a direct gauge for the quantitative distribution between crystalline and amorphous portions;
2. the sorptive power with respect to water vapour runs parallel to the percentage of amorphous substance,

then the density d and sorption ratio r of various fibres must be in the reverse order. This, in fact, is the case.

[21] In this respect there is satisfactory agreement with the densities previously determined by *W. Moll*, Beih. zu "Die Chemie", 47, (1943) 105, likewise by the suspension method in CCl_4, but employing a somewhat less reliable experimental technique. *Moll* moreover found some extremely low values for staple fibres, for which, however gas-locks were probably responsible.

Let us take the simple case of the specific volume of the fibrous substance being a linear function of the fraction of amorphous substance and let

φ_{cr} = the spec. volume of the crystalline substance = 0.630 [22]

φ_n = the spec. volume of the native fibre $\frac{1}{1.550} = 0.645$

φ = the spec. volume of the relevant object,

then the sorption ratio would be:

$$r = \frac{\varphi - \varphi_{cr}}{\varphi_n - \varphi_{cr}} \qquad (3.1)$$

Table XXIV bears this out, provided the mean density of 1.530 be taken for mercerized ramie

TABLE XXIV

Sorption Ratios computed from the Density and those Observed

	Density	Spec. Vol.	Sorption Ratio r	
			Comp.	Observed
Wood pulp	1.538	0.650	1.3	1.3
Merc. ramie	1.530	0.654	1.6	1.5 — 1.6
Rayon	1.518 1.525	0.656 0.659	1.7	1.9 — 2.0

We shall find that agreement is better still if we bear in mind (as on p. 188) that the sorption ratio for rayon is roughly 10% higher than would follow from the ratio of the fractions of amorphous substance for rayon and cotton.

It should be noted that, in the case of regenerated fibres, both the sorptive power and specific volume decrease slightly as orientation increases (cf. Tables XVII and XXIII).

These results go to show that in this way we actually are dealing with the density of packing of the fibre wall substance and that this represents (approximately, at all events) a linear function of the percentage of crystalline substance.

P. H. Hermans and co-workers have now attempted to estimate the absolute quantity of the crystalline substance with the aid of density measurements. Assuming that the difference between the specific volume of the crystalline substance and that of the glassy, amorphous state is of the same order for cellulose as it is for other organic substances, such as butyl alcohol, they thus find roughly 25% of crystalline substance in regenerated, and 60% in native fibres. There is other evidence that these figures are approximately correct (cf. p. 316).

It should be added that there is certain evidence available, the quantitative interpretation of which could not be fitted into the line of thought developed in the foregoing. Thus *P. H. Hermans* and co-workers [23] found that, in the

[22] The mean value, 1.588, of the densities of cellulose I (1.592) and cellulose II (1.583) was taken here as the density of the crystalline substance (cf. page 20).

[23] Contrib. p. 68.

conversion of regenerated fibres to cellulose IV by heating in glycerol to 250°, the sorptive power decreases very much more than the comparatively slight increase in density would seem to warrant. Nevertheless, it is difficult to foresee what changes will be brought about in the fibres by heating to such high temperatures.

§ 3. DENSITY OF MOIST FIBRES. (VOLUM RELATIONS DURING SWELLING)

Let us consider 1 g of dry fibrous substance of d_0 density and $\frac{1}{d_0} = v_0$ volume. Now a g of water are absorbed, when the volume will increase to v_a. v_a will then be the specific volume of swelling and

$$q = \frac{v_a}{v_0} \qquad (3.2)$$

will be the degree of swelling of the fibre. It is the practice to denote the swelling value SV as being equal to the water content of the swollen fibres as a percentage referred to dry substance. Thus

$$SV = 100\, a \qquad (3.3)$$

The equation

$$d_a = \frac{1+a}{v_a} \quad or \quad v_a = \frac{1+a}{d_a} \qquad (3.4)$$

applies, of course, if the density d_a of the moist fibres is being determined. Thus, with the water content known, the specific swelling volume v_a can be derived from density measurements by (3.4).

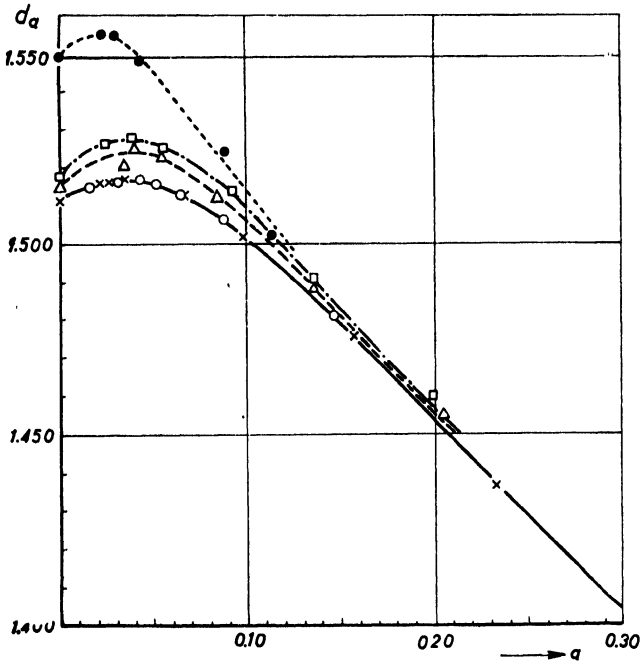


Fig. 58. Density d_a of cellulose fibres as a function of the regain (in grams per gram of cellulose).
x Isotropic filaments (absorption); □ 100- X-filaments;
○ „ „ (desorption); ● Cotton;
△ H. M. W.-filaments.

A. J. Stamm and *M. Seborg*[24] thus determined the density of moist fibres, using native cotton and the pyknometric method in benzene, and *P. H. Hermans*[25], using the three kinds of model filaments shown in Table XXI illustrates how, on the evidence

[24] *A. J. Stamm* and *M. Seborg*, J. physik. Chem., 39, (1935) 133.
[25] *P. H. Hermans*, contrib. p. 79.

of these investigations, the density d_a of the moist fibres stands in relation to the quantity of water a absorbed.

In all cases the curves run through a maximum value which corresponds to a lower water content in native cellulose than in the regenerated article. The initial increase in density depends, of course, upon the contraction resulting from water absorption, which used to be ascribed (cf. § 1) to compression of the water in the pores of the material. The result represented in Fig. 58 is analogous to that of the density measurements performed many years ago by *A. T. King* [26] upon moist wool.

Hermans and co-workers are of opinion that the results are clearer if the specific swelling volume v_a instead of d_a is plotted against a, when curves of the shape shown diagrammatically in Fig. 59 are obtained (precise indications in the original).

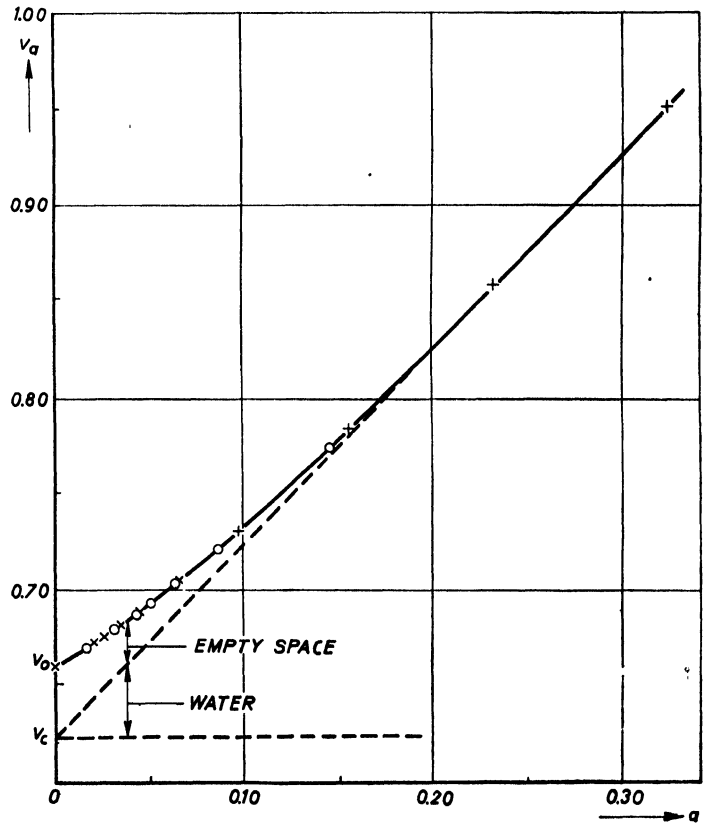


Fig. 59. Course of the specific volume of swelling v_a of cellulose fibres in dependence upon the water content a Explanation given in the text. (x absorption; o desorption).

It will be seen that the volume v_0 of one gram of the dry fibrous substance increases as soon as water absorption begins. The tangent of the angle of

[26] *A. T. King*, J. Text. Inst., 17 (1926) T 53; 18 (1927) T 274.

inclination of the curve towards the abscissa gives apparent spec. volume with which the water is absorbed; therefore the cotangent gives its apparent density d_s. The latter is at first far above 1, a token that the water is apparently compressed.

Round about a water content of 4% the inclination of the curve rapidly becomes greater, approaching the value 1 asymptotically, which is reached in the neighbourhood of 25% water content. Hence from 4% to 25% the apparent density d_s of the water decreases till it reaches the normal value. From now on, if more water is absorbed, the increased volume of the fibre is equal to the volume of the absorbed water, which means to say that contraction in the cellulose-water system has ceased.

Figure 60 portrays the course of the apparent density d_s of the absorbed water as a function of the water content for cotton (I) and regenerated cellulose (II). The position of the maxima in Fig. 58 is marked by the rapid decline of d_s that of a = 0.25 by the attainment of value 1.

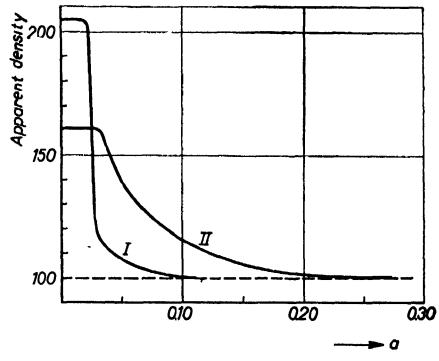


Fig. 60. Apparent density d_s of the absorbed water dependent upon the water content a in grams per gram of cellulose. I for cotton; II for regenerated fibres (isotropic model filaments).

Hermans and co-workers explain this as follows. If the v_a curve above a = 0.25 (Fig. 59) is extrapolated, it meets the ordinates at a point v_c (Fig. 59) representing the specific volume of the fibre measured in water as buoyancy liquid, i.e., the reciprocal value of the density d_w measured in water. (For, if the density of the water is put at 1, the volume v_c is equal to the buoyancy of the fibre fully swollen in water).

Now if we turn to our simple illustration of § 1, in which the rules governing the volumetric conditions of swelling were represented as similar to those applying to the packing of spheres of two different sizes, we shall have a clearer picture of the implications of Figure 59.

Volume $v_0 - v_c$ represents that part of the "empty space" between the cellulose molecules in the dry fibre which the water molecules are able to occupy. The fibre volume v_0 is then considered as the sum of this occupiable portion of empty space $v_0 - v_c$ and of the unchangeable portion of space occupied by the cellulose v_c. The latter is represented by the horizontal dotted line starting from v_c. The dotted line leaving v_c at 45° gives the sum of v_c and the volume of the bound water with the normal density 1. The remaining vertical distance to the v_a curve, therefore, gives us the still available portion of "occupiable empty space".

Hermans and co-workers maintain that the first part of the curves (Figs.

59 and 60) corresponds to the formation of the first hydrate (cellulose hydrate I). The position of the maxima both for native and regenerated cellulose is, within the margin of accuracy of measurement, exactly where consideration of the balance of bound water set forth on page 188 would give one to suppose it to be. The point of coincidence of the curve and its tangent in Fig. 59 corresponds to that phase of swelling in which the monomolecular covering of the chains in the amorphous regions has been completed. For cotton it is roughly at 10 to 12% of water; for regenerated cellulose at 22 to 25% of water. Assuming once again 40% of amorphous substance for the former and 75% for the latter, this point will correspond in both cases to approximately 2½ to 3 moles of H_2O per $C_6H_{10}O_5$ in the amorphous portions, which, on the whole, is a reasonable figure. From now on, water molecules are no longer added on to glucose groups, but begin to attach themselves to their own kind, and contraction therefore ceases.

We now have grounds for believing that the volumetric interplay in the process of swelling can be made to fit intelligibly into the picture — now complemented to some extent by numerical data - that has been built up of fibrous structure, sorption and swelling. As we shall see in Chapter IV, quantitative data bearing on these volumetric relationships are a necessary preliminary to any proper understanding of the optics of moist fibres.

Before concluding this Paragraph, we wish to mention research work carried out by *E. Filby* and *O. Maas*[27] on the density of moist cotton fibres in helium gas. This likewise led to a decided density maximum which, however, these authors found to coincide with about 6% of water. *Hermans* and co-workers[28] have advanced arguments to show that in all probability an error is responsible for this figure.

Once the course of the volume of swelling v_a with the water content a is known, it will henceforth be possible to connect the characteristic indices referred to at the beginning of this section, viz., swelling value SV and degree of swelling q, a facility which may prove useful for practical purposes.

We can now submit a general formula for regenerated fibres if we assume that the swelling of all technical artificial fibres is as measured by *Hermans* and co-workers for orientated model filaments, which will be found to be very nearly the case. We then have:

$$q = (SV + 62)/66 \qquad (3{\cdot}5)$$

This equation, however, only holds good for water contents above 25 to 30%. (For lower water contents it is necessary to resort to the measurements made by the authors mentioned).

The degree of swelling of regenerated fibres in standard atmosphere at 65% r.h. amounts to 1.16 -- 1.17.

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[27] *E. Filby* and *O. Maass*, Canad. J. of Research, 7, (1932) 62, p. 131.
[28] Contrib. p. 84.

§ 4. POROSITY AND BIOSTRUCTURE OF NATIVE FIBRES

It was stated in the foregoing that regenerated fibres can only be said to be porous if they contain microscopically visible gaspockets. Native fibres are, on the contrary, porous by nature. They contain a lumen in addition to other microscopically visible voids and probably a system of minute capillaries as well, by which the lumen is connected with the outside world.

Whereas the gas pockets in regenerated fibres are n o t reached when the dry objects are steeped in organic liquids such as benzene and carbon tetrachloride, the lumen of native fibres is readily filled up with them and it is likely that the same happens with all the voids [29]. That is why the porosity of native fibres does not affect the density determination of fibrous wall substance discussed in the previous section.

This t r u e (macroscopic) porosity of native fibres is nevertheless a property which we should not overlook, being, as it is, one in which native fibres are essentially different from regenerated fibres.

Cotton fibres are so porous that this porosity can easily be determined by microscopic measurement. Whereas the density of model filaments calculated from the microscopically measured fibre volume (within the 1 — 2% margin of accuracy) agrees with the density determined in the buoyancy test [30], this is not so with cotton fibre. Admittedly, the material published on this subject is very scanty, no doubt on account of the difficulty of determinations of this kind. We have, however, the reliable evidence of *G. C. Clegg* and *S. C. Harland* [31] respecting cotton fibre, which shows the specific gravity calculated from the microscopically determined fibre volume to be 1.05 [32]. Starting from 1.55 as the true specific gravity, the volume of the pores calculated amounts to no less than 30%.

L. Balls [33], without stating by what method it was determined, reports the porosity of cotton fibre to be 20%. We have similar measurements for ramie fibre, performed by *A. Frey-Wyssling* and *H. Speich* [34], who put the porosity at 12½%. (By mistake, these authors took the density of crystallized cellulose into account, instead of the measured density of ramie fibres in organic liquids. Upon correcting for this error, the porosity of ramie fibres is found to be 10.5%).

Optical measurements likewise provide evidence of the porosity of native fibres (cf. p. 225). The considerable pore volume of native fibres is altogether truly remarkable. There is some reason to believe that certain

[29] The fibre lumen readily fills up if dry woodpulp and cotton fibres are introduced into organic liquids with due care (using vacuum).
[30] Contrib. 45.
[31] *G. C. Clegg* and *S. C. Harland*, Shirley Inst. Mem., 2, (1923) 353; J. Text. Inst., 14, (1924) 489.
[32] The apparent volume of the hairs was estimated from the microscopic measurement of many cross sections, the average weight per unit of length being likewise ascertained.
[33] *W. L. Balls*, Studies in Quality of Cotton, 1928, p. 71.
[34] *A. Frey-Wyssling* and *H. Speich*, Helv. chim. acta 25, (1942) 1474.

properties of native fibres of special technological value (such as the lasting great bending strength of cotton) are by no means unconnected with it, as suggested in various quarters.

Since the aforementioned experimental evidence obtained from model filaments, it has become fairly certain that the same conditions do not obtain in artificial fibres. Determinations such as those conducted by *Clegg* and *Harland* upon cotton have not yet been applied to rayon, though this would presumably be the easier material, particularly when handling fibres of circular cross section [35].

§ 5. DENSITY OF CELLULOSE FIBRES IN WATER

Using water as the buoyancy medium for the determination of the density of a cellulose fibre, the value found is d_W which we may define as its "apparent density in water". The reciprocal value v_c is its apparent specific volume in water, a value to which we have already assigned a formal meaning in § 3 (Fig. 59). Actually, it represents the "partial volume of the cellulose in its mixture with water" and the terms "specific volume" and "density" are in fact as inapt as would be "density" applied to cane sugar in its aqueous solution.

It will be evident from the foregoing exposition that, the greater the amount of amorphous substance contained by the cellulose, the greater will be penetration of water into it and that the lower will be the apparent specific volume v_c of the cellulose in water and, therefore, the higher its apparent density. The density d and the apparent density in water d_W of various objects may consequently be expected to rum antiparallel and d_W will obviously always be greater than the density of the crystalline cellulose, while conversely, d will invariably show a lower figure than the latter.

Referring to the original for further details, we shall here only briefly touch on the most salient points of systematic and exact density determinations conducted recently in water by *P. H. Hermans* and co-workers[36] with the hydrostatic balance.

The density in water proves to be dependent upon the preliminary treatment and upon the time which has eleapsed since immersion. Constant and reproducible figures are obtained after briefly boiling in water and an interval of 15 hours, though these figures are still to some extent subject to the

[35] True, *P. Heermann* and *A. Herzog*, Mikroskopische und mechanisch-technische Textiluntersuchungen, Berlin, 1931, p. 232) have given 0.93 as the conversion factor for titrations of viscose rayon from the measured surfaces of microscopical cross sections. Assuming a true spec. gr. of 1.47 (at 65% r.h.), the computed apparent sp.gr. would be 1.37 and, therefore, the pore volume 7%. Probably, however, the empirical conversion factor other than 1 should here be interpreted differently. This matter needs to be investigated further.

[36] Contrib. p. 91.

temperature (even after a correction has been made for the temperature of the water).

Some of the d_W values — accurate to within about 0.02% — and of the d values — accurate only to about 0.15% — are collected in Table XXV.

TABLE XXV

Density d and Apparent Density d_W in Water of some Cellulose Fibres after P. H. Hermans and Co-workers [37]

	d	d_W
Native Fibres		
Cotton A	1.547	1.6108
Ramie fibres	1.553	1.6116
Ditto mercerized II	1.526	1.6126
Viscose Rayon		
LA 0% „	1.518	1.6178
„ 30% „	1.523	1.6174
„ 50% „	1.524	1.6171
„ 70% „	1.525	1.6165
HA 10% „	1.521	1.6203
„ 50% „	1.521	1.6180
„ 80% „	1.520	1.6187
„ 120% „	1.523	1.6143
Lilienfeld Rayon		
Sedura A	1.520	1.6168
Sedura B	1.524	1.6166
Sedura C	1.525	1.6138
Bemberg Rayon	1.524	1.6150
*Model Filaments**		
Isotropic	1.512	1.6179
Orientated	1.518	1.6153

* According to Table XXI

In broad outline, the expected antiparallelism between d and d_W is there. Leaving the first two figures (for native fibres) out of consideration, we even find an approximately linear connection, as Fig. 61 will illustrate.

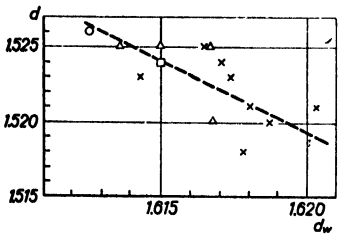


Fig. 61. Negative correlation between density d and apparent density in water d_W.
○ Mercerized ramie fibres; × viscose rayon; △ Lilienfeld rayon; □ Bemberg rayon.

The data relating to native fibres, however, do not fit into this scheme at all. We must refer to the original for a discussion of these circumstances, but would point out that the maximum variation of d_W for all fibres in Table XXV is no more than 0.6%, while that of d amounts to 2.7%.

The d_W values cited above were determined in material that had never been dried absolutely. Reduction of d_W takes place after

[37] For the meanings of the descriptive symbols in this table see the footnotes to Table XXIII.

drying over phosphorus pentoxide at 100° and also after conversion to cellulose IV [38].

The d_W values of freshly prepared, still considerably swollen regenerated filaments are, on the contrary, noticeably higher (about 1.625) and as much as 1.642 was found for fresh samples still containing undecomposed cellulose hydrate II [39]. Here we have an example of the maximum density of packing between cellulose and water, when all the chains of the cellulose are surrounded on all sides by water molecules.

[38] Contrib. p. 99.
[39] Contrib. p. 97.

CHAPTER IV

OPTICAL PROPERTIES OF FIBRES

§ 1. INTRODUCTION

Many of the structural traits of fibres are manifested in their optical properties, the study of which, therefore, is a valuable accessory in fibre research, and one that has hitherto been sorely neglected where artificial fibres are concerned. It could profitably be turned to better account in future and we shall therefore deal at some length with the subject in this book.

§ 2. GENERAL REMARKS ON THE REFRACTIVE POWER AND BIREFRINGENCE OF FIBRES AND THE METHODS BY WHICH THEY CAN BE DETERMINED

Cellulose fibres with orientated micellar structure are known often to be very strongly birefringent. Superficially, they are reminiscent in their behaviour of positive, uniaxial birefringent crystals. The optical axis lies in the fibre axis. With bodies of this kind, the velocity of propagation of the light and, therefore, the refractive power, depend upon the direction in which the light travels in them. A ray of natural light falling in any direction on the body passes through it in the form of two separate, polarized rays, called *extraordinary* and *ordinary rays*. The electric vector of the *extraordinary ray* vibrates in the plane through the ray and the optical axis; the *ordinary ray* vibrates perpendicularly to the former. The refractive index n_o of the ordinary ray is independent of the direction of propagation of the light through the fibre, that of the extraordinary ray n_e varies with this direction. The difference between n_e and n_o is maximal if the light passes perpendicularly to the optical axis. In this case the refractive indices of the ordinary and extraordinary rays are denoted by $n_{/\!/}$ and $n_\perp$ respectively (Fig. 62). The *index ellipsoid* drawn in this Fig. represents the entire optical character of the fibre. The values of the refractive indices and the directions of their vibrations for light passing in any direction are given by the lengths and the spatial situation of the ellipse of intersection formed by this ellipsoid and a plane perpendicular to the beam of light.

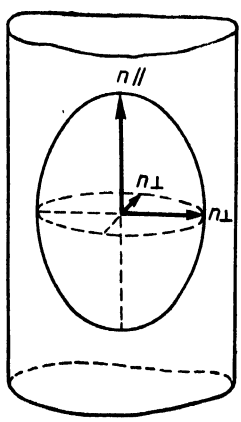


Fig. 62. Position of index ellipsoid in the fibre; $n_{/\!/}$ and $n_\perp$ are the main refractive indices of the fibre.

The difference $n_{/\!/} - n_{\perp}$ is called the *birefringence*. For cellulose it is positive, in cellulose nitrate fibres the b.r.[1] is negative.

Both the principal refractive indices of a fibre can be determined with the aid of a polarizing microscope by either of the well-known immersion methods devised by *Becke* and by *Schröder—van der Kolk*. Briefly, these methods consist in plunging the completely dry fibre into liquids (also dried) of differently graded refractive power which do not give rise to swelling; then choosing that liquid in which, viewed in linearly polarized monochromatic light (polarizer in condenser, analyser cut out), the outlines of the fibre disappear, or certain optical criteria are manifested[2]. This procedure is carried out with the polarizing plane of the light parallel to the fibre axis and is repeated with that plane perpendicular to it, the first producing $n_{/\!/}$, the second $n_{\perp}$.

A. Frey-Wyssling[3] introduced into fibre research an excellent modification of this method, which is commonly used in mineralogy, whereby the extinction of the fibre outline is effected by varying, not the immersion liquid, but the wave-length of the monochromatic light used for the observation (dispersion method). This necessitates the use of a monochromator of strong intensity for illumination.

In a paper by *C. P. Saylor*[4] it is stated that the use of an objective with a not too high aperture around 0.25 yields the highest accuracy. When observing the *Becke* line a low aperture of illumination (narrow diaphragm) below the condenser should be used and when employing the shadow method of *Schroeder van der Kolk* the aperture of illumination should be large. A very useful improvement of the latter method, called the "double diaphragm method" is also published in that paper.

When the two main refractive indices have been determined in either of these ways, the specific birefr. is derived from the difference between them. In favourable cases this latter value can also be determined independently under the polarizing microscope with the help of some compensating process. One then dispenses with the phase difference γ between the ordinary and extraordinary ray, expressed as wave-lengths λ of the monochromatic light used.[5] $\Gamma = \gamma\lambda$ denotes difference in path and, therefore, represents length. It is proportional to the thickness d of the layer traversed by the light. The birefr. is then derived as follows:

$$n_{/\!/} - n_{\perp} = \frac{\Gamma}{d} = \frac{\gamma\lambda}{d} \qquad (4.1)$$

---

1 The word "birefingence" will hereinafter be abbreviated to "b.r.".

2 Full description in: Anleitung zu optischen Untersuchungen mit dem Polarisationsmikroskop, Leipzig 1934, by *F. Rinne* and *M. Berek;* Modern Textile Microscopy, London, 1933 by *J. M. Preston.*

3 *A. Frey-Wyssling,* Helv. chim. acta, 19, (1936) 900.

4 *C. P. Saylor,* Accuracy of Microscopical Methods for Determining Refractive Index by Immersion, Natl. Bur. of Standards J. Res. 15, (1935) 277.

5 For details see *H. Ambronn* and *A. Frey,* Das Polarisationsmikroskop, Leipzig 1926, or the books by *F. Rinne* and *M. Berek* or *J. M. Preston* previously cited.

Hence, the thickness d has likewise to be determined microscopically and expressed in the same unit of length as the wave-length λ [6].

Owing, however, to the irregular cross-sectional shapes of most technical fibres, it is difficult, if not impossible, to determine thickness microscopically and this can only be done if the fibres are to some extent cylindrical in shape. The applicability of formula (4.1) can then be tested by determining the refractive indices $n_{/\!/}$ and $n_{\perp}$ separately. It is found to apply to crystals and also, with fair approximation, to model filaments; but serious discrepancies often arise with native fibres, which may be attributed to the porosity of those fibres (cf. Chap. III § 4).

The method for the determination of the b.r. commonly employed is that of the separate determination of the two main refractive indices by means of suitable imbibition liquids. *P. H. Hermans* and co-workers [7] describe a sure means by which such determinations can be carried out with the complete exclusion of moisture. These authors recommend mixtures of butyl stearate, tricresyl phosphate and diphenyl amine as suitable, non-volatile liquids, which suffice in the realm of cellulose fibres.

J. M. Preston has recently published a very interesting method of measuring the refractive indices of air-dry fibres in mass without the aid of a microscope. A parallel wound pad of fibres is examined in a relatively simple apparatus, called "fibre refractometer" [8].

The magnitude of the b.r. depends upon the orientation of the micellar frame (§ 6). If we wish to compare the optical refractive power of various fibres, we require a standard independent of their respective orientations. This would be provided by the refractive index which the fibre would possess if only its orientation were disturbed, without involving any change in density of packing; hence, the refractive index n_{iso} of the isotropic material. This is given by the formula

$$n_{iso} = \frac{1}{3} \quad (n_{/\!/} + 2n_{\perp}) \qquad (4.2)$$

which will be explained later (p. 231).

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[6] The difference in path Γ found by the compensation method is dependent, not only upon the thickness of the layer d, but also upon the angle of vision with respect to the position of the index ellipsoid in the object. The standard for Γ is the axial ratio of the, generally elliptical, cross-section of the ellipsoid at the plane which stands perpendicular to the line of vision. Looking at the cross section of a fibre (sliced vertically to the fibre axis), this, as an exception, will be found to be a circle and the difference in path is therefore equal to zero. In this direction the body appears to be isotropic. If, as in Fig. 62, the angle of vision is perpendicular to the fibre axis, the axial ratio and, therefore, the difference in path Γ are at a maximum. This case comes into the method of determination here described and it is to it that formula (1) applies.

[7] *P. H. Hermans*, Contrib. 217; J. Polymer Sci., 1, (1946) 162.

[8] *J. M. Preston* and *K. Freeman*, J. Text. Inst. 34, (1943) T 19.

§ 3. RELATIONSHIP BETWEEN REFRACTIVITY, BIREFRINGENCE AND DENSITY

We saw in Chapter III, § 2, that *Gladstone* and *Dale's* law applies to all cellulose fibres in the dry state and, therefore, the refraction

$$\frac{n_{iso} - 1}{d} \qquad (4.3)$$

represents a constant if density and refractive power are always determined in the same, comparable manner. *P. H. Hermans, J. J. Hermans* and *D. Vermaas*[9] have found from many determinations 0.3570 as the value of the constant (4.3), with a probable error of 0.0006, following the procedure they themselves had advocated for density measurement.

The *Gladstone* and *Dale* relation can now be applied individually to the two main refractive indices of anisotropic fibres, viz.,

$$\frac{n_{\parallel} - 1}{d} = c_1 \text{ and } \frac{n_{\perp} - 1}{d} = c_2 \qquad (4.3a)$$

where c_1 and c_2 are constants. Therefore

$$\frac{n_{\parallel} - n_{\perp}}{d} = constant \qquad (4.4)$$

With the help of these formulas comparison is made possible between the optical constants of fibres of different densities, since they are all converted to the same density [9a].

It should be noted that, whereas the determination of the refractive indices of fibres by the immersion method gives us the refractive power at the periphery of the fibre, density measurement, of course, produces a mean value for the entire section. The consistency of the refractions found for all the fibres examined goes to show that:

1°. Any differences in density there may be within the cross section cannot be appreciable.

2°. The lumen and pores of native fibres are well and truly filled by the buoyancy medium used for the density determinations.

§ 4. INFLUENCE OF REGAIN ON REFRACTIVITY AND BIREFRINGENCE

The effect of the lower regains may conveniently be considered before we proceed to discuss the optics of the more highly swollen fibres.

4.1 The Simple Rule of Miscibility in Low Degrees of Swelling

The effect of the regain upon the optical constants of cellulose fibres was investigated first by *A. Frey-Wyssling* and *M. Meyer*[10], with ramie fibres as the test material, and subsequently by *P. H. Hermans* and *P. Platzek*[11],

[9] *P. H. Hermans, J. J. Hermans*, and *D. Vermaas*, Contrib. p. 111; J. Polymer Sci., 1, (1946) 162.

[9a] Reservation made that the crystal structure and the percentage of amorphous substance be equal in the objects compared, as will be explained further on.

[10] *A. Frey-Wyssling* and *M. Meyer*, Helv. chim. acta, 18, (1935) 1425.

[11] *P. H. Hermans* and *P. Platzek*, Rec. trav. chim., 58, (1939) 1001.

using isotropic model filaments from regenerated cellulose. These authors, however, did not succeed in expressing their findings quantitatively by a physical formula, but recently *P. H. Hermans, J. J. Hermans* and *D. Vermaas*[12] were able to elucidate the whole matter conclusively with the aid of the exact data in their possession relating to the increase in volume entailed by the swelling of model filaments.

By a simple rule of miscibility it was possible to render the change in the refractive index n_{iso} of isotropic filaments as well as that in the two main refractive indices $n_{/\!/}$ and $n_{\perp}$ of anisotropic model filaments coincident with increasing regain up to about 20% water content. This generally applicable rule[13] to homogeneous mixtures of several substances states that the refraction according to *Gladstone* and *Dale* is an additive quantity for the mixture.

Let v_1, v_2, v_3..... be the volumes and n_1, n_2, n_3..... the refractive indices of the individual components of the mixture and v_m and n_m the corresponding quantities for the mixture, then

$$v_m (n_m - 1) = v_1 (n_1 - 1) + v_2 (n_2 - 1) + v_3 (n_3 - 1) + \ldots (4.5)$$

In our case, taking 1.3333 as the refractive index of the water, we shall have for the mixture of cellulose and water:

$$v_a (n_a - 1) = v_o (n_o - 1) + 0.333\, a \qquad (4.6)$$

where n_a and n_o represent the refractive indices of the moist and of the dry cellulose and v_a, v_o and a have the significance introduced in Chapter III, § 3.

Experimental results show that formula (4.6) proves exactly correct for n_{iso} of isotropic filaments and also for $n_{/\!/}$ and $n_{\perp}$ of anisotropic filaments. Figure 63 shows, for instance, the course of $n_{/\!/}$ and $n_{\perp}$ of an orientated filament as the function of the regain a. The full curve was calculated according to the postulates of equation (4.6); the circles represent the observed facts. The calculated and observed values also agree in the case of ramie fibres. The course of the b.r. $n_{/\!/} - n_{\perp}$ with the regain will now

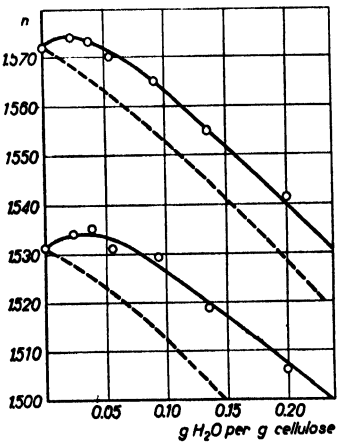


Fig. 63. Course of the two principal refractive indices $n_{/\!/}$ and $n_{\perp}$ of an orientated model filament, dependent upon the water content a in g per g of cellulose, after *P. H. Hermans* and coworkers. Solid curve calculated in conformity with the additive miscibility formulas; broken curves calculated in accordance with the *Wiener* formulas. Points = observed values.

[12] *P. H. Hermans, J. J. Hermans,* and *D. Vermaas,* J. Colloid Sci. 1, (1946) 251; cf. Contrib. p. 77.

[13] For this cf. e.g., *C. Dieterici,* Ann. d. Physik. 67, (1922) 337.

also be clear without further amplification from equations (4.6) and (4.4) on p. 217. It is simply in inverse ratio to the degree of swelling q ($= v_a / v_o$):

$$(n_{/\!/} - n_{\perp})_a = \frac{(n_{/\!/} - n_{\perp})_o}{q} \qquad (4.7)^{14}$$

The fact that the simple miscibility formula (4.6) proves correct affords further strong support for the assumption that sorption represents a homogeneous mixing process. *Hermans* and his associates state that formula (4.6) also provides the exact refractive index of all mixtures of sulphuric acid and water (in which contraction and the formation of hydrates likewise occur).

It is worthy of note that, within the region here dealt with, the water in the cellulose-water mixture behaves like an isotropic component. We know that at moderate regain the water molecules are, for the most part at all events, bound as water of hydration. We might therefore expect them to be orientated in relation to the cellulose. If the cellulose chains exhibit preferential orientation, as is the case in anisotropic fibres, we should really expect a component of b.r. coming from the water molecules (likewise orientated). As was demonstrated by *D. Vermaas*[15] not long ago, a very considerable component of b.r. is, in fact, liable to occur occasionally in orientated gels through orientated adsorbed liquid molecules[16]. For reasons which are not yet clear, this phenomenon, which *Vermaas* called "adsorptive birefringence", does not occur in the cellulose-water system, though the anisotropy of the water molecule would in itself entitle us to expect an adsorptive birefringence.

The peculiar course of the curves in Fig. 63, where the refractive index initially remains almost unchanged while passing through a very shallow maximum, after which it drops, is, of course, due to the relevant change of the volume (cf. Fig. 58) and the gradual filling up of empty spaces (Fig. 59). Formulas (4.6) and (4.7) have been found to hold good for regenerated cellulose up to about 15% water content, to within 10^{-3}. Above that there are deviations, in that the birefringence gradually increases, more rapidly than calculated according to equation (4.7). (See section 4.2).

P. H. Hermans[17] has given generally valid formulas for the computation of the optical constants of regenerated fibres in the absolutely dry state from observations made in standard atmosphere.

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[14] This equation had been used before by *O. Kratky* and *P. Platzek*, Kolloid-Z., 84, (1938) 268.
[15] *D. Vermaas*, Z. physik. Chem., B. 52, (1941) 131.
[16] Also cf. *P. H. Hermans*, Kolloid-Z., 96, (1941) 148. A similar case was reported by *A. Mohring*, Kolloid chem. Beih., 23, (1927) 152, who interpretated it in a similar way.
[17] Contrib., p. 129.

4.2. *Additional Structural Birefringence in Higher Degrees of Swelling*

a *Wiener's Theory*

For many years past, *Wiener's* theory of anisotropic mixed bodies[18] has provided the theoretical basis for the treatment of the optics of swollen cellulose. It deals with the ideal case of a body constructed of parallel cylindrical rodlets embedded in a medium of different refractivity from that of the rodlets. (See diagrammatic presentation in Fig. 64).

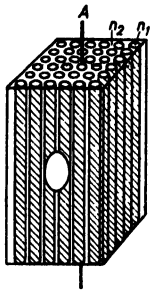


Fig. 64. Diagram of the *Wiener* mixed body of rodlets (after *W. J. Schmidt*). A. Optical axis. The effective index ellipsis is introduced on the anterior surface.

According to *Wiener*, a body of that kind is fundamentally birefringent, even if the rodlets and the imbibition medium are themselves entirely isotropic; optically, its behaviour is that of a uniaxial crystal with the optical axis parallel to the rodlet axis (see subscript to Fig. 64). Structural birefringence is the name given to that phenomenon by which components of a mixed body which, in themselves, are optically isotropic, impart optical anisotropy to the whole body solely on account of a regular, geometrical arrangement. The structural b.r. discussed a little further back is called rodlet birefringence. The size of this b.r. is governed entirely by the refractive indices n_1 of the rodlets and n_2 of the imbibition medium and by the relative part by volume δ_1 and δ_2 of these two. It is therefore independent of the absolute thickness of the rodlets provided this does not exceed the order of magnitude of the wave-length of the light.

For our purposes we prefer the "degree of swelling" q of the body to the two quantities δ_1 and δ_2. This represents the volume of the whole body divided by the total volume of the rodlets it contains and is therefore related to δ_1 and δ_2 as follows:

$$\delta_1 = \frac{1}{q} \quad \text{and} \quad \delta_2 = \frac{q-1}{q} \tag{4.8}$$

Then, according to *Wiener:*

$$n_{/\!/}^2 = \frac{1}{q} n_1^2 + \left(1 - \frac{1}{q}\right) n_2^2 \tag{4.9a}$$

and

$$n_\perp^2 = n_2^2 \cdot \frac{(q+1)n_1^2 + (q-1)n_2^2}{(q+1)n_2^2 + (q-1)n_1^2} \tag{4.9b}$$[19]

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[18] *O. Wiener*, Abh. Sächs. Akad. d. Wiss. Math. phys. Kl., 32, (1912) 507, 604. We shall here only deal with the case of the *Wiener* rodlet mixed body, leaving out of account the analogous layer mixed body, for which latter reference may be made to the appropriate text-books. Also cf. the recently published article by *W. J. Schmidt*, Kolloid-Z., 96, (1941) 135.

[19] These formulas only hold good if the two components of the polarized light are absorbed with equal intensity. If there is any selective absorption by one of the components, that alters matters. Cf. *O. Wiener*, Kolloid-Beih., 23, (1927) 189.

As can easily be proved, the birefr. $n_{/\!/} - n_{\perp}$ which is calculated from this is always positive. We get $n_{/\!/} = n_{\perp}$ for $n_1 = n_2$ (same refractive power of the components of the mixed body) and in this case the body will be isotropic.

It is as well to bear in mind that the *Wiener* theory rests on the following presuppositions [20]:

1°. That the thicknesses of, and distances between the rodlets are small compared to the wave-length of the light.

2°. That sharply defined phase boundaries exist between the rodlets and the imbibition medium.

In the next section we shall consider whether these assumptions are or are not applicable to the case now in point.

If the rodlets of the mixed body are in themselves birefringent, this b.r. proper to the rodlets is added to the structural b.r. of the mixed body. As *A. Möhring* [21] has demonstrated, to calculate the latter one can then, without falling into any serious error, insert into the *Wiener* miscibility formulas (4.9) as refractive index n_1 of the anisotropic rodlets the mean value of their two principal refractive indices n_γ and n_α, though it is better to put in the refractive index of the isotropic state according to formula (4.2).

The total birefr. of the swollen anisotropic body can now be formulated as the sum of the "intrinsic b.r." of the rodlets and of the *Wiener* structural b.r. as follows:

$$(n_{/\!/} - n_{\perp})_q = \frac{(n_{/\!/} - n_{\perp})_o}{q} + (n_{/\!/} - n_{\perp})_W \qquad (4.10)$$

This is no more than equation (4.7) to which the *Wiener* component, according to formula (4.9), has been added. The first term of the second expression of equation (4.10), to which the anisotropy of the molecules is attributable, is called the intrinsic birefringence; the second term, the structural birefringence of the object.

We have now two important questions to consider:

a. How does the *Wiener* structural b.r. with given n_1 and n_2 vary with the degree of swelling q ?

b. How, with given refractive index n_2 of the rodlets and given degree of swelling q of the mixed body, does it vary with the refractive index n_2 of the imbibition medium?

Re a) the evidence is that the b.r. always reaches a maximum for $q = 2$ (i.e., for the same volume of the rodlets and of the imbibition medium).

[20] It was evolved from the so-called continuum theory of the refraction of light.
[21] *A. Möhring*, Kolloid chem. Beih., 23, (1927) 126.

Figure 65 represents the course of $n_{/\!/} - n_{\perp}$ as a function of the degree of swelling q, notably by way of example for $n_1 = 1.565$ upper curve and $n_2 = 1.333$ (n_D^{20} for water), or alternatively for $n_1 = 1.535$ lower curve and $n_2 = 1.333$ [22].

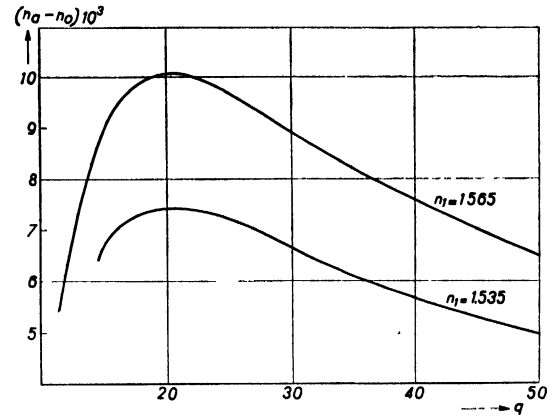


Fig. 65. Course of the rodlet birefringence as a function of the degree of swelling q after *Wiener*; $n_2 = 1.333$. I for $n_1 = 1.565$, II for $n_1 = 1.535$.

With regard to b) we have the familiar result that, in the case of isotropic rodlets with increasing n_2, the b.r. of the mixed body first decreases, reaches zero for $n_1 = n_2$ and then increases again. (The curve is a hyperbola [23]). Figure 66 is the diagram of an "imbibition curve" in the event of the rodlets having a positive intrinsic b.r., where G represents the total birefr. resulting from the addition of intrinsic b.r. and rodlet b.r. At the minimum of the curve $n_1 = n_2$; the birefringence continuing there of AB size has its source in the intrinsic b.r. of the rodlets [24]. It is given in formula 4.7.

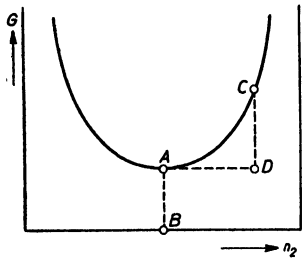


Fig. 66. Rodlet birefringence with given degree of swelling for positively birefringent rodlets as a function of the refractive index n_2 of the imbibition medium; AB = intrinsic birefringence; CD = rodlet birefringence.

Thus, by varying the refractive power of the imbibition liquid, a mixed body of rodlets with a liquid imbibition medium can in this way be subjected to comprehensive optical analysis. If it be found that an intrinsic birefringence remains in the minimum of the curve, this may be taken as evidence that the rodlets are birefringent.

β *Structural Birefringence in Cellulose Fibres*

H. Ambronn [25] was the first to investigate experimentally the structural birefringence of gels, including swollen orientated cellulose objects, finding that the behaviour of the latter was, optically, that of rodlet mixed bodies,

[22] Calculations in accordance with the *Wiener* formulas must be carried through to at least six places of decimals to obtain sufficiently accurate figures.
[23] For a more exact analysis of these curves and for comments on their position and shape see *A. Frey-Wyssling*, Kolloid-Z., 90, (1940) 33.
[24] If the intrinsic b.r. of the rodlets is negative ($n_\gamma < n_\alpha$), the negative intrinsic b.r. superimposes the positive structural birefringence. A curve is then obtained similar to that of Fig. 66, though shifted downwards so that its minimum has a negative ordinate and the abscissa axis therefore intersects it at two points.
[25] For literature see p. 20.

with the rodlets exhibiting intrinsic birefringence. This, concording so handsomely with the theory that the fibres are built up of crystalline particles resembling rodlets, was held to vindicate *Nägeli's* hypothesis.

Imbibition curves, similar to those shown in Fig. 66, were established by *A. Möhring*[26] for ramie fibres and by *P. H. Hermans* and *P. Platzek*[27] for model filaments of regenerated cellulose.

Nowadays, while conceding that the coherent, orientated micellar frame of the fibres actually will behave in a manner similar to a rodlet mixed body, we realize that the idealised geometrical conditions of the *Wiener* model body do not prevail. This in itself lays the quantitative applicability of the *Wiener* theory open to doubt. Other questions, however, also arise which are of paramount importance to the analysis of the optical phenomena inhering in swollen fibres. For example: To what extent are the assumptions, mentioned on p. 221, of the *Wiener* theory borne out here?

Being well below the microscopic visibility limit, the lateral dimensions of the particle and of the intermicellar interstices[28] are sufficiently small with respect to the wave-length of visible light. It remains to be seen, however, whether they could also become optionally small and whether, say, the individual molecular chains in the molecularly disperse micellar system (molecular frame, see page 32) can also occur as "rodlets" of the mixed body. Allowance has to be made for the occurrence — at all events locally — of such structures in swollen fibres, especially in highly swollen artificial fibres. (Part I, Chap. II, § 7).

According to *A. Frey-Wyssling*[29], the second condition, viz., that there must be well-defined phase boundaries, provides the answer. We have already seen that a system of the kind has to be considered as a one-phase system, so there cannot be any phase boundaries at all (p. 28). The question as to where, in colloidal dimensions, defined phase boundaries begin or end, cannot be answered[30]. *Frey-Wyssling* also pointed out that possibly the molecules of the imbibition liquid are strongly adsorbed to the inner surface of the micellar system, in which case there might be a density gradient which effaces the phase boundary[31]. The assumptions of the theory would then, therefore, not be borne out.

In point of fact, the evidence of more exhaustive investigations has invariably been that, although the optical behaviour of swollen orientated micellar systems often fits in qualitatively with *Wiener's* theory, there is usually no quantitative agreement. It has moreover been found

[26] *A. Mohring*, Kolloid chem. Beih., 23, (1927) 162.
[27] *P. H. Hermans* and *P. Platzek*, Z. physik. Chem., A 185, (1939) 269.
[28] The reader is reminded that in this book we use the term "intermicellar" in the sense of the definition given on p. 32.
[29] *A. Frey-Wyssling*, Die Stoffausscheidung der höheren Pflanzen, Berlin 1935; Submikroskopische Morphologie des Protoplasmas und seiner Derivate, Berlin 1938.
[30] For this see, e.g., *Wo. Ostwald*, Kolloid-Z., 84, (1938) 258.
[31] For a recent discussion of this question by several authors *(F. H. Müller, H. A. Stuart, H. H. Weber, W. J. Schmidt)* see Kolloid-Z., 96, (1941) 147-149.

that, in the case of cellulose fibres, even qualitative agreement is confined to a small number of imbibition liquids (alcohols and bases such as quinoline, toluidine). (See further below).

The utmost caution should, therefore, be observed in applying the *Wiener* theory quantitatively [32].

A. Frey-Wyssling and *M. Meyer* [33] had already shown that the *Wiener* theory does not help to explain the effect of moisture upon the optical properties of ramie fibres. We have seen in the previous section that the optical behaviour of all cellulose fibres in the first phases of swelling is represented by the simple miscibility rule formulated by *Gladstone* and *Dale*. (The broken curves in Fig. 63 show the course of the two refractive indices calculated in accordance with *Wiener's* formula's (4.9).

As formula (4.7) holds good for the first phases of swelling, *there is in this case no component of structural birefringence at all.* It is only above a given regain that the birefringence exceeds the figure it should attain according to formula (4.7) and a component therefore results which might be designated as structural b.r.

P. H. Hermans, J. J. Hermans, and *D. Vermaas* [34] state that this component becomes noticeable as from approximately 20% regain, though it remains well below the value calculated by means of formula (4.9): for instance, only about half the value thus calculated was observed in the case of model filaments swollen in water ($q = 2.12$). The explanation offered by these authors was the following:

The components of the mixed bodies are not cellulose and water, but the crystalline regions on one hand and, on the other, the amorphous regions mixed with water, for, in a certain sense, each of these can be regarded as a homogeneous phase. There is far less difference in refractive power between these two phases, of course, than between cellulose and water and, where the regains are low, it is so slight that the structural birefr. as yet evades detection [35].

The immersion method (p. 215) is again used for the *determination of the refractive indices* of swollen fibres. The choice of *immersion* liquids is, naturally, confined to those which will not mix with the swelling agent, i.e., the *imbibition* liquid. Should the immersion liquid likewise penetrate *into* the fibre, the results will be incorrect. It is sometimes difficult to avoid this source of error [36]. *P. H. Hermans* and co-workers (loc. cit.) obtained excellent results

[32] According to calculations made by *J. J. Hermans*, the *Wiener* calculations even contain an error and formula (9b) should read as follows:

$$n_{\gamma}^2 = n_2^2 \left(1 + \frac{2}{q} \frac{n_1^2 - n_2^2}{n_1^2 + n_2^2}\right).$$

This formula produces appreciably higher values for the structural birefringence than the *Wiener* version. (Unpublished results).

[33] *A. Frey-Wyssling* and *M. Meyer*, Helv. chim. acta, 18, (1935) 1425.

[34] *P. H. Hermans, J. J. Hermans,* and *D. Vermaas*, J. Colloid Sci, 1 (1946) 251.

[35] Contrib. p. 126.

[36] For this see *A. Frey-Wyssling* and *M. Meyer*, Helv. chim. acta, 18, (1935) 1425 and *A. Frey-Wyssling*, Helv. chim. acta, 19, (1936) 900.

with mixtures of butyl stearate and tricresyl phosphate as the immersion liquid for regenerated fibres.

We shall not discuss the optical behaviour of nitrated and acetylated cellulose in the form of fibre, for which the reader may be referred to the text-book by *H. Mark* [37] and to investigations published by *H. R. Kruyt, D. Vermaas* and *P. H. Hermans* [38]. Some attention must here be paid, however, to the optical behaviour of cellulose fibres with the imbibition of liquids other than water. As was stated above, though *Wiener* imbibition curves have often been observed with reference to cellulose objects, it is only possible to do so with certain imbibition liquids. We shall consider this phenomenon in the light of investigations carried out by *A. Frey-Wyssling* and *A. Speich* [39], who steeped ramie fibres in different liquids of increasing refractive power and measured the path difference using the compensation method. The thickness of the fibres being likewise measured, they were then able to determine the birefringence in accordance with formula (4.1) (page 215).

With alcohols, aldehydes and certain nitrogen bases, such as aniline and quinoline, they obtained a regular W i e n e r imbibition curve of the type shown in Fig. 66. In so-called "lipophilic" liquids like amyl bromide, xylene, toluene, benzene, chlorobenzene and bromobenzene, α-bromonaphthalene, on the contrary, the same birefringence was almost invariably found, in the mean 0.0657, although the refractive indices of these substances range from 1.441 to 1.658. The value 0.0657 was a little lower than that found in the minimum of imbibition curves found with the alcohols, etc.

The authors take this result to show that the "lipophilic" liquids do not penetrate into the fibre and therefore act only as i m m e r s i o n liquid and not as i m b i b i t i o n liquid. The fact that the b.r. measured in it by the compensation process is lower by 0.0029 than the difference in refractive indices, likewise measured by them in the same object, is ascribed to the porosity of the fibre wall, the "intermicellar voids" not coming into this picture. The "porosity" calculated from the difference of 0.0029 between the b.r. values measured in the two ways is 4.4%. The same authors determined the porosity of the ramie fibres by the direct method as well, finding 10.5% (see Chap. III, § 4). Discussing the lack of agreement between the two results, they come to the conclusion that the fault lies with inadequate precision in the physical definition of the capillary system.

If, however, the value 0.0708 measured by H e r m a n s and co-workers from the refractive indices of the ramie fibre (cf. Table XXVIII, p. 235 is inserted, the difference becomes 0.0052 and the porosity is found to be 8%. (The remaining difference between 10.5 and 8% might easily be due to experimental errors made during the difficult operation of measuring thickness).

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[37] *H. Mark*, Physik und Chemie der Cellulose, Berlin 1932.
[38] *H. R. Kruyt, D. Vermaas*, and *P. H. Hermans*, Kolloid-Z. 99, (1942) 251 100, (1942) 111.
[39] *A. Frey-Wyssling* and *H. Speich*, Helv. chim. acta, 25 (1942) 1474.

A probably better interpretation of the experimental evidence might conceivably be this [40]: When the fibres are placed in the "lipophilic" liquids, the coherent capillary system present in the fibre wall is filled with liquid. No structural b.r. takes place because the capillaries are too coarse. (The *Wiener* theory calls for dimensions which are small compared to the wavelength of the light). The deficiency in birefringence, however, exists, of course, just the same. The density determinations themselves go to show that the liquid penetrates into the fibre wall, since the density determined in organic liquids (1.55) is much higher than that derived from microscopic measurements. The coarseness of these capillaries which follows from optical observations now also makes it clear why they are so readily filled and do not interfere with density measurements.

Other liquids, like alcohols, aldehydes, nitrogen bases, also penetrate into this capillary system, of course, but they go even further, into the fibre wall itself; that is to say, the amorphous portions of the fibre are also in some degree accessible to them, for which reason a *Wiener* effect is observed. This is borne out by the fact that abnormally high density values are found in those liquids.

Regenerated fibres display similar phenomena. *P. H. Hermans* and *P. Platzek* [41] caused swollen model filaments to imbibe 26 different organic liquids and here too obtained a regular *(Wiener)* imbibition curve only when alcohols and nitrogen bases were used; with all other liquids the behaviour was more or less irregular. With these liquids the b.r. was always far higher than with the alcohols of the same refractive index. The reason for this is as yet unexplained. As the procedure in these experiments was, after the objects had been swollen in a high degree in water, to place them first in alcohol to displace the water and then in the organic liquid under test to replace the alcohol, the facts are not as conveniently presented as otherwise, for it is difficult to tell how exactly the organic liquid is distributed in the gel.

§ 5. ON THE MICROSTRUCTURAL BASES OF OPTICAL ANISOTROPY AND THE DEFINITION OF ORIENTATION

5.1. General

Ambronn's classical research into the b.r. of fibrous substances in the sense of *C. v. Nägeli's* theory (p. 26) had initially led to the view that optical anisotropy is caused by the presence of orientated, birefringent anisodiametric crystals. These investigations infused new life into the "Micellar theory" and at the same time relied on the phenomena of birefringence which have been dealt with in greater detail in the previous section.

It took some time for the current view that the existence of the intrinsic b.r. of the fibres does not necessarily depend upon the presence of "crystalline"

[40] Contrib. p. 153.

[41] *P. H. Hermans* and *P. Platzek*, Rec trav. chim. 58, (1939) 1001; Z. physik. Chem., A. 185, (1939) 269; Kolloid-Z., 88, (1939) 68.

particles, to find general acceptance. As long as ten years after the appearance of *H. Ambronn's* classical researches (p. 26), *O. Wiener* [42] himself considered it necessary to discuss the question whether the failure to detect crystalline components by X-ray meant that real birefr. did not exist. He ends, however, by denying that that is the implication. Later on, *H. Zocher* [43] also pointed out in respect of liquid crystals that molecular orderliness also produces intrinsic birefringence. Then *F. Horst Müller* [44] quite emphatically claimed that the birefr. of polymers with linear molecules was traceable to preferred molecular orientation. He expresses the opinion that this is how the b.r. of artificial cellulose fibres is also primarily to be understood and that in native fibres the crystalline components may possibly constitute an additional influence (see further below).

Generally speaking, optical anisotropy occurs with anisotropic distribution of the atoms, or with anisotropy of the inner electromagnetic field. In the case of fibres it can as a rule be considered as a result of their ordered structure [45]. A molecular chain in cellulose, or its individual constituent glucosidic groups, will be variously polarizable in different directions and will therefore represent optically anisotropic systems. Superposition of the optical effects of these elementary structural units is responsible for the optical properties of a cellulose object. If the statistical distribution of the position of the glucosidic groups is not entirely chaotic, optically the object will be anisotropic [46].

Following the example of *F. H. Müller* [47], therefore, any description of the orientation governing the optical anisotropy may conveniently be based on the spatial distribution and polarizability of the individual members of the chain (hence in this case the glucose residues). This also simplifies its mathematical treatment. The majority of the earlier authors pursued their quantitative researches on the assumption that the b.r. of the object is brought about by the superposition of the b.r. of very many elementary crystalline particles [48]. The resulting optical anisotropy was then computed by means of formulas borrowed from crystallographic optics. As we shall see presently (§ 6), we then get more complicated formulas which, however, do not produce better results than the simpler ones which will be presented below.

The optical anisotropy of the glucosidic group is biaxial, conforming to its

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[42] *O. Wiener*, Kolloid chem. Beih. 23, (1927) 198.

[43] *H. Zocher*, Z. Kristallogr., Vol. A (1931) 79.

[44] *F. Horst Müller*, In *R. Houwink*, Chemie und Technologie der Kunststoffe, Berlin 1939, Chap. 3, p. 150; Wiss. Veröff. Siemens W. 19, (1940) 110; Z. angew. Chem., 53, (1940) 425.

[45] For a synopsis of the connections between structure and birefringence see *A. Frey*, Kolloid chem. Beih. 20, (1925) 209 and *W. J. Schmidt*, Kolloid-Z., 96 (1941) 135.

[46] Cf. the alignment of the molecules in a liquid through flow (b.r. of flow), or in an electric field (*Kerr* effect).

[47] *F. H. Müller*, In *R. Houwink*, Chemie und Technologie der Kunststoffe, Berlin 1939, Chap. 3, p. 150; Kolloid-Z. 95, (1941) 138, 306.

[48] *O. Kratky*, Kolloid-Z., 64, (1933) 213; *O. Kratky* and *P. Platzek*, ibid., 88, (1939) 78; *A. Frey-Wyssling*, Protoplasma, 35, (1941) 534; Cellulosechem., 20, (1942) 53; Jahrb. für wiss. Bot., 90, (1942) 705; Helv. chim. acta, 26, (1943) 833; *K. Atsuki* and *S. Okajima*, J. Soc. Chem. Ind. Japan, 43, (1940) 150; *S. Okajima* and *I. Iwamoto*, ibid., 43, (1940) 1463.

structure; that is to say, its polarizability in three spatial directions will be different; it has three principal polarizabilities, the axis of the greatest polarizability being that which lies parallel to the direction of the chain.

For this reason a cellulose crystal should likewise be considered as optically biaxial and therefore possesses three principal refractive indices, while the index ellipsoid (cf. p. 214) is triaxial.

The orientation in a cellulose single crystal with ideal lattice arrangement of the molecules represents, of course, the condition of maximum orientation of a cellulose object. The order in a cellulose crystal is characterized not merely by the parallel alignment of all the chain axes of the glucose residues (*longitudinal orientation*, but also by an ideal orderliness in directions perpendicular to them *(lateral orientation)*.

In fibres, however, we are always dealing with uniaxial symmetrical bodies [49]. The maximum orientation of a fibre, therefore, is the state of ideal longitudinal orientation, when the longitudinal axes of all chain molecules or crystalline regions are parallel to the fibre axis. In this case the lateral orientation may still be random.

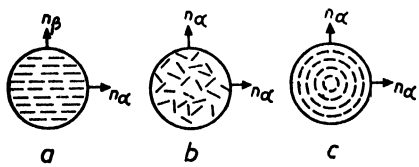


Fig. 67. Cross section of a bundle of parallel cellulose molecules perpendicular to the direction of the chain (diagrammatic). a. In lattice order with lateral orientation. b. without lateral orientation. c. with tangential orientation.

The difference may be seen in the diagram of Fig. 67. Fig. 67a represents a cross-section perpendicular to the fibre axis with combined longitudinal and lateral orientation; Fig. 67b shows the same with only longitudinal orientation, such as we meet with in orientated fibres having no lateral orientation. The case represented by Fig. 67c may likewise occur, where there is also lateral orientation, but axially symmetrical. Optically the instances of Figs. 67b and c are equivalent if observed lengthwise.

Thanks to this uniaxial symmetry of the fibre we are now able to simplify the theoretical treatment by classifying both the glucose group and the cellulose single crystal as optically uniaxial objects with only two principal polarizabilities (or two main refractive indices), one in the direction of the chain and one perpendicular to it [50]. The contribution of a glucose residue or of a crystallite to the total anisotropy of the object is then perfectly clear, provided the position of its longitudinal axis parallel to the direction of the chain with respect to the fibre axis be known.

The state of orientation in a fibrous object can, therefore, be described by suitably indicating the spatial arrangement of the longitudinal axes of all monomeric residues. (The mathematical form will be given later; see p. 392).

[49] Cf. *W. A. Sisson*, J. Phys. Chem., 40, (1936) 343; ibid., 44, (1940) 513.

[50] *A. Frey-Wyssling* states in: "Die Stoffausscheidung der höheren Pflanzen", Berlin, (1935) that, moreover, the two main refractive indices of the crystal of Cellulose I perpendicular to the fibre axis differ only slightly.

This will not suffice for cell walls, films and other like objects which may exhibit a "higher orientation" similar to that represented by Fig. 67a[51]; moreover, the lateral distribution has to be given, in which case the elementary structural units have, naturally, likewise to be treated as optically biaxial.

5.2. *Limiting Cases of Orientation*

There are two extreme boundary cases of orientation which it would be well to bear in mind when considering the quantitative data relating to the connection between optical properties and orientation of fibres.

First limiting case: No orientation at all.

This case includes isotropic objects. The distribution of the monomeric residues in the amorphous portions, and also of the crystallites, is such that their anisotropies cancel each other out on the average. The experimental experience dealt with in § 3 suggests that the polarizability, or the refractive index, of a body of that kind depends only upon its density of packing according to equation (4.3) and, therefore, can only be given if its density is known.

Second limiting case: Ideal orientation.

By this is not meant the state of orientation in the single crystal, but the ideal l o n g i t u d i n a l (uniaxial) orientation; that is to say, it is merely supposed that the longitudinal axis of all the glucose residues or crystallites lies parallel to the fibre axis. Here, too, it is assumed for the moment that the optical constants then only depend upon the average density of packing according to (4.3a) and (4.4), and not, therefore, upon the quantitative distribution between crystalline and amorphous substance.

We still regard as an exceptional case of ideal orientation that in which the fibre displays ideal orientation and the density of crystalline cellulose. We shall call such a fibre "a n i d e a l f i b r e".

If the two principal refractive indices of the ideal fibre are n_α and n_γ, their b.r. will be $n_\alpha - n_\gamma$, n_α being, of course identical to the principal refractive index of the cellulose single crystal in the direction of the fibre axis and n_γ equal to the average value of its other two main refractive indices.

The states of orientation within these boundary cases of isotropic and ideal fibres are defined by the particular distribution of the glucose residues in the object. (For this cf. p. 392). The optical constants always are a function of this spatial distribution and the density of the object.

§ 6. QUANTITATIVE RELATIONS BETWEEN OPTICAL CONSTANTS AND ORIENTATION

6.1. *The Optical Orientation Factor*

We shall take the birefringence of a fibre as a measure of its orientation, comparing it with the birefringence of the ideal fibre $n_\alpha - n_\gamma$ (see preceding section). First of all we must, of course, reduce the optical constants of the fibre in question (with density d) to the density of the crystalline cellulose d_{cr}.

[51] *G. van Iterson,* Chem. Weekblad, 30 (1933) 2. Also cf. *W. J. Schmidt,* Kolloid-Z., 96, (1941) 135.

If the two principal refractive indices of the fibre are $n_{//}$ and $n_{\perp}$, making its birefr. $n_{//} - n_{\perp}$, its birefr. with density d_{cr} would be

$$(n_{//} - n_{\perp}) \cdot \frac{d_{cr}}{d}$$

The orientation factor f of the fibre is then defined as follows:

$$f = \frac{n_{//} - n_{\perp}}{n_{\alpha} - n_{\gamma}} \cdot \frac{d_{cr}}{d} \qquad (4.11)$$

Factor f is a measure of the orientation. $f = 0$ for an isotropic fibre and is 1 for a fibre with ideal orientation. We may henceforth conveniently omit the density correction, writing merely:

$$f = \frac{n_{//} - n_{\perp}}{n_{\alpha} - n_{\gamma}} \qquad (4.12)$$

But it will always be necessary to make the correction for density in any practical application of this formula.

The directional distribution of the monomeric glucose residues governs the value of the factor f. The mathematical expression of this directional distribution will be discussed later (p. 392). The optical properties reveal only a mean value for orientation; they do not furnish us with any information on the details of the spatial distribution.

Let α_1 and α_2 be the principal polarizabilities of the monomeric glucose residue parallel and perpendicular to the chain axis,

β_1 and β_2 the polarizabilities of the ideal fibre parallel and perpendicular to the fibre axis.

$\beta_{//}$ and $\beta_{\perp}$ the polarizabilities of a particular fibre parallel and perpendicular to the fibre axis,

N_0 the number of glucose residues in 1 cm³ of the dry fibre.

Then the polarizabilities of the fibre with ideal orientation will be:

$$\beta_1 = \alpha_1 N_0 \qquad (4.13a)$$

$$\beta_2 = \alpha_2 N_0 \qquad (4.13b)$$

It may further be said [52] that

$$\beta_{//} = [\tfrac{1}{3}(\alpha_1 + 2\alpha_2) + \tfrac{2}{3} f (\alpha_1 - \alpha_2)] N_0 \qquad (4.14a)$$

$$\beta_{\perp} = [\tfrac{1}{3}(\alpha_1 + 2\alpha_2) - \tfrac{1}{3} f (\alpha_1 - \alpha_2)] N_0 \qquad (4.14b)$$

where f represents the orientation factor defined above. N_0 is here a measure for the density of the fibre.

It follows from (4.13) and (4.14) that

$$f = \frac{\beta_{//} - \beta_{\perp}}{\beta_1 - \beta_2} \qquad (4.15)$$

The mathematical relation between polarizability β and refractive index is given by

$$\frac{n^2 - 1}{n^2 + 2} = 4/3\,\pi\beta$$

[52] Contrib. p. 195.

It can now be easily shown that $n_\alpha - n_\gamma$ is proportional to $\beta_1 - \beta_2$ and $n_{//} - n_\perp$ to $\beta_{//} - \beta_\perp$ provided the differences between the refractive indices be small as against the value of the refractive indices themselves, a condition which is always met in cellulose fibres. Equation (4.12) is therefore identical to eq. (4.15).

6.2. *The Refractive Index of Isotropic Cellulose*

By inserting $f = 0$ in eq. (4.14) we now find the polarizability of the isotropic fibre:

$$\beta_{iso} = \frac{1}{3} (\alpha_1 + 2\alpha_2) N_0 \qquad (4.16)$$

and from (4.16) and (4.14) we then find

$$\beta_{//} - \beta_{iso} = 2 (\beta_{iso} - \beta_\perp)$$

But then

$$n_{//} - n_{iso} = 2 (n_{iso} - n_\perp)$$

and therefore

$$n_{iso} = \frac{1}{3} (n_{//} + 2 n_\perp) \qquad (4.17)$$

This simple equation enables us to predict from the two principal refractive indices of an anisotropic fibre what would be its refractive index in the isotropic state, and thus to express its refractive power in a single number. Far more complicated formulas are to be found for n_{iso} in the literature; e.g., that of *A. Frey-Wyssling* [53]:

$$n_{iso} = \sqrt{\frac{3 n^2_{//} n^2_\perp}{2 n^2_{//} + n^2_\perp}} \qquad (4.18)$$

and of *K. Atsuki* and *S. Okajima* [54].

$$n_{iso} = \frac{n_{//} \cdot n_\perp}{(n^2_{//} - n^2_\perp)^{\frac{1}{2}}} \arcsin \frac{(n^2_{//} - n^2_\perp)^{\frac{1}{2}}}{n_{//}} \qquad (4.19)$$

which were founded on the conception of a polycrystalline fibre and derived from the laws applying to crystal optics with the introduction of certain approximations. But for slight variations affecting only the fourth decimal equations (4.17), (4.18) and (4.19) produce the same numerical values [55].

The r_{iso} of all cellulose fibres will obviously have the same value if it is referred to the same density, a fact which the author has verified experimentally in a variety of the most divergent fibres [56], thereby fixing 1.5425 as the mean value with density at 1.520 [57]. Some examples are given in Table XXVI.

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[53] *A. Frey-Wyssling*, Helv. chim. acta, 26, (1943) 833.
[54] *K. Atsuki* and *S. Okajima*, J. Soc. chem. ind. Japan, 43, (1940) 150.
[55] Contrib. p. 137.
[56] Contrib. p. 113.
[57] Reservation made that the density be determined in the same way as in the relevant paper.

TABLE XXVI

Refractive Indices $n_{/\!/}$, $n_{\perp}$ and n_{iso} for some Cellulose Fibres Reduced to Density 1.520

	$n_{/\!/}$	$n_{\perp}$	n_{iso}
Native ramie fibres	1.588[1]	1.519[1]	1.542[1]
Mercerized ramie fibres (stretched)	1.577[4]	1.523[1]	1.541[1]
Viscose fibres (highly orientated)	1.572[6]	1.527[6]	1.542[6]
Lilienfeld rayon	1.573[1]	1.527[6]	1.542[1]

We shall again take the density $d = 1.520$ as the standard density for comparison of the optical constants of cellulose fibres, corresponding as it does approximately to the average density of regenerated fibres.

6.3. The Course of the Refractive Indices as Depending upon Orientation.

It follows from formulas (4.14) and (4.16) that $\beta_{/\!/} - \beta_{iso}$ and $\beta_{iso} - \beta_{\perp}$ are linear functions of f; therefore $n_{/\!/} - n_{iso}$ and $n_{iso} - n_{\perp}$ will be linear functions of f. The solid curves in Fig. 68 show the course of $n_{/\!/}$ and $n_{\perp}$ as dependent upon f. With $f = 0$ they converge at the value n_{iso}. The vertical distance between the curves represents the birefringence; with $f = 1$ the optical constants of the ideal fibre are reached. It follows primarily from the foregoing that:

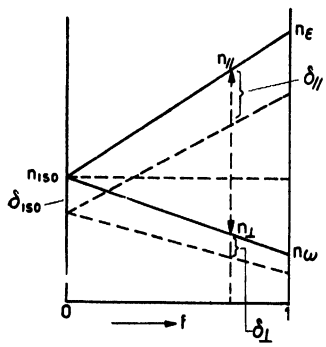


Fig. 68. Refractive indices of a dry fibre (full lines) and of a moist fibre (broken lines) in dependence upon the orientation factor f.

$$n_{/\!/} = \frac{n_\alpha + 2n_\gamma}{3} + \frac{2}{3} f\,(n_\alpha - n_\gamma) \qquad (4.20a)$$

$$n_{\perp} = \frac{n_\alpha + 2n_\gamma}{3} - \frac{1}{3} f\,(n_\alpha - n_\gamma) \qquad (4.20b)$$

Thus the angle formed by the upper curve with the horizontal is exactly twice that formed by the lower curve.

Precisely the same relations obtain for moist fibres within the regain range defined in § 4.1 [58], except that the refractive indices are a little lower (dotted curves in Fig. 68). If the reduction in the refractive index owing to water absorption is designated as δ, the result is invariably

$$\delta_{iso} = \tfrac{1}{3}\,(\delta_{/\!/} + \delta_{\perp}) \qquad (4.21)$$

Hence eq. (4.17) can also be applied to moist objects.

The validity of formula (4.20) is likewise demonstrable by plotting the observed values of $n_{/\!/}$ and $n_{\perp}$ against those reduced to the same density for a number of fibres of different orientation. The result must be a straight line,

[58] Contrib. p. 141.

whose angle of inclination α with the horizontal is given by $tg\alpha = 2$. The author has shown [59] that this actually does apply to native and mercerized ramie fibres as well as to a variety of artificial fibres of different orientation [60]. The like was demonstrated for atmospherically moist model filaments of different orientation but with the same regain.

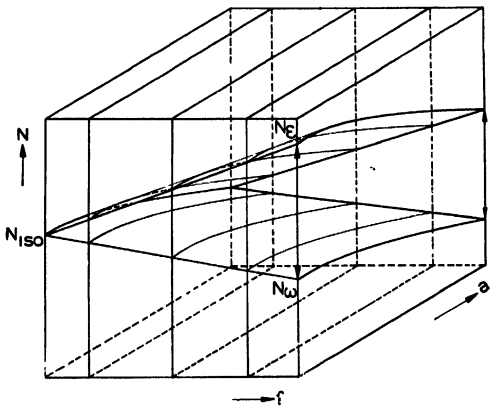


Fig. 69. Three-dimensional diagram of the relations between refractive indices n, orientation factor f and regain a

By means of a three-dimensional diagram, we are now in a position to give a comprehensive description of the optical constants of cellulose fibres for a given density as a function of the orientation factor f and of the moisture content. This diagram, which is reproduced in Fig. 69, is made up of a combination of the correlations set out in Figs. 63 and 68 and will require no explanation.

Finally, the refractive indices $n_{\parallel}$ and $n_{\perp}$, determined by direct measurement, of a number of fibres in the dry state are given in Table XXVII as recorded by *P. H. Hermans* and co-workers [61]. Density d is also shown.

TABLE XXVII

Density and Refractive Indices of Various Cellulose Fibres in the Dry State. (For meaning of symbols see Table XXIII)

	Density	$n_{\parallel}$	$n_{\perp}$	n_{iso}
Native Fibres				
Native ramie	1.553	1.601[5]	1.530[7]	1.554[3]
Mercerized ramie (a. Without tension)	1.526	1.579[3]	1.528[8]	1.545[6]
Mercerized ramie (b. Re-orientated)	1.546	1.587[1]	1.532[5]	1.550[8]
Viscose Rayon				
LA 0% stretch	1.518	1.556[0]	1.533[6]	1.541[1]
LA 70% „	1.525	1.567[3]	1.532[0]	1.543[1]
HA 10% „	1.521	1.560[0]	1.533[5]	1.542[3]
HA 80% „	1.520	1.568[9]	1.531[9]	1.543[1]
HA 120% „	1.523	1.573[0]	1.528[9]	1.542[9]
Lilienfeld Rayon *				
Sedura A	1.520	1.570[0]	1.529[3]	1.542[9]
Sedura B	1.524	1.572[2]	1.529[7]	1.543[9]
Sedura C	1.525	1.575[2]	1.528[8]	1.544[1]
Bemberg Rayon	1.524	1.571[4]	1.534[4]	1.546[7]
Model filaments (orientated)	1.522	1.572[4]	1.531[4]	1.544[7]
Model filaments (isotropic)	1.519	—.—	—.—	1.544

* The samples are given in the order of increasing stretch during spinning.

[59] Contrib. p. 140.
[60] Cf. also *S. Okajima* and *T. Iwamoto*, J. Soc. Chem. Ind. Japan, 43, (1942) 1463.
[61] Contrib. p. 113.

6.4. *Orientation Factor and Average Angle of Orientation*

For clarity the orientation factor f may conveniently be connected with an average angle of orientation of the elementary particles. Relevant investigations made by *P. H. Hermans* and *P. Platzek*[62] make it plain that this average angle may best be defined as follows. Imagine a fibre in which the main axis of the collective particles (monomeric glucose residues or crystallites) forms an angle α_m with the fibre axis (fibre with "uniform orientation"; cf. the diagram in Figure 70). The average angle of orientation in a fibre is then equal to the angle of orientation α_m of that fibre with uniform orientation which possesses the same birefringence as the fibre under consideration. Then

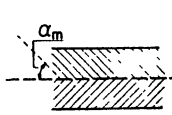


Fig. 70. Diagram of a fibre of "uniform orientation", all particles being orientated at an angle of αm to the fibre axis

$$f = 1 - \tfrac{3}{2} \sin^2 \alpha_m \qquad (4.22)$$

In the isotropic state $f = 0$ and $\sin^2 \alpha_m = 2/3$.

Inserting (4.22) into (4.20) and taking (4.17) into account, we find the following:

$$n_{/\!/} = n_\alpha - (n_\alpha - n_\gamma) \sin^2 \alpha_m \qquad (4.23a)$$

$$n_\perp = n_\gamma + \tfrac{1}{2}(n_\alpha - n_\gamma) \sin^2 \alpha_m \qquad (4.23b)$$

These equations establish the relationship between the optical constants and the average angle of orientation.

It may now be asked how the orientation factor (or the quantity α_m) is to be derived from the experimentally determined optical constants of a fibre. It follows from the above fundamental formulas that this is only possible if the refractive indices of the ideal fibre n_α and n_γ are given, as these enter into all equations. Therefore, only if n_α and n_γ can be determined will our theoretical arguments serve any useful purpose. This is dealt with in the next section.

6.5. *The Optical Constants of the Ideal Fibre*

According to our definition in Section 5.2 of the ideal fibre, n_α is equal to the refractive index of a cellulose single crystal in the direction of the fibre axis and n_γ is equal to the average value of its two principal refractive indices perpendicular to the fibre axis. Having no such objects at our disposal, however, we cannot verify these quantities by direct measurement.

There are some native fibres, however, whose orientation is almost ideal. Typical examples are ramie and hemp fibres, the pitch of whose spiral structure (p. 171) is only very small, so that the cellulose molecules are almost entirely parallel to the fibre axis. Moreover, these fibres contain a relatively large

[62] *P. H. Hermans* and *P. Platzek*, Kolloid-Z., 88, (1939) 68.

percentage of crystalline substance (probably about 70% according to *P. H. Hermans*, Chapter III, § 2).

Now, with the help of the optical constants of such fibres one may try to ascertain those of the ideal fibre. The b.r. would have to be determined from the refractive indices measured in accordance with the immersion method. The values resulting from polarizing optical determination of the b.r. according to e.q. (4.1) are too low owing to the "porosity" of these fibres (page 225).

Records of determinations of the optical constants of native fibres are fairly frequent in the literature. Some are collected in Table XXVIII, which includes one performed by *G. van Iterson* upon fibrillæ prepared from the cell wall of marine algæ, notably Valonia Macrophysa.

In the case of fibres with spiral structure, like cotton fibre, the larger refractive index $n_{/\!/}$ of the fibrillæ is greater than that determined for the fibre, whereas the smaller refractive index is the same for both at a first approximation. If the pitch of the spiral structure is Θ and if the indices measured in the fibre are $n_{/\!/}$ and $n_{\perp}$, the larger index of the fibrillæ n_γ can be computed according to the formula:

$$\frac{1}{n^2_{/\!/}} + \frac{\sin^2 \Theta}{n^2_{\perp}} = \frac{\cos^2 \Theta}{n^2_\gamma} \qquad (4.24)$$

TABLE XXVIII

Principal Refractive Indices and Birefringence of Native Fibres for Sodium Light according to Various Authors

Object	Author	$n_{/\!/}$	$n_\perp$	$n_{/\!/} - n_\perp$
Ramie	*H. Frey* [63]	1.595	1.534	0.061
Nettle	"	1.595	1.533	0.062
Flax	"	1.594	1.532	0.062
Cotton*	"	1.594	1.534	0.060
Callotropia	"	1.593	1.532	0.061
Ramie and flax	*J. M. Preston* [64]	1.596	1.528	0.068
Valonia	*G. v. Iterson* [65]	1.598	1.533	0.065
Ramie	*K. Kanamaru* [66]	1.596	1.525	0.071
Ramie	*A. Frey* [67]	1.599	1.531	0.068
Ramie Cotton*	*K. Atsuki* and *S. Okajima* [68]	1.595	1.533	0.062
" "	" "	1.595	1.533	0.062
Ramie	*A. Frey-Wyssling* and *K. Wuhrmann* [69]	1.599[6]	1.531[9]	0.067[7]
Ramie	*P. H. Hermans* [70]	1.601[8]	1.530[7]	0.070[8]

* Corrected for the pitch of the spiral structure.

Except in the last instance of Table XXVIII, the density was not determined, but it is safe to assume that the density of the preparations is. everywhere approximately the same. The latest measurements made by *Frey-Wyssling*

[63] *A. Frey-Wyssling*, Kolloid chem. Beih. 23, (1927) 40.
[64] *J. M. Preston*, Trans. Faraday Soc., 29, (1933) 65.
[65] *G. v. Iterson*, Chem. Weekbl. 30, (1933) 2.
[66] *K. Kanamaru*, Helv. chim. acta, 17, (1934) 1037,, 1425.
[67] *A. Frey*. Helv. chim. acta, 19, (1936) 911.
[68] *K. Atsuki* and *S. Okajima*, J. Soc. chem. Ind. Japan, 40, (1937) B 360.
[69] *A. Frey-Wyssling* und *K. Wuhrmann*. Helv. chim. acta, 22, (1939) 981.
[70] Contrib. p. 113.

and *Wuhrmann* and those of *Hermans* agree fairly well. (It was only in the last case that the exclusion of all moisture during the determination was fully guaranteed).

P. H. Hermans and co-workers [71] computed the optical constants of the ideal fibre, with due regard to the remaining slight deviation from the ideal orientation of ramie fibres established by quantitatively evaluated X-ray diagrams, and allowing for the measured density and that of the crystalline native cellulose, finding:

$$n_\alpha = 1.618^0 \qquad n_\gamma = 1.543^6 \qquad (n_\alpha - n_\gamma) = 0.074^4$$

When comparing with the optical data of artificial fibres it should be borne in mind that in the latter the "crystalline" portions consist of cellulose II instead of cellulose I. For this reason the lastnamed authors applied the same method to mercerized ramie fibres as well.

Older measurements of the optical constants are few and far between. As a rule there is no telling from the indications given whether the orientation had deteriorated during mercerization and whether it was complete mercerization. The known data are given in Table XXIX.

TABLE XXIX

Refractive Indices and Birefringence of Mercerized Native Fibres.

Object	Author	$n_{\parallel}$	$n_\perp$	$n_{\parallel} - n_\perp$
Flax	*J. M. Preston* [72]	1.571	1.517	0.054
Ramie a	*A. Frey* [73]	1.574	1.525	0.049
Ramie b	"	1.571	1.525	0.046
Ramie c	*K. Atsuki* and *S. Okajima*	1.584	1.524	0.060
Ramie d	" " "	1.5775	1.5156	0.062
Ramie e	*P. H. Hermans* [74]	1.5873	1.5325	0.055

a Mercerized under tension.
b Mercerized without tension.
c Merc. under tension (still containing cellulose I).
d Corrected figures.
e Mercerized without tension, then again orientated.

The Japanese investigators attempted to correct in a roundabout way for the incomplete mercerization of their objects. The process to which they had recourse, however, is not unexceptionable and the refractive index of the isotropic cellulose which they assumed for their purpose was decidedly too low. *Hermans* and co-workers used single fibres completely transformed into cellulose II by mercerization without tension and afterwards re-orientated to their original length by stretching in the caustic solution; they were measured by X-rays and their density was also determined.

On the basis of their measurements they computed for the ideal fibre (with the density of the crystalline cellulose II):

$$n_\alpha = 1.605^9 \qquad n_\gamma = 1.548^4 \qquad n_\alpha - n_\gamma = 0.057^5$$

71 Contrib. p. 144.
72 *J. M. Preston*, Trans. Faraday Soc. 29, (1933) 65.
73 *A. Frey*, Kolloidchem. Beih., 23, (1927) 40; Jahrb. wiss. Bot., 67, (1927) 597.
74 Contrib. p. 150.

These figures differ very materially from those (cited above) obtained with reference to native ramie, even if related to the same density. *Hermans* and co-workers discussed the reason of this deviation fully [75] and attributed it to the difference in the percentage of crystalline substance and in lattice modification. This argument gained support from the fact that the difference was reduced by about half when half the crystalline portion of the mercerized fibres was converted to the cellulose IV modification (which is very similar to cellulose I) [76].

Therefore, when considering artificial fibres, whose crystalline portion likewise consists of cellulose II, the values of n_α and n_γ derived from determinations applied to mercerized ramie should be used.

We get, then, for a fibre of ideal orientation and with density 1.520:

$$n_\alpha^* = 1.578^2 \qquad n_\gamma^* = 1.523^2 \qquad n_\alpha^* - n_\gamma^* = 0.055$$

There remains the question as to the influence of the percentage of crystalline substance. This is practically equal in all regenerated fibres but slightly lower than in mercerized ramie. A thorough discussion of this matter has shown that the value of $n_\alpha^1 - n_\gamma^1$ for artificial fibres at a density of 1.520 must lie between 0.050 and 0.055, *but that 0.050 may be considered as the most probable figure.*

In many cases it is more convenient to apply measurements to moist fibres conditioned in standard atmosphere of 65 r.h. than to bone-dry fibres. As the regain of almost all regenerated fibres at the same r.h. differs only nominally, a universal value can be fixed for the size of the birefringence of fibres of ideal orientation in standard atmosphere, without the risk of incurring any serious errors. On the basis of the degree of swelling $q = 1.17$ resulting from measurements made by *Hermans* and co-workers, we then find:

$$(n_\alpha^* - n_\gamma^*)_{65\%\ r.h.} = 0.043.$$

The optical orientation factor f_0 of a fibre now therefore appears from the proportion of the observed birefr. to $(n_\alpha^* - n_\gamma^*)$.

The question as to the best value of $n_\alpha^* - n_\gamma^*$ for regenerated fibres will be considered once again with reference to X-ray data in Chapter V (§ 3).

§ 7. THE BIREFRINGENCE OF CELLULOSE FIBRES COMPARED WITH THAT OF THE IDEAL FIBRE

Some years ago, *P. H. Hermans* and *P. Platzek* [77] drew attention to the considerable gap between the birefr. of the most highly orientated artificial fibres and that of well-orientated native fibres. If the comparison is made with the optical constants derived from mercerized ramie with ideal orientation, the gap narrows appreciably, but by no means disappears.

[75] Contrib., p. 146.
[76] Contrib., p. 175; *P. H. Hermans* and *A. Weidinger*, J. Colloid Sci. 1, (1946) 495.
[77] *P. H. Hermans* and *P. Platzek*, Kolloid-Z., 98, (1942) 62.

The birefringence of a number of dry fibres, measured by *P. H. Hermans* and co-workers [78] and reduced to density 1.520 is given in Table XXX together with the orientation factor f on the basis of $n_\alpha^* - n_\gamma^* = 0.050$. Only in the case of native ramie was the orientation factor based on $n_\alpha^* - n_\gamma^* = 0.071$, a value likewise related to density 1.520. (The density of the ramie fibre is 1.553; that of the crystalline cellulose I, 1.593).

TABLE XXX

Birefringence (reduced to Standard Density 1.520) and Orientation Factor of Various Cellulose Fibres. (See Table XXIII for meaning of symbols)

Object.	$n_{/\!/} - n_\perp$	fo
Native Fibres.		
Native ramie	0.069	0.97
Ramie mercerized without tension	0.050	0.92
Ditto subsequently re-orientated	0.054	0.98
Viscose Rayon.		
LA 0% stretch	0.022	0.45
LA 70% „	0.035	0.70
HA 10% „	0.026	0.53
HA 80% „	0.037	0.74
HA 120% „	0.044	0.88
Lilienfeld Rayon		
Sedura A	0.041	0.82
Sedura B	0.042	0.85
Sedura C	0.046	0.93
Bemberg Rayon	0.037	0.74
Model filaments (orientated)	0.041	0.82

Note that the highest orientation factor (found in a greatly stretched *Lilienfeld* rayon) amounts to 0.93. For normal, good quality rayon it remains well below 0.75 (with stretch generally below 80%). These facts go to show that even artificial fibres spun under optimum conditions as regards orientation fall far short of the state of ideal orientation [79].

Before we proceed, we should do well to recall that cellulose fibres of inferior orientation also occur in Nature, a few examples of which, collected by *J. M. Preston* [80], are given in Table XXXI.

TABLE XXXI

Optical Constants of a few Native Fibres, arranged in Declining Order of Micellar Orientation (after J. M. Preston)

Object	$n_{/\!/}$	$n_\perp$	$n_{/\!/} - n_\perp$
Ramie and flax	1.596	1.528	0.068
Cotton	1.578	1.532	0.046
*Adansonia digitata**	1.564	1.531	0.033
*Yucca gloriosa**	1.559	1.536	0.023
*Agave perfoliata**	1.554	1.537	0.017

* Measured by *A. Frey*.

[78] Contrib. p. 153.
[79] This holds good even more pronounced if we put $n_\alpha^* - n_\gamma^*$ at the 10% higher value mentioned in the preceding section.
[80] *J. M. Preston*, Trans. Faraday Soc., 29, (1933) 65.

The objects are arranged in descending order of orientation. The last three species of fibre belonging to the ductile category of fibres [81], the morphology and properties of which indicate that the cellulose molecules within them are no longer even approximately parallel to the fibre axis. It should not be forgotten, however, that the ductile fibres do not consist of pure cellulose, but contain impurities in a substantial quantity, which are bound to affect the optical behaviour in some degree.

§ 8. REMARKS ON OPTICAL ANISOTROPY IN THE CASE OF NON-UNIAXIAL ORIENTATION

In the foregoing we have only considered uniaxially orientated fibres whose structure has symmetry of rotation around the fibre axis. Fibre research, however, is sometimes confronted with less simple cases. When a fibre is subjected to other than axial deformations, biaxial optical anisotropy occurs. If, for instance, a swollen fibre is laterally pressed between two plates, or is rolled out to a flat band, it will exhibit three principal refractive indices, one in the direction of the fibre axis, one parallel and one perpendicular to the direction of the pressure.

It is important to note that this biaxial anisotropy can be accounted for without assuming other than uniaxial elementary structural units. True, the possible biaxial anisotropy of the particles themselves may also interfere, since deformations of the kind referred to here may give rise to selective lateral orientation of the particles. However, if such biaxial particles be assumed, the quantitative, and even the qualitative, analysis of the optical phenomena becomes exceedingly complicated.

In the absence of conclusive evidence of the necessity of taking biaxial optical anisotropy of the structural units in cellulose gels into account, the wise course is to adhere to interpretations on the basis of uniaxial particles. No such conclusive evidence has yet come to the knowledge of the author.

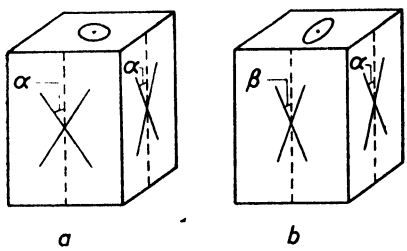


Fig. 71. Diagrammatic representation of the tangential orientation of the lamellar planes (on fiber cross-sections).

In certain favourable cases there is a quantitative standard by which it is possible to decide whether or not biaxial anisotropy of the fibre can be explained on the basis of uniaxial particles. In several of such cases actually investigated, there was, however, no reason to assume biaxial particles.

Let us briefly consider some instances of biaxial anisotropy. Take a rectangular prism out of a partly orientated uniaxial fibre with the fibre axis vertical (Fig. 71 A) and project the axes of the elementary particles on the

[81] Cf. *G. van Iterson*, Chem. Weekbl., 30, (1933) 2.

side planes of the prism. Now we can determine the average angle of those projections relative to the fibre axis. If the structure has uniaxial symmetry, the average angles α will be equal on all side planes. But if the fibre is biaxially anisotropic, the average angles will be different on the front and back planes as compared to the left and right-hand planes ($\beta < \alpha$ in Fig. 71 A, covered by a lateral compression in the direction from left to right).

When examined in the direction of the fibre axis (from the top in Fig. 71), the body A appears isotropic, its index ellipsoid is a circle. Contrarily, the body B appears birefringent. The largest diameter of the index ellipsoid and, consequently, the direction of the largest refractive index, lie perpendicular to the direction of compression.

We shall use these facts later for the interpretation of the optical phenomena exhibited by rayon cross-sections when examined in the polarization microscope (page 369).

§ 9. DICHROISM

Dichroism occurs when one of the manifestations of the anistropy of a body consists in the absorption to different extents of polarized light passing through it in different directions. It is frequently found in dyed fibres[82]. If such a dyed fibre is viewed under a microscope in polychromatic, linearly polarized light, the transmitted light will be seen to vary according to whether the plane of polarization is set perpendicular or parallel to the fibre axis. Either intensity or colour change. Formally, dichroism can be treated like birefringence, i.e., by constructing the ellipsoid of absorption, the radius vectors of which represent the coefficients of absorption for the different directions in space.

Taking the case of dyed fibres and assuming the validity of the *Lambert-Beer* law, the following formulas hold good for the intensities of monochromatic light polarized parallel and perpendicular to the optical axis:

$$I_{/\!/} = I_0 e^{-k_{/\!/} d} \quad \text{and} \quad I_{\perp} = I_0 e^{-k_{\perp} d} \qquad (4.25)$$

where I_0 is the intensity of the incident and $I_{/\!/}$ or $I_{\perp}$ that of the transmitted light and d the thickness of the irradiated layer; $k_{/\!/}$ and $k_{\perp}$ are the coefficients of absorption in the two principal axes for that particular kind of light.

From this it follows that:

$$k_{/\!/} - k_{\perp} = \frac{(\ln I_{\perp} - \ln I_{/\!/})}{d} = \frac{\ln I_{\perp}/I_{/\!/}}{d} \qquad (4.26)$$

This formula is analogous to equation (4.1) on page 215 for the birefringence and it provides a measure, for a certain wave-length, of the specific dichroism coinciding with a given concentration of dyestuff. This can be determined by

[82] *H. Ambronn*, Ber. d. deutsche Bot. Ges., 6 (1888) 85, 255.

ascertaining $I_\perp/I_\parallel$. All that is required, therefore, is to measure the ratio of the intensities of the transmitted light with the plane of polarization set parallel and perpendicular to the fibre axis. A quantity independent of the thickness can be determined by including the intensity I_0 of the incident light; for, from (4.25) it is also found that:

$$\frac{ln\ (I_\parallel/I_0)}{ln\ (I_\perp/I_0)} = \frac{k_\parallel}{k_\perp} = p \qquad (4.27)$$

J. M. Preston [83] called the quantity p the "dichroitic constant" and he found that it was also independent of the concentration of the dyestuff in the case of cellophane films coloured with substantive dyes.

Dichroism according to formula (4.20) is at its strongest when light is used whose wave-length is within the range of the maximum absorption of the dyestuff [84].

As in birefringence, so there is in dichroism a distinction between *intrinsic dichroism* and *structural dichroism*. The latter occurs in its pure form, for instance, if the, intrinsically isotropic, rodlets of a mixed body are dyed and therefore absorb the light differently from the imbibition medium. If the rodlets are themselves both anisotropic and dichroitic, the two forms occur side by side. *O. Wiener* [85] has extended his theory of mixed bodies to include just such a case, but the results in their general form are incomparably more complicated than when the absorption is left out of account. Thus, with the refractive indices of the rodlets the same as for the imbibition medium, the b.r. need no longer be nil and the b.r. of the rodlets may even be negative.

Dichroitic fibre colouring is obtained with iodine-zinc chloride solution, with most substantive dyestuffs (such as Congo red) and with the infiltration of finely divided colloidal metals [86].

Metallic colouring results from soaking the fibres in gold, silver or mercury salts followed by reduction. *A. Frey-Wyssling* gave the matter careful attention in his exceedingly informative studies respecting the microstructure of fibres. (Literature, see p. 33). With the aid of X-ray photographs he found that the particles of metal are themselves isotropic and not orientated, particularly those of liquid mercury. Hence this is clearly a case, not of intrinsic dichroism, but only of structural dichroism. The infiltrated metal particles in the oblong voids of the micellar system are aligned more or less parallel to the fibre axis, or are packed there in rodlet-shaped aggregates, with the result that rodlet dichroism is produced.

Since iodine crystals display marked intrinsic dichroism, it was thought, that, with iodine staining, orientated iodine crystals might be present; but *F. Bion* [87] maintained that there is nothing in the X-ray evidence to warrant the

[83] *J. M. Preston*, J. Soc. Dyers and Colourists, 47, (1931) 312.
[84] *K. S. Gibson* and *E. P. T. Tyndall*, Natl. Bur. Standards Bull. 19, (1913) 131.
[85] *O. Wiener*, Kolloid Beih. 23, (1927) 189.
[86] *H. Ambronn* and *A. Frey*, Das Polarisationsmikroskop, Leipzig 1926.
[87] *F. Bion*, Helv. phys. acta 1, (1928) 165.

assumption that iodine crystals are present. Rather must one, therefore, imagine an orientated accretion of iodine molecules at the inner-micellar surface, which results in a kind of intrinsic dichroism (also see *A. Frey*[88]). This is also how, no doubt, the dichroism of dyed fibres comes to pass, viz. by orientated adsorption of dyestuff molecules in the fibre[89]. This has recently been substantiated by *A. Frey-Wyssling* and *O. Wälchli*[90].

The *Wiener* theory states that simplification is achieved when the absorbing, as compared to the non-absorbing components of the mixed body, occupy but very little space, as is certainly always the case with metal staining. Similarly, conditions are simplified if one of the components is only lightly tinted, as in moderate colouring with dichroitic dyes. If, moreover, the refractive indices of the fibre and imbibition components are equal (e.g., as is approximately the case in the imbibition of cellulose fibres with benzyl alcohol), again the structural dichroism becomes equal to nil and it is, therefore, pure intrinsic dichroism that is being measured.

There exists only one paper by *A. Frey-Wyssling* and *O. Wälchli* where it was attempted to check the *Wiener* theory on structural dichroism. Approximate confirmation was found with cellulose fibres stained with metallic silver[91].

Quantitative investigations on the dichroism of fibres stained with substantive dyes are still scarce. Yet such measurements hold promise of furnishing information in many respects where, in the research of artificial fibres, birefringence measurements fail, as for instance, is the case in swollen fibres. *J. M. Preston*[92] has quantitatively measured the dichroism of fibres and films coloured with direct dyes and related his findings to their state of orientation. For ramie fibres he found, in accordance with formula (4.27) : $k_{/\!/}/k_{\perp} = 9$.

Analogously, the formula (4.24) given on page 235 may be written thus:

$$\frac{1}{k_{/\!/}} = \frac{\sin^2\Theta}{k^2{}_{\alpha}} + \frac{\cos^2\Theta}{k^2{}_{\gamma}} \quad \text{and} \quad \frac{1}{k_{\perp}} = \frac{\sin^2\Theta}{k^2{}_{\gamma}} + \frac{\cos^2\Theta}{k^2{}_{\alpha}} \qquad (4.28)$$

Since the dyes exhibit maximum absorption in one direction of the two principal axes and practically none in the other, it is permissible to state $k_{\alpha} = 0$, and we then get:

$$\frac{k_{/\!/}}{k_{\perp}} = \frac{\cos^2\Theta}{\sin^2\Theta} = \operatorname{cotg}^2\Theta \qquad (4.29)$$

From *Preston's* datum, i.e., $k_{/\!/} / k_{\perp} = 9$, *A. Frey-Wyssling*[93] in this way calculated the pitch of the spiral texture of ramie fibre, declaring it to be $\Theta = 6°$.

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[88] *A. Frey*, Kolloid chem. Beih. 23, (1927) 40.
[89] *H. Zocher* and *F. C. Jacoby*, Kolloid chem Beih. 24, (1927) 365.
[90] *O. Wälchli*, Thesis, Zürich 1945.
[91] *A. Frey-Wyssling* and *O. Wälchli*, J. Polymer Sci., 1 (1946) 266.
[92] *J. M. Preston*, J. Soc. Dyers and Colourists, 47, (1931) 312.
[93] *A. Frey-Wyssling*, Die Stoffausscheidung der höheren Pflanzen, Berlin, 1935.

Recently *J. M. Preston* and *P. C. Tsien* have published further contributions to the subject [93a]. They have found that distinct dichroism is observed when light reflected from pads of rayon filaments is examined through a polaroid screen. They worked out a method to measure this effect and showed that it is affected by the degree of orientation of the fibres.

§ 10. POLARIZATION OF FLUORESCENT LIGHT

We shall here only touch on the investigations carried out by *D. R. Morey* [94] on the polarization of fluorescence light in fibres tinted with fluorescent dyes. He related this phenomenon to orientation measurements. The fibres were exposed to ultraviolet light and the intensity of the fluorescence light they reflected was measured photometrically after passing through a rotating analyzer. With suitable dyes the fluorescence light of orientated absorbed dyestuff molecules is polarized in the direction of the fibre axis. From the ratio of the intensities of the light polarized parallel and perpendicular to the fibre axis, *Morey* derives a measure of the average orientation of the dyestuff molecule, which is also a measure of the orientation of the cellulose.

He maintained that in this way only the orientation of the outer layer of the fibre turned towards the observer is thus measured. Where fibres of spiral structure are involved, the maximum intensity of the fluorescence light falls with the analyzer adjusted not to coincide with the fibre axis, but forming an angle with it equal to the pitch of the spiral.

This method produced characteristic differences for various native fibres. Broadly speaking, the results as to orientation corroborated the information obtained from other data. *Morey's* investigations nevertheless show that the method cannot be recommended in a general way for the estimation of orientation [95], for which it is hampered by a number of disadvantages and uncertainties. It might, however, render valuable service in special cases, but for these, reference must be made to the original treatises.

[93a] *J. M. Preston* and *P. C. Tsien*, J. Soc. Dyers and Colourists, 62, (1946) 368.

[94] *D. R. Morey*, Textile Research, 3, (1933) 325; 4, (1934) 491; 5, (1935) 105, 483, 538. Abstracts of these publications are given by *E. Valkó*, Kolloidchemische Grundlagen der Textilveredlung, Berlin 1937, p. 74.

[95] In particular, see Textile Research, 5, (1935) 483.

CHAPTER V

THE X-RAY EXAMINATION OF FIBRES

§ 1. THE X-RAY DIAGRAM OF CELLULOSE IN ITS FIBROUS FORM

1.1 *The Fibre Diagram of Highly Orientated Fibres*

Of recent years the behaviour of fibrous material, as revealed by X-rays, and the principles assumed by theory to underlie such behaviour, have formed the subject of many comprehensive and excellent treatises[1]. While referring the reader to these for fuller treatment, we shall here only consider those facts of which some knowledge is indispensable to a proper grasp of the material to be dealt with later in this book.

It need hardly be said that X-ray evidence is conclusive only in regard to the portions of the fibre which are arranged in a lattice order. These are ordinarily present in a more or less marked degree in unswollen, and often also in swollen cellulose fibres.

The diagrams obtained after X-rays have passed through native fibres are called "Fibre diagrams". The ideal type of fibre diagram is obtained with an agglomeration of well-formed crystallites, all of which are orientated with one of their three crystallographic main axes entirely parallel, the distribution of the other two principal axes being wholly un-orientated, corresponding, that is, to the "ideal cellulose fibre" discussed in Chapter IV, § 5. Here all the b-axes of the elementary cells (see p. 16) are parallel to the fibre axis.

An exactly similar fibre diagram would result if a cellulose monocrystal, with irradiation perpendicular to the b axis, were to rotate around that axis.

The ideal fibre diagram is a point diagram[2]. The interferences corresponding to the crystallographic planes giving rise to selective diffraction

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[1] E.g., *K. H. Meyer* and *H. Mark*, Der Aufbau der hochpolymeren Naturstoffe, Leipzig, 1930, p. 94; the same authors: Hochpolymere Chemie, Leipzig, 1940, Vol. I, p. 2; Vol. II, pp. 33, 221; *H. Mark*, Physik und Chemie der Cellulose, Berlin, 1932, p. 126; *A. Frey-Wyssling*, Die Stoffausscheidung der höheren Pflanzen, Berlin, 1935, p. 12; *O. Kratky* in *W. R. Rohrs, H. Staudinger* and *R. Vieweg*, Fortschritte der Chemie, Physik und Technik der makromolekularen Stoffe, Berlin, 1939, Vol. I, p. 172. Also see list of literature appended to Part I, Chapter I. (p. 40).

[2] For a detailed and lucid account of the formation of a fibre diagram see *A. Frey-Wyssling's* book cited above.

– as shown diagrammatically in Fig. 72 for native cellulose – are found on the equator (horizontal line marked A), on the meridian (line perpendicular to it) and on the layer lines (the hyperbolic group sketched into the figure).

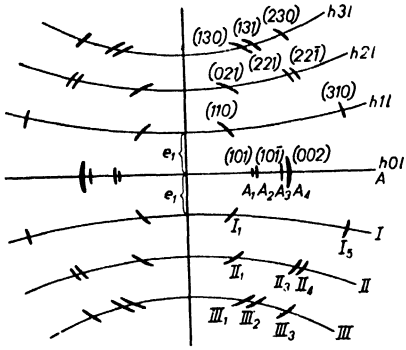


Fig. 72. Outline of Fibre Diagram of native cellulose (after *A. Frey-Wyssling* 1935). I, II, III (h 1 l), (h 2 l), layer lines; A equator (h O l). The interference points above the equator are marked by the *Miller* indices and below the equator bear the designations devised by *R. O. Herzog*. The basic reflexes on the meridian (O k O) are not shown.

For purposes of comparison, the actual radiograph of a purified ramie fibre, behaving very much like an ideal fibre, borrowed from *H. Kiessig*[3], is reproduced in Fig. 73.

Every diffracting lattice plane produces four interference points, arranged symmetrically around a focal point, if they lie on the layer lines. With lattice planes standing parallel to the fibre axis (paratropic planes), the four points converge to two situated on the equator, one to the left, and one to the right of the central point; lattice planes perpendicular to the fibre axis (diatropic planes) likewise produce only two points, i.e., situated on the meridian above and below the central point. (These are not shown in Figure 72, but in Fig. 73 a few faint diatropic interferences are just visible on the meridian). In the upper part of Fig. 72 the interference points are indicated by the conventional signs introduced by *R. O. Herzog*, and in the lower part by the crystallographic indices devised by *Miller* for the proper lattice planes.

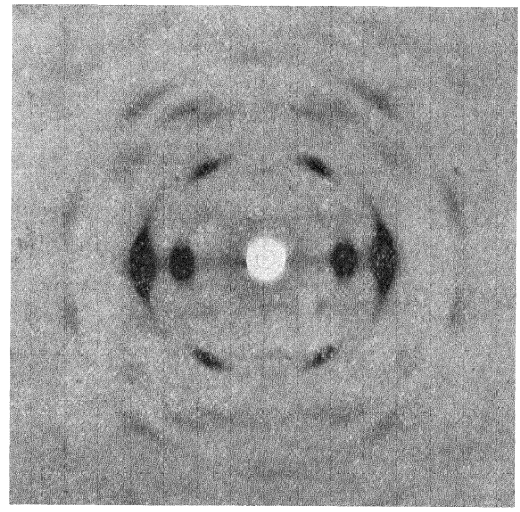


Fig. 73. X-ray diagram of ramie taken with pure Cu Kα radiation, after *H. Kiessig* (by kind permission of Professor *K. Hess* and *H. Kiessig*).

The intensity of the interferences varies with the density of the coating of the lattice planes by scattering atoms. The intensest interferences of the

[3] *H. Kiessig*, Z. physik. Chem., B. 43, (1939) 33.

native cellulose lattice are those paratropic interferences lying on the equator, i.e., A_1 (101), A_2 ($10\bar{1}$) and A_4 (002), also interference II_1 (021) [4].

As has been stated, diatropic interferences — that is to say, those connected with lattice spacings in the direction of the fibre axis — are not shown in Figure 72, but (020) and (040) are faintly visible in Fig. 73. (These interferences become more distinct when the incident rays are oblique to the fibre axis). According to *Bragg's* equation, the distance e_1 from the central point to the first layer line is co-ordinate with the "fibre period" of 10.3 å (dimension of the elementary cell in the *b* direction).

The most important interferences for practical purposes are those three intensest which lie on the equator. They correspond, therefore, to lattice spacings running perpendicular to the fibre axis (i.e., lattice planes lying parallel thereto). Let us consider these a little more closely. They are again represented in the diagram of Fig. 74 A and beside them, in Fig. 74 B, the three intensest interferences of hydrate cellulose (cellulose II). Figures 74 C and D show how they are connected with the appropriate lattice planes. These illustrations represent diagrammatic sections through the elementary cell perpendicular to the fibre axis; the arrangement of the glucosidic rings is also shown in diagram.

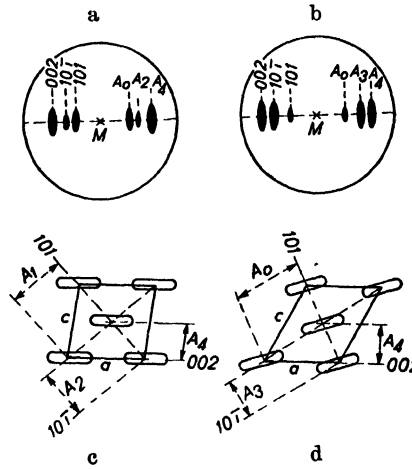


Fig. 74. Diagram of the paratropic interferences (equator) of native cellulose (a) and of cellulose hydrate (b) with their associated lattice planes (c and d) shown in section through the elementary cell perpendicular to the fibre axis.

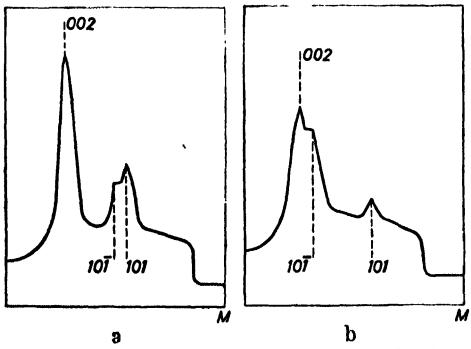


Fig. 75. Photometer curves of blackening intensity along the equator up to the central point, a for the diagram of native cellulose, b for that of cellulose hydrate. (After *W. Schramek*).

Fig. 75 A and B shows how intensity is distributed and represents curves of blacking intensity [5] recorded by *W. Schramek* [6]. It will be observed that (002) occurs in both cases as the most

[4] The fainter paratropic interference A_3 placed beside A_4 in Fig. 73 only occurs with Cu-Kα radiation not entirely free from β-radiation; it too belongs to (002). As complete monochromatization of Cu-Kα radiation requires special apparatus (reflection on a rock-salt crystal), it is seldom undertaken in practice. The (002) interference then often appears to be doubled.

[5] The utmost care was taken to make the conditions (such as thickness of the object, time of exposure) strictly comparable.

[6] *W. Schramek*, Z. physik. Chem., B. 13, (1931) 462.

intense interference; it corresponds to the lattice planes most densely occupied by atoms.

With cellulose I, where the densely charged glucosidic rings are exactly in the (002) plane (Fig. 74 C), the blacking is the heaviest; with cellulose II (Fig. 74D), where the glucosidic rings are slightly deflected from the (002) plane, it is less marked. Corresponding to the denser packing as compared with Fig. 74A the $(10\bar{1})$ interference has become more intense in the case of cellulose II and, at the same time, it has deflected further outwards from the central point as a result of the reduced lattice spacing. In like manner the (101) interference of cellulose II has shifted somewhat nearer the central point owing to the larger lattice spacing as compared with native cellulose. *Schramek* used photometric curves of this kind for quantitative determination of the mixing proportions of native cellulose and cellulose II in composite objects (determination of degree of mercerization).

The symbols standing for the three most important interferences of the two types of lattice are collected in Table XXXII.

TABLE XXXII

Symbols for the most important Paratropic Interferences of Cellulose I and Cellulose II

CELLULOSE I		CELLULOSE II	
After *Herzog*	After *Müller*	After *Herzog*	After *Müller*
A_1	101	A_0	101
A_2	$10\bar{1}$	A_3	$10\bar{1}$
A_4	002	A_4	002

1.2. *Deviations from the Ideal Fibre Diagram due to Incomplete Orientation*

We have already encountered (pp. 21 ff., 31) some of the instances of deviation from the ideal fibre diagram made up of punctiform interferences, such as widening of the interferences, blurring of the contour lines, etc.

One of the "aberrations" from the fibre diagram to be discussed now, takes place the moment there ceases to be strict parallelism of all the b axes of the crystallites with respect to the fibre axis. This condition of parallelism is only approximately met in the case of highly orientated fibres such as ramie. To obtain a perfect fibre diagram from fibres distinctly spiral in texture, like cotton fibre, the highly orientated elementary fibrillæ had first to be isolated and parallelized. If cotton fibres are X-rayed just as they are, the imperfect orientation with regard to the fibre axis is manifested by a spreading of the interference points of the fibre diagram to sickle-shaped interferences

encircling the central point *(Debye-Scherrer* circles). Blacking is known to spread uniformly over the entire circle with objects in which the crystallites are oriented entirely at random *(Debye-Scherrer* diagrams).

The pitch of the spiral texture can be deduced from the angular width of the sickles; and it will be found that, at a first approximation, the two quantities are equal [7]. Figure 76 reproduces in outline the sickle diagram of a cotton fibre in relation to the microscopically visible spirally fibrillar structure of the fibre after Sisson.

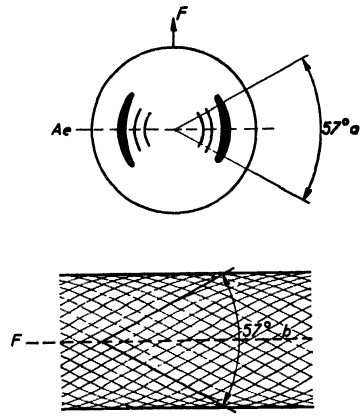


Fig. 76. Crescent-shaped equatorial interferences of a cotton fibre (a) and connection between their angular width and the pitch of the spiral striation of the secondary wall (b). (Diagrammatically after *W. A. Sisson*. In the upper figure: Ae Equator, F direction of the fibre axis when photographed.

As artificial fibres are never ideally orientated, their interferences produce sickles whose distention varies with their orientation.

Quantitative evidence as to the distribution of the crystalline regions in a fibre can be obtained by recording photometrically the course of the blacking intensity along the sickles. This is dwelt on in § 2.

§ 1.3. *Deviations from the Ideal Fibre Diagram due to "higher orientation"*

As we saw on page 244, a "fibre diagram" is drawn up on the premise that no order at all underlies the orientation of the a and c axes of the crystallites in relation to the direction of radiation. As a result, all the paratropic planes capable of interference are manifested in the diagram. This is actually the case with well-orientated vegetable fibres, but different conditions may obtain both in native and artificial objects of cellulosic origin. If the orientation of certain lattice planes with reference to the direction of radiation is not entirely without order, then it depends upon the reciprocal position whether an interference is or is not manifested; that is to say, whether the glancing angle necessary for reflection chances to be attained or not. We have seen an example of this above, *viz.*, in the diatropic planes of the ramie fibre parallel to the direction of radiation. They appear faintly in the usual fibre diagram and only become more sharply defined with oblique irradiation at an angle deviating from 90° with respect to the fibre axis. If there is in a cellulose object, in addition to an orientation of the primary valency chains in the direction of the fibre axis (longitudinal order), also an arrangement in perpendicular directions thereto (lateral order), we speak of "higher orientation" and examination by X-rays discloses fresh phenomena. Orien-

[7] *W. A. Sisson*, Ind. Eng. Chem., 27, (1935) 51.

tation of this kind is found, e.g., in the cell wall of the algæ gen. Valonia[8]. In the individual layers of the wall all the crystallographic axes of the crystallites (or of the primary fibrillæ) are parallel to each other.

We cannot now dwell on the various aspects of higher orientation and its concomitants as revealed by X-rays. *W. A. Sisson*[9] fully described them in connection with his deformation experiments as applied to membranes and rodlets of bacterial cellulose and, later, regenerated cellulose[10]. At present we refer the reader to that fundamental research and shall revert to the matter in Part III.

The following respecting the structure of native cellulose fibres may be pointed out here. Although, taking the fibre section as a whole, the fibre diagrams show the paratropic planes to occur in every conceivable state of orientation, this does not necessarily mean that this holds good in smaller regions of the fibre. Higher orientation almost certainly exists in the individual fibrillæ, closely resembling that of a cellulose monocrystal, and it is very probable that neighbouring fibrillæ in a fibrillar bundle are similarly orientated (cf. Fig. 21).

The structural analysis of the cell-wall of Valonia has made it clear that the (101) plane forms a tangent; that is to say, it forms the outer border of the cell-wall layers. This is the plane which is most densely packed with hydroxyl groups, as will be obvious from a comparison of Figures 9 A, 10, 11, 74 C and D. This plane is, therefore, turned outwards in the cell-wall[11]. The same probably likewise occurs in the individual concentric layers of the wall of native cellulose fibres.

In the same way, the (101) plane of films prepared from cellulose is preferentially always more or less perfectly parallel to the film plane. If this orientation of the (101) plane is almost perfect, its corresponding interference does not appear in the X-ray diagram resulting from radiation at right angles to the film plane, because its glancing angle is nowhere attained[12].

With the usual perpendicular X-raying of an entire fibre, it cannot be ascertained, of course, whether the alignment is that of Fig. 67 B or of 67 C. To establish this fact it would be necessary to take individual portions of the fibre (e.g., a film of rind) and X-ray each separately.

As we shall see later, preferential tangential orientation of the (101) plane often occurs in artificial fibres as well.

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8 *O. L. Sponsler*, Protoplasma, 12, (1931) 2; *R. D. Preston* and *W. T. Astbury*, Proc. Roy. Soc. London, B. 122, (1937) 76.
9 *W. A. Sisson*, J. Phys. Chem., 40, (1936) 343.
10 *W. A. Sisson*, J. Phys. Chem., 44, (1940) 513.
11 If isotropic foils of regenerated cellulose are allowed to dry up on a solid stand, the (101) plane likewise tends to be orientated in the plane of the foil. Here too, therefore, the OH groups come to lie outside.
12 Cf. *W. A. Sisson*, J. Phys. Chem., 44, (1940) 513.

1.4. *Further Details*

The structure of the crystalline components derived from X-ray diagrams is identical for all preparations of native cellulose [13]. The conditions of orientation to be deduced from the number or crescent expansion of the interferences are liable to vary with the origin and preliminary treatment of the object. Other variables in natural objects are the distinctness (width) of the interferences and other blackening in the diagrams pointing to non-crystalline components, such as wide "amorphous" rings, or diffuse blackening. The interferences in the majority of cellulose objects are less sharply defined than is to be expected of those for ideal lattice structure. In well-orientated fibres the interferences of the paratropic planes are broader (therefore less sharp) than those of the diatropic planes. Yet the indistinctness of the paratropic planes varies from fibre to fibre: In some bast fibres (lignified fibres), like ramie and wood fibres, the intereferences are very broad, in Valonia they are very distinct and in this respect the cotton fibre holds an intermediate position [14].

Indistinctness of the interferences may be due to a variety of causes, such as the size of the crystallite (p. 20), imperfect lattice structure (lattice distortion; p. 22), the presence of contaminations in the lattice, or a combination of these factors. Chief among these may be the non-crystalline cellulose portions — usually termed the amorphous portions [15] — where they gradually merge, without any determinate borderline, into the crystalline portions, so in the outer regions of the latter. On the other hand, many non-cellulosic components become associated with cellulose while it matures in Nature and they might to some extent be built into the lattice, or be deposited in the inner surfaces (cf. page 325).

W. A. Sisson [16] states that diffuse blacking, varying from object to object, appears in the diagram of native fibres and overlies the actual cellulose diagram. In some cases wide, diffuse circles are to be seen, which resemble the diagram of a liquid; in others will be found disc-like blacking extending to the point of penetration. He affirms that these are due to the presence of foreign substances and are very greatly reduced in well-cleaned fibre objects. The non-crystalline portion of cellulose ever present then still gives rise to a certain amount of diffusely scattered radiation, which, however, is not easily recognizable as such on either visual or photometrical examination of the photographs, since it represents only one of the components of the diffuse "background" on which the peaks of the crystalline interferences are superimposed. Whereas in the case of rubber the amorphous constituents

[13] One exception is provided by the algae Halicystis, the cell-wall of which contains the lattice of cellulose hydrate (*W. A. Sisson*, Science, 87, (1938) 350). In point of fact, according to recently published investigations by *T. Kubo*, Z. physik. Chem., A. 187, (1940) 297, fine distinctions in the native lattice also occur in various vegetable fibres.

[14] *W. A. Sisson*, Chemical Reviews, 20, (1940) 187.

[15] There will generally be a fairly determinate longitudinal orientation in these amorphous components.

[16] *W. A. Sisson*, Chemical Reviews, 20 (1940) 187.

produce wide rings similar to those observed in liquids, a distinct maximum does not appear in the background of cellulose photographs, even in artificial fibres which consist for the greater part of amorphous substance.

Until recently very little attention, if any, had been given to this question and X-ray investigation has contributed little to the study of the amorphous components of fibres. Full knowledge of the microstructure of fibres can, however, never be attained by the study merely of their crystalline components, for the part played by the non-crystalline portion is at least as important, not to say the more decisive. Recently a closer analysis of the diffuse background in cellulose photographs, accounting for the diffuse scattering due to radiation scattered by the air in the camera and to contamination of the radiation by its non-monochromatic component, has revealed that the amorphous component of cellulose fibres, as well, produces a broad diffuse band whose actual shape is masked by the superposition of the other kinds of diffuse radiation referred to. We shall revert to this subject in § 4 of this Chapter.

§ 2. QUANTITATIVE EVALUATION OF X-RAY PHOTOGRAPHS WITH REFERENCE TO THE ORIENTATION OF THE CRYSTALLINE CONSTITUENTS OF THE FIBRE

2.1. *Introduction*

Polanyi[17] was the first to recognize a quantitative relation between the intensity distribution of the interferences along the *Debye-Scherrer* circles for imperfectly orientated objects, and the distribution of orientation of the crystalline regions. Thus reliable information as to the statistical state of orientation of these regions can be obtained by measuring this distribution of intensity.

Here the X-ray method is more useful than the optical, since the latter furnishes information merely as to the a v e r a g e orientation (Chapter IV, § 6). As against this, however, the average orientation derived from optical data is that of the entire fibrous substance, whereas the X-ray method provides indications of the orientation of the crystalline components only, though the a v e r a g e orientation of the latter can also, of course, be deduced from those indications. Then, by comparing the average orientation derived from both the optical and X-ray data, it is possible to tell whether the average orientation of the amorphous and crystalline portions is or is not the same.

It is not within our province to enter fully into the theory of the quantitative evaluation of the X-ray diagram. We must content ourselves with outlining its principles and referring the interested reader to the literature.

It should be added that the quantitative measurement of the blacking intensity[18] along the *Debye-Scherrer* circles was introduced for the first

[17] *M. Polanyi*, Z. Physik., 7, (1921) 149.

[18] As a rule, of course, some connection exists between the blackening of the film and the irradiated X-ray intensity, which depends upon the "blackening characteristic" of the photographic material. Generally, however, the prevailing conditions are such that the two quantities may be assumed to be proportional. Photometric processes do exist which automatically eliminate the blackening characteristic.

time by *W. A. Sisson* and *G. L. Clark* [19] for the examination of cotton. By means of this method *E. E. Berkley* [20] was able to follow quantitatively the different kinds of orientation of the fibrillæ in the primary and secondary walls in growing cotton hairs of increasing age (cf. p. 163). At a later date the method was adapted to practical cotton testing (see p. 280).

R. Hosemann [21] applied a similar method to artificial fibres. As, however, these methods are not exact enough for our particular purpose, we shall not dwell on them.

More recently, *O. Kratky* has materially assisted in developing the theoretical and technical determination of orientation on the basis of X-Ray diagrams (see below), yet the method still suffers from serious defects. The amplifications described in this book rest on theoretical arguments advanced by *J. J. Hermans* [22] from the principles laid down by *Polanyi*.

2.2. *Elementary Statement of the Principles Underlying Quantitative Evaluation of Diagrams*

For the sake of simplicity we shall limit ourselves to a consideration of the case of cellulose II. (The process is, mutatis mutandis, the same for native cellulose).

O. Kratky [23] has proved that the crystalline regions of cellulose II are not of the rodlet type, but are lamelliform (which very probably also applies to cellulose I [24]. Figure 77 represents a lamella of the kind in diagram, with the *YY'* fibre axis vertical.

It is in this direction, therefore, that the chain of primary valencies lies, corresponding to the *b* axis of the elementary cell (page 16). At right angles to *YY'* lie the diatropic planes, as e.g., the (020) plane, which corresponds to the II_0 interference, and the interferences of which are on the meridian (cf. Figures 74 and 79).

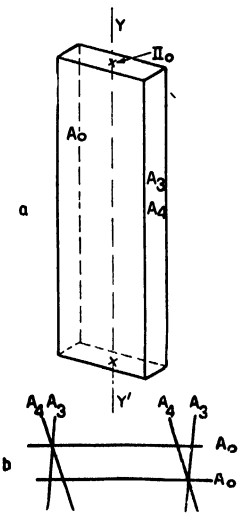


Fig. 77. Diagram of a lamellar crystallite of cellulose II. Below: cross-section perpendicular to the fibre axis YY'; A_0 = lamellar plane.

The position of the paratropic planes (101), ($10\bar{1}$) and (002) (all of which lie parallel to the main axis *YY'*) is shown in the lower part of Fig. 77 in a cross section perpendicular to *YY'*. The lamellar plane corresponds to the

[19] *W. A. Sisson* and *G. L. Clark*, Ind. Eng. Chem. Anal. Ed., 5, (1933) 296.
[20] *E. E. Berkley*, Textile Res., 9, (1939) 335. Also cf. *W. A. Sisson*, Contrib. Boyce Thompson Inst., 9, (1938) 239.
[21] *R. Hosemann*, Z. physik. Chem., 179A, (1937) 356.
[22] Contrib. p. 158, 195; cf. *J. J. Hermans, P. H. Hermans, D. Vermaas* and *A. Weidinger*, Rec. trav. chim. 65, (1946) 427.
[23] *O. Kratky*, Z. physik. Chem., B. 50, (1941) 255; Z. Elektrochem. 48, (1942) 587.
[24] The crystallographic planes, which are distinguished as cleavage surfaces in the crystals, are ordinarily those most densely packed with atoms. In cellulose these are obviously the (101) planes most closely occupied by hydroxyl groups.

(101) plane co-ordinate with the A_0 interference. The two planes ($10\bar{1}$) and (002) together form only a small angle. Their associated interferences A_3 and A_4 (see Fig. 74) are close together on the equator. It is generally hard to separate one from the other in photometric measuring of the blackening intensity. For orientation determination they may conveniently be taken together and thought of as a single plane described as A_3A_4 lying perpendicular to the lamellar plane. (This involves no noticeable error [25]).

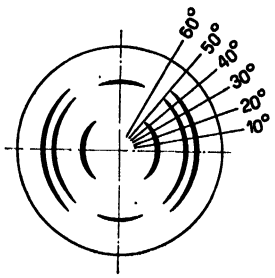


Fig. 78. Outline of the X-ray diagram of an imperfectly orientated fibre (with cellulose II).

Figure 78 is the X-ray diagram in outline of an imperfectly orientated fibre. The interferences form crescent-shaped arcs along *Debye-Scherrer* circles. What we now have to do is to infer the distribution of the orientation of the crystallites from the distribution of intensity along the crescents. If only the longitudinal orientation is required, i.e., the position of the main axes *YY'* of the crystallites (Fig. 77), all that is required is to consider the orientation of a diatropic plane perpendicular to this axis, the interferences of which, with radiation at right angles to the fibre axis, are to be found on the meridian of the diagram.

Figure 79 represents diagrammatically how matters stand with a) complete lack or orderly spatial distribution of the crystallites (isotropy) and b) with partial orientation towards the fibre axis.

The upper part of the figure shows in diagram the appearance of a diatropic interference in the X-ray diagram. Owing to random orientation, there is circular blacking at the left; at the right these is crescent-shaped interference.

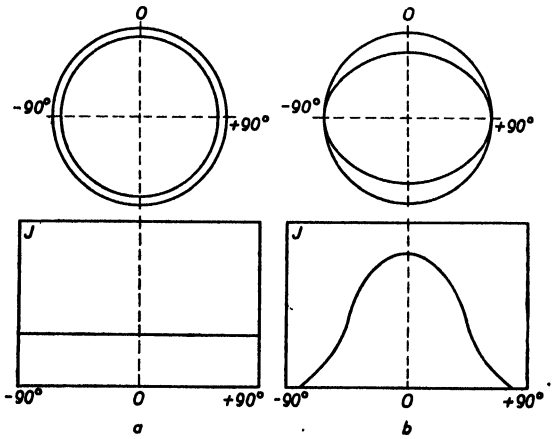


Fig. 79. Diagram of a diatropic X-ray interference and concomitant blackening curve along the *Debye-Scherrer* circle for a. an entirely unorientated object; b. a fibre with partial orientation in the direction of the fibre axis. I = intensity of blackening.

The lower part of the figure displays the concomitant course of the blackening intensity obtained by measuring the blackening of the film along the circle, starting from the equator, over 180°. In Fig. 79 A the blackening intensity is evenly spread along the circle and the blackening curve is therefore a

[25] Similarly, with native cellulose the interferences A_1 and A_2 are taken together and A_1A_2 and A_4 are regarded as the two decisive paratropic interferences.

horizontal straight line; in Fig. 79 B, on the contrary, we have a curve with a maximum in the meridian.

The theory teaches us that the curve representing the X-ray intensity I, irradiated in the angular range of 0 to 90° (Fig. 80), at the same time stands for the distribution of the orientation of the crystallites' main axes YY'. That means to say that the ordinate of this curve proper to an angle α gives the appropriate fraction $\frac{dN}{N}$ of the particles whose axis YY' forms an angle α with the fibre axis (where N represents the total number of particles). The intensity of the diatropic interferences in the diagram of the fibres, however, is only slight and they are therefore not very suitable for exact measurements. One must consequently have recourse to the paratropic interferences A_0 and A_3A_4, an expedient which has the added advantage of disclosing certain details respecting the state of lateral orientation. The course of the intensity is, then, measured along the crescents of the paratropic interferences, not, however, from the meridian at an angle α (see Fig. 81), but from the equator at an angle β, or γ.

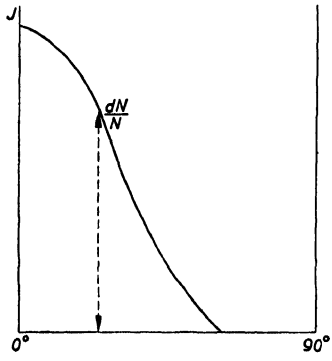


Fig. 80. Course of intensity along the *Debye-Scherrer* circle of a diatropic interference from the meridian ($\alpha = 0$) to the equator ($\alpha = 90°$).

Curves are then obtained which, in analogy to Fig. 80, represent the spatial distribution of the surface norms of planes A_0 and A_3A_4 (Fig. 77) with reference to a plane perpendicular to the fibre axis.

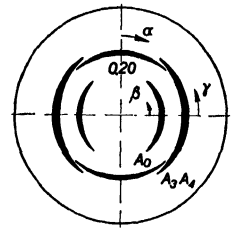


Fig. 81. Plan of the marking of angular distances along the Debye Scherrer circles; α for the diatropic planes; β and γ for A_0 and A_3A_4 respectively.

On mathematical grounds, nevertheless, it is denied that it is possible to calculate from the given distribution of orientation of the surface normals at A_0 and A_3A_4 that of the main axes YY'; for, a given distribution of the paratropic planes may be compatible with various distributions of the diatropic planes and does not therefore unequivocally determine them [26].

All the same, it is possible to determine the a v e r a g e orientation of the diatropics with the aid of the two paratropic distributions. This means to say that the o r i e n t a t i o n f a c t o r of the crystallites (Chapter IV, § 6) can be definitely determined by measuring the two paratropic intensities.

[26] Conclusions as to the diatropic distribution can only be drawn in the exceptional case of identical intensity curves of A_0 and A_3A_4, but, mathematically, these things are rather complicated. Cf. the papers cited in footnote 22. See also *O. Kratky*, Oesterr. Chem. Ztg. Nr. 8 (1939) and *C. Matano*, J. Soc. Chem. Ind. Japan, 40, (1937) 358.

Mathematical calculations [27] have made the following clear:

Let the function $I = F(\alpha)$ stand for the distribution curve represented in Fig. 80 for the d i a t r o p i c plane. Then the orientation factor is determined by the equation:

$$f = 1 - {}^3/_2 \int_0^{\frac{1}{2}\pi} F(\alpha) \sin^3 \alpha \, d\alpha \qquad (5.1)$$

According to Chapter IV, § 6.4., the relation between f and the average angle of orientation α_m is

$$f = 1 - {}^3/_2 \sin^2 \alpha_m \qquad (5.2)$$

Thus $\sin^2 \alpha_m$ is equal to the integral from eq. (5.1). *J. de Booys* and *P. H. Hermans* [27a] have since indicated how, starting from the experimentally determined intensity curve $F(a)$ (see Fig. 80), the numerical value of the integral from eq. (5.1) can be ascertained.

Operating with the paratropic interferences, the numerical value of their average angle of orientation β_m and γ_m can be determined by a similar process [28]. This is then given by the equations:

$$\sin^2 \beta_m = \int_0^{\frac{1}{2}\pi} F(\beta) \sin^2 \beta \cos \beta \, d\beta \qquad (5.3)$$

$$\sin^2 \gamma_m = \int_0^{\frac{1}{2}\pi} F(\gamma) \sin^2 \gamma \cos \, d\gamma \qquad (5.4)$$

when the orientation factor is

$$f = 1 - {}^3/_2 (\sin^2 \beta_m + \sin^2 \gamma_m) \qquad (5.5)$$

For convenience the orientation factor of the whole fibrous substance derived from optical measurements will be symbolized as f_o while that of the crystallites obtained from X-ray data will be distinguished by the symbol f_x.

We shall have occasion to consider these matters again in the third part of this book. Meanwhile, to sum up, we may say that the spatial distribution of the planes A_o and A_3A_4 of the crystallites and, furthermore, the orientation factor can be determined from the distribution of intensity of the two paratropic interferences A_o and A_3A_4 (A_3 and A_4 being regarded as a single

[27] See *P. H. Hermans* and *P. Platzek*, Kolloid-Z., 88, (1939) 68.
[27a] *J. de Booys* and *P H. Hermans*, Kolloid-Z. 97 (1941) 229.
[28] *J. J. Hermans*, Contrib. p. 195.

interference and measured together). Ordinarily, these data suffice for the study of fibre orientation and the processes of deformation [29].

A few words may here be appropriate respecting the practical aspect of these determinations.

By a procedure devised by *O. Kratky* et al[30], photometer curves were recorded along a series of radii of increasing angle from the equator (see Fig. 78). By this means the evidence obtained as to blackening on A_0 and A_3A_4 with deduction of the so-called underground blackening, due to diffusely scattered radiation, non-monochromatic radiation, etc., is more exact than that produced by the methods employed by *Hosemann* or *Sisson* and *Clark* (page 252). For details we refer to the literature cited. The expedient formerly resorted to by *Kratky* and also *Hosemann, viz.*, taking the width at half of maximum intensity, and the formula suggested by *Y. Go* and *T. Kubo* [31] to express the degree of orientation, are either inexact or have no clear physical meaning.

There arises a further complication in the practical evaluation of the diagrams of fibres of relatively poor orientation. The interference of the (021) plane (of medium intensity) lies, with its centre of gravity at an angular distance of 60° from the equator (cf. Fig. 72), upon the second layer line, practically at the same distance from the central point of the diagrams as A_3. With fibres of better orientation the crescents of A_3 and (021) remain separated, but below a certain degree of orientation the two interferences merge.

The upper part of Fig. 82 reproduces the X-ray diagrams of (a) a well-orientated and (b) a less well orientated artificial fibre. Below these are shown the intensity curves (broken lines) ascertained by the procedure described above over 90° along the *Debye-Scherrer* circle of interference A_3, starting from the equator.

In the former case A_3 and 021 remain apart, but in the second case they overlap partly, so that it is no longer possible to determine straight forwardly the intensity curve for A_3 alone, a circumstance which was formerly not taken into account. In that event, however, the determination of the distribution of A_3, or even of reliable data as to the average orientation, must be deemed illusory. There nevertheless remains a means of correctly determining at any rate the a v e r a g e orientation of A_3, simply by taking as the basis the curve arising from the superposition of A_3 and (021) over the entire quadrant and deriving from it, mathematically, $\sin^2 \gamma_m$ for A_3 alone. A method whereby this can be done has been suggested by the author and co-workers; by it the

[29] The above mathematical principles hold where the crystallites may be treated as optically uniaxial and in this respect are an approximation. The relations become appreciably more complicated for optically biaxial crystallites.

[30] See *P. H. Hermans, O. Kratky* and *P. Platzek*, Kolloid-Z., 86, (1939) 245; *P. H. Hermans, O. Kratky* and *R. Treer*, Kolloid-Z., 96 (1941) 30.

[31] *Y. Go* and *T. Kubo*, J. Soc. Chem. Ind. Japan, 39, (1936) 458B.

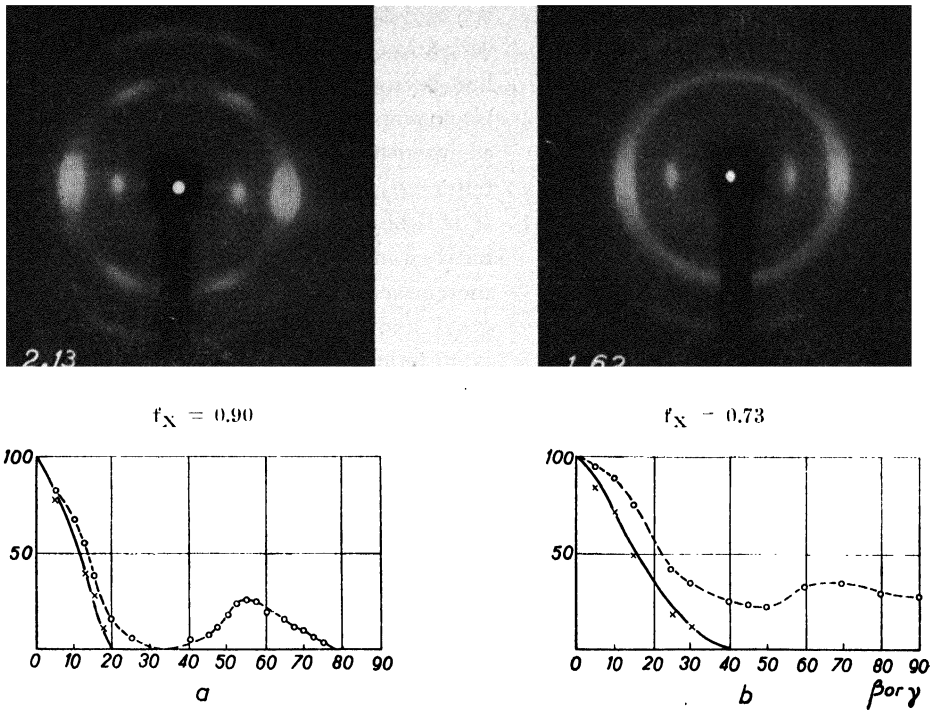


Fig 82. X-ray photographs and the distribution of intensity along the *Debye-Scherrer* circle of the paratropic interferences ascertained from it: a) of a well-orientated, b) of a less well orientated rayon. In the former case the interferences A_3 and 021 are apart, but in the latter they merge. The full-line curves represent the course of the intensity of the A_0 interference, the broken curves that of the A_3 and (021) interference.

orientation factor f_X can be determined for fibres of any orientation. It utilizes in stead of (5.5) the formula:

$$f_X = 1.25 - 1.72 \sin^2 \beta - 2.06 \sin^2 t \qquad (5.6)$$

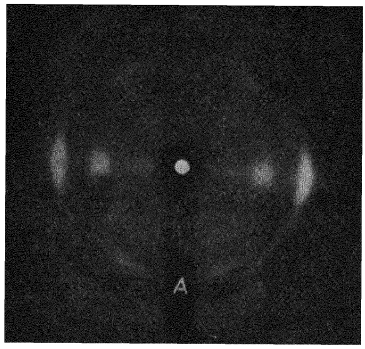
where t is the angle along the A_3-021 circle, relating to the total intensity of the two overlapping interferences [32].

§ 3. THE STATE OF ORIENTATION OF SOME FIBRE SPECIMENS

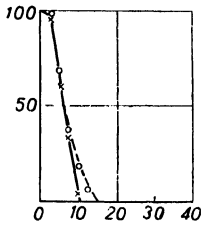
We shall now consider the state of orientation of some specimens of fibre, taking as our criteria the results obtained from the method alluded to in the preceding section [33].

We begin by showing in Fig. 83 the X-ray photographs of (a) a native, (b) a ramie fibre mercerized without tension which, during mercerization, shrank to about 0.8 of its original length, and (c) the same fibre stretched again to

[32] Full details of this procedure are given in Rec. trav. chim., 65, (1946) 427.
[33] Contrib., p. 166.



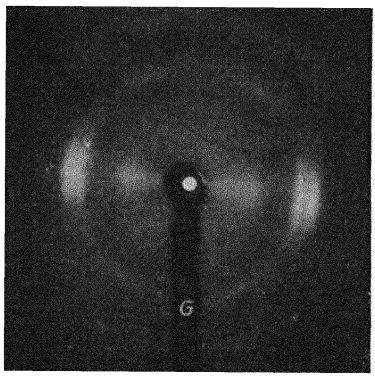
$f_X = 0.97$

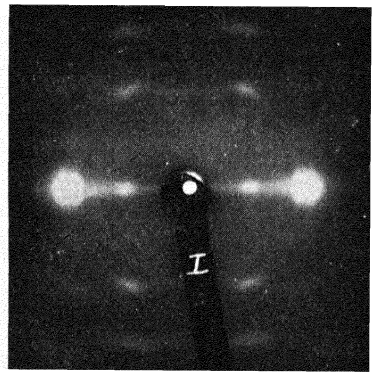


a

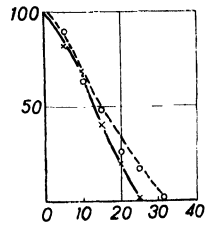
its initial length immediately after mercerization, i.e., before the caustic solution had been washed out. Below these X-ray photographs are given the distribution of intensity curves of the inner (×) and outer (o) paratropic interferences.

It will be seen that the orientation of the native ramie (a) and of the re-orientated mercerized ramie (c) is exceptionally good and that the remaining scattering is practically the same for both paratropic planes. The scattering is far more marked in the case of the specimen which became somewhat disorientated during mercerization. Furthermore, the Λ_3-Λ_4 plane (cf. Fig. 77) is slightly more disorientated than the lamellar plane Λ_0. Through stretching, the original orientation (Fig. 83a) was re-established, in fact, was even slightly improved upon.



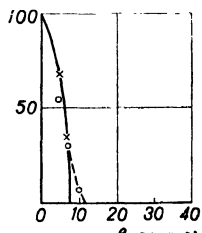


$f_X = 0.90$



b

$f_X = 0.98$



c

Fig. 83. X-ray photographs and distribution of the inner (full-line curves and x) and of the outer (broken-line curve and o) paratropic interference for: (a) native ramie, (b) ramie fibre mercerized without tension having contracted somewhat during mercerization; (c) the same after mercerization, having been re-orientated to original length by stretching. The orientation factor f_X of the crystallites is shown in print

Figure 84 reproduces similar particulars respecting (a) a very strong rayon resulting from the ordinary viscose double-bath process (with 120% stretch), and (b) a likewise highly stretched Lilienfeld rayon of very high tensile strength. The orientation of the crystallites is inferior to that of the native

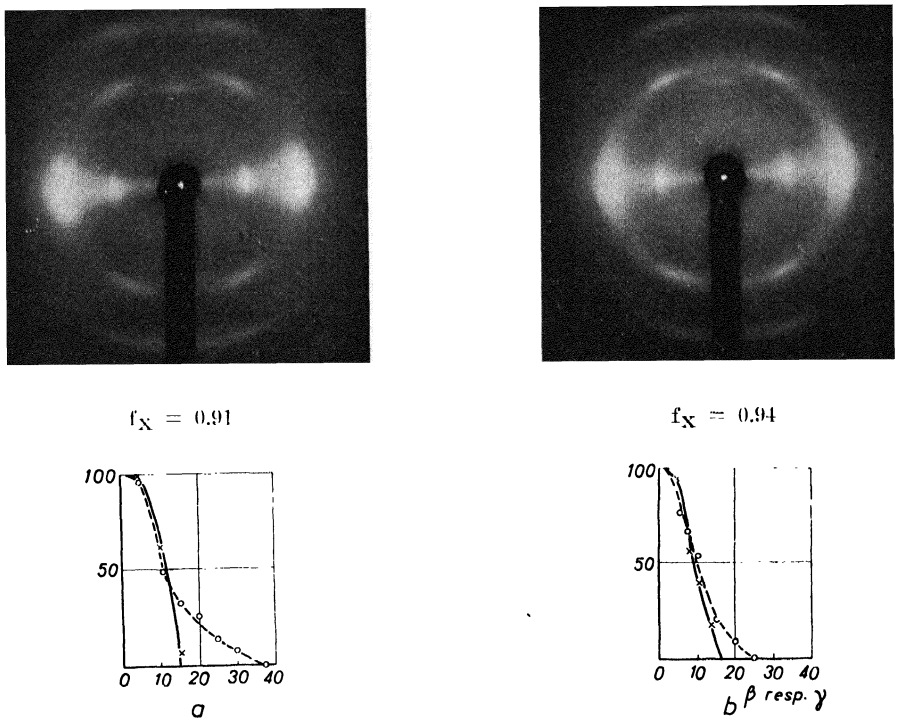


Fig. 84. X-ray photograph and distribution of intensity of the paratropic interferences for (a) a highly stretched viscose rayon; (b) a highly stretched *Lilienfeld* rayon. (In the former the orientation of the A_3 plane lags behind that of the A_0 plane; in the latter the two planes are orientated more or less alike). The orientation factor f_X is shown.

ramie, but in both cases is fairly close to it for the lamellar plane A_0. It is clear from the intensity curves that in the viscose rayon (a) the orientation of the A_3-A_4 plane lags behind that of the lamellar plane A_0 to a greater extent than it does in the *Lilienfeld* rayon.

We have the same thing in the artificial fibres shown in fig. 82; it is obvious even visually from the diagrams that the A_0 interference describes a smaller arc than the A_3 and A_4 interferences.

In cellulose fibres the orientation of the A_3-A_4 plane is often found to lag behind that of the lamellar plane. In the deformation of many artificial filaments it has been observed that the orientation of the A_0 plane runs

ahead of that of the A_3A_4 plane. This means that the lamellar planes of the crystallites tend to become orientated parallel to the fibre axis by preference. On the other hand, when native fibres, such as ramie, are mercerized under tension, the orientation of the lamellar plane scarcely alters at all, whereas the A_3A_4 plane becomes disorientated. The obvious assumption is that the lamellar plane, when originally orientated tangentially, somewhat as represented in Fig. 85, tends to maintain this position, whilst the A_3A_4 plane rotates.

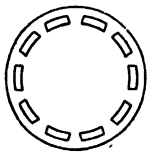


Fig. 85. Diagram of the tangential orientation of the lamellar plane of the crystallites (on fibre cross-section).

These are examples of how certain details as to the state of orientation of fibres may be inferred from X-ray analysis. In Part III we shall see how this reasoning may be applied to the study of the mechanism of deformation of artificial fibres.

Another interesting point is the comparison of the orientation factor f_O derived from optical data (cf. Table XXX) with the orientation factor f_X of the crystallites arrived at in X-ray analysis. These quantities are placed side by side for a number of fibres in Table XXXIII, which also includes the objects dealt with in Figs 83 and 84. Other quantities as well appear in the table and to these we shall revert directly (see heading).

Taking f_O and f_X first, we see that these quantities are only alike in the case of ramie fibre and *Lilienfeld* rayon. For the first and third objects given in the table, this result is trivial, for the equality of the two quantities was assumed in Chapter IV, Section 6.5 for the establishment of the birefringence $n\alpha^*-n\gamma^*$ at ideal orientation. The figures 0.071 and 0.055 in the last column represent the respective values.

But, within the experimental accuracy, f_O and f_X are equal also for the disorientated mercerized ramie (without tension)[34], and for the *Lilienfeld* rayons, which means to say that here the crystalline and non-crystalline components of the fibre were orientated to the same extent. For the factor f_O expresses the orientation of the whole substance and factor f_X merely that of the crystallites.

[34] This has been confirmed for a larger number of mercerized fibres variously orientated. (Contrib. p. 180).

TABLE XXXIII

Birefringence $n_{//} - n_{\perp}$ (converted to density 1.520), Orientation factor f_O from the birefringence and orientation factor f_X of the crystallites from X-ray analysis, the f_O / f_X ratio and the $(n_{//} - n_{\perp})/f_X$ ratio for a number of fibres. (See Table XXVII for meaning of distinguishing marks of the objects.)

Object	$n_{//}-n_{\perp}$	f_O	f_X	$\frac{f_O}{f_X}$	$\frac{n_{//}-n_{\perp}}{f_X}$
Native ramie	0.069	0.97	0.97	—.—	0.071
Ditto mercerized without tension	0.050[5]	0.92	0.90	1.02	0.056
Ditto re-orientated	0.054	0.98	0.98	—.—	0.055
Viscose rayon					
HA 10% stretch	0.026[5]	0.535	0.78	0.62	0.034
HA 80% „	0.037	0.745	0.89	0.76	0.041[5]
HA 120% „	0.44	0.88	0.91	0.88	0.049[5]
LA 70% „	0.035	0.70	0.85	0.74[5]	0.041
Lilienfeld rayon					
Sedura a	0.041	0.82	0.82	1.0	0.049[5]
Sedura b	0.042[5]	0.855	0.87[5]	0.98	0.048[5]
Sedura c	0.046[5]	0.93	0.94	0.99	0.049[5]
*Model filaments**	0.041	0.82	0.87[5]	0.955	0.047
Bemberg rayon	0.037	0.745	0.86	0.86	0.043

* Stretched 100% in xanthate condition.

In the other fibres, f_O is patently inferior to f_X which signifies that, on the average, the crystalline components of the fibre are better orientated than the non-crystalline portions. In ordinary viscose rayons the difference diminishes as orientation increases. The orientated model filaments match the viscose rayon and fit in between HA 80% stretch and HA 120% stretch. In Part III we shall consider what interpretation is to be put upon these facts. (p. 456).

Were the whole orientation of the fibre substance to correspond to that of the crystallites, the quantity given in the third column, viz., $(n_{//} - n_{\perp})/f_X$ would represent the birefringence $n_\alpha^* - n_\gamma^*$ with ideal orientation. In *Lilienfeld* rayon this value (0.050; see p. 237) is actually reached; in the other rayons it is only approached if the orientation is high, owing to the inequality between f_O and f_X

If the percentage of crystalline substance in a fibre is known, the portion of the birefringence which falls to its share and that falling to the share of the non-crystalline portion can be calculated separately on the basis of the figures given in Table XXXIII.

It is in any event evident from these results that the correct value for $n_\alpha^* - n_\gamma^*$ for regenerated fibres must be between 0.050 and 0.055, probably nearer the lower limit [35]. The assumption is that the slightly higher value of 0.055 as deduced from mercerized ramie fibres is due to a slightly higher percentage of crystalline substance in the latter (also see Chap. VIII).

We would mention in conclusion that the same author [36] found that the birefringence of the fibres increases substantially in the partial conversion of

[35] Contrib. p. 172.
[36] Contrib. p. 175.

the crystalline component of mercerized ramie fibres to cellulose IV resulting from heating in glycerol (cf. page 155), whereas X-ray analysis shows the orientation of the crystallites to have remained unchanged. Since it is hardly to be assumed that this operation entails increased orientation of the amorphous components, the increase in birefringence was taken to be the result, either of conversion of the lattice to that of the IV modification, or of an increased percentage of crystalline substance brought about by the thermal treatment, or else of the two effects combined. Some of the relevant figures are listed in Table XXXIV.

TABLE XXXIV

Optical constants and X-ray Orientation Factor of Ramie and Rayon before (B) and after (A) Partial Transformation into Cellulose IV

	$n_{//} - n_{\perp}$ (d = 1.520)	f_x	$\frac{n_{//} - n_{\perp}}{f_x}$
Mercerized ramie			
B	0.054	0.98	0.055
A	0.061$_5$	0.98$_5$	0.062$_5$
Lilienfeld rayon			
B	0.046$_5$	0.94	0.049$_5$
A	0.050$_5$	0.95	0.053$_5$

§ 4. THE CONTRIBUTION OF THE AMORPHOUS FIBRE PORTION TO X-RAY DIFFRACTION

It was stated at the end of § 1 that the amorphous component of cellulose fibres likewise gives rise to a diffuse scattering of X-rays and thus contributes to the diffuse background blackening of the film. As, however, this background blackening contains other components as well, special technique is required to distinguish them. Until recently this matter had been practically ignored, but the author and his co-workers have been giving it their attention latterly [37]. The work they have done will be discussed briefly here, as it may prove helpful towards a quantitative evaluation of the percentage of crystalline and amorphous substance in fibres.

The components of the diffuse background are:

a) Radiation scattered by the amorphous substance.

b) Radiation scattered by the air in the camera and by the edges of the diaphragm.

c) Non-monochromatic radiation diffracted by the crystalline and amorphous components.

The usual copper Kα radiation from a copper anticathode and filtered through nickelfoil is always contaminated by a certain amount of harder, non-monochromatic radiation. Naturally, the diffraction of this radiation through the crystalline component does not produce maxima of intensity; it is, rather, spread in a black patch of a certain width. This component can be removed

[37] See *P. H. Hermans* and *A. Weidinger*, Rev. trav. chim., 65, (1946) 620. (cf. Chap. VIII)

by using entirely monochromatized radiation, but a simpler method is to use two films, one above the other, with an aluminium foil 0.3 mm thick in between. This absorbs practically all the Cu$K\alpha$ radiation (98%) and transmits nearly all hard radiation (91%), so that the second film shows only the blacking caused by the hard radiation. This can be photometered and deducted from the background on the first film.

To determine the radiation scattered by the amorphous substance a photo is taken of the object by the double-film method in a "comparison camera" as designed by Astbury, two quadrants of the film being covered by lead sectors (see Fig. 86). After five minutes the object is removed from the path of the rays and the lead sectors are turned 90°. Then only the radiation scattered by the air and the diaphragm is photographed on the unexposed sectors of the film. This cycle is repeated every five minutes until both pairs

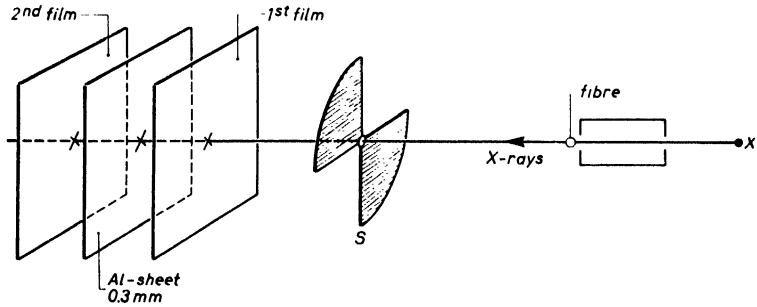


Fig. 86. Diagram showing the two-film method in conjunction with *Astbury's* comparison camera. X = source of X-rays; D = diaphragm; S = lead sector. The films are separated by an aluminium foil 0.3 mm thick. (For clarity the sector and the films have been drawn at some distance from each other, but in reality they are superimposed).

of sectors have been sufficiently exposed, when it is safe to assume that the total intensity of the primary ray has been the same for each sector. Fig. 87

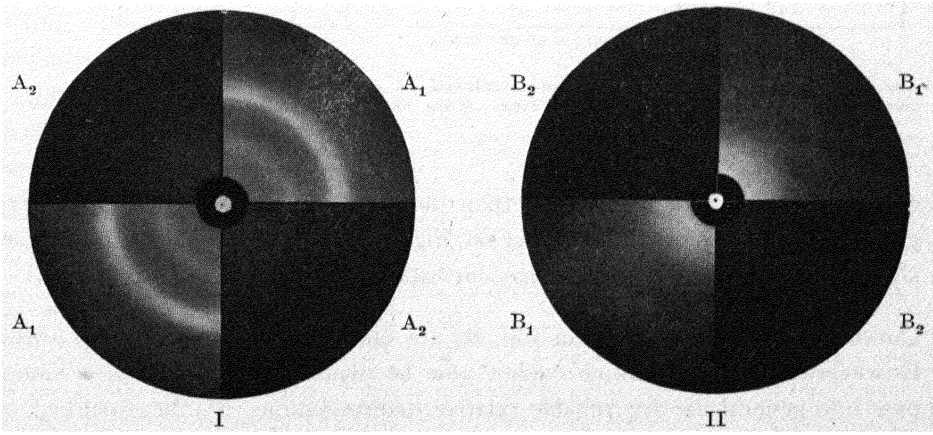


Fig. 87. Exposures of an isotropic filament according to Fig. 80; I first film; II second film. A_1 and B_1 cellulose quadrants; A_2 and B_2 air quadrants.

reproduces the two films obtained from an isotropic model filament. Fig. 88a illustrates a radial photometer curve A_1 taken of the cellulose quadrant and a photometer curve A_2 taken of the air quadrant of the first film. A_1 consists of the maxima of the crystalline interferences (101), ($10\bar{1}$) and (002) superimposed upon the diffuse underground (dotted line). In Fig. 88b we have the photometer curves of the quadrants B_1 and B_2 of the second film. The difference B_1-B_2 of the two latter curves is now determined and plotted above the air curve A_2 in Fig. 88a. The sum of A_2 and B_1-B_2 represents the intensity which has to be subtracted from the background A_1 to find the blacking A_m of the amorphous substance. The result is represented in Fig. 89 where it will be

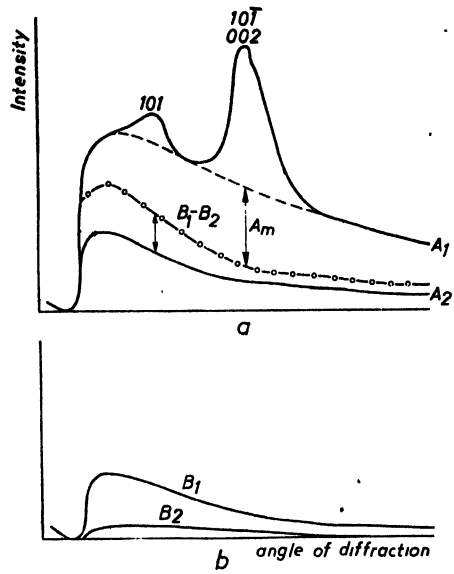


Fig. 88. Radial photometer curves over the cellulose and air quadrants of a) the first and, b) the second film. The background of A_1 less the intensity $A_2 + B_1 - B_2$ produces the intensity Am of the radiation scattered by the amorphous substance.

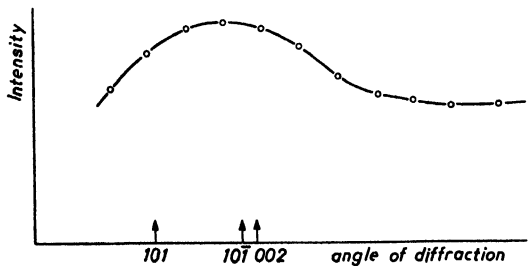


Fig. 89. Intensity of the radiation scattered by the amorphous substance, derived from Fig. 88 (on enlarged scale).

seen that a curve with a broad maximum was obtained. The position of this maximum is in between those of the two main crystal interferences (the place of which is shown on the abscissa). This procedure is not quite impeccable until a correction has been made for the absorption in the cellulose object (which makes the intensity of the air-blacking in the cellulose quadrants a little lower than indicated). This correction leaves the general configuration of the curve in Fig. 89 unchanged, but the maximum shifts slightly to the left and then corresponds with a period of 5—6 å.

Curves of the shape shown in Fig. 89 are obtained with all cellulose fibres. However, for reasons which cannot now be explained [87] this method cannot pass into general use for reliable relative determinations of the quantity of amorphous substance in various fibres. Only in one favourable case it was applied to the estimation of the percentage of crystalline substance formed

in the recrystallization of amorphous cellulose powder obtained by grinding ramiefibres in the dry state [38]. (Cf. Chapter II § 5).

A similar powder sealed in a thin glass capillary tube was photographed before and after recrystallization in the comparison camera, each time compared with an empty tube of the same thickness.

In Fig. 90 we see the photometer curves of the amorphous (A) and of the recrystallized powder (B), which converge in the right-hand part of the figure. Both curves have been corrected for the scattering by the air and by the glass capillary tube. The amorphous powder no longer produces crystal interferences; only a broad band. Assuming that the powder is all amorphous, the ratio between the height *qr* of the underground of curve B (where the maximum is) and the height *pr* of the maximum of curve A provides us with a measure of the fraction of amorphous substance in the recrystallized object. In this way Hermans and Weidinger found 62%, a figure which correction for absorption increases by about 5%. In order of magnitude, this figure tallies most satisfactorily with the percentage derived from the sorption ratio, the heat of moistening and other data (see page 191).

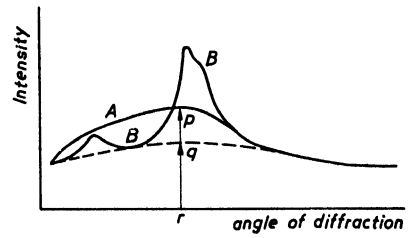


Fig. 90. Photometer curves (corrected for radiation scattered by the air and by the thin gass capillary tube) of, A amorphous cellulose powder from ramie fibres and, B the same preparation after recrystallization by heating with water. The ratio qr : pr represents the fraction of amorphous substance in the recrystallized powder.

An improved technique also permitting the investigation of the crystalline-amorphous ratio in fibres will be dealt with in Chapter VIII

[38] *P. H. Hermans* and *A. Weidinger*, J. Am. Chem. Soc., 68, (1946) 2547.

CHAPTER VI

MECHANICAL PROPERTIES

§ 1. INTRODUCTION

It is the mechanical properties of a fibrous material which are of prime importance from the technological point of view, for it is they which govern its reaction to external mechanical action; e.g., its deformation under applied stress, its behaviour under mechanical durability tests, such as bending, friction, etc.

In the realm of fibrous material, its mechanical properties in the narrower sense are understood to imply its reaction to the strain of extension in the fibre axis, a comparatively easy matter to ascertain and one which has been the primary objective of the practice of fibre testing from earliest times. It is not too much to say, however, that the evidence of precisely these tests as to the usefulness of the material has often been over-estimated and that their results have frequently been neither properly understood nor interpreted. Nowadays there is a growing tendency to apply supplementary tests, such as those for bending resistance, resistance to wear and tear, etc.

Physically, the deformation of solid substances is the sum of very complicated processes, the principles of which cannot yet be rightly understood, despite the great bulk of labour expended upon the matter, and the elucidation of which is still in its beginnings. In this province, therefore, we are still very far indeed from establishing an obvious connecting link between the perceptible phenomena and the intrinsic structure of the material.[1] Here the greatest progress has been made in research on metallic industrial materials; where organic high-polymers are concerned, only the preliminary attempts have been made to attack the problem.

We shall be reverting to this matter in Part III and shall here merely describe, from their phenomenal aspect, some of the most salient mechanical properties of cellulose fibres, only here and there touching on the theoretical aspects. We shall restrict ourselves almost entirely to the properties that come into play under mechanical tests in the longitudinal direction, for the very good reason that our fundamental knowledge of other properties is practically non-existent. We shall thereby first consider those much-used terms "strength" and "elongation" and the principles underlying their determination in fibrous materials generally, and shall then deal with the mechanical properties of fibres individually.

[1] "Even the simpler problems of the solid state are baffling in the extreme", *H. J. Gough* and *W. A. Wood*, J. Inst. of Civil Eng., (1937/38) 249.

§ 2. GENERAL REMARKS ON TENSILE STRENGTH AND ELONGATION

What we are here concerned with is the deformation of a fibrous material resulting from stress applied in the direction of the fibre axis. This is comparable to loading a cylindrical test rod of q cm² cross-section with p grams weight. Then, according to the classical rule of elasticity, a tensile stress is set up in the rod:

$$\sigma = \frac{p}{q} \text{ g/cm}^2 \qquad (6.1)$$

under the influence of which the rod is stretched from its initial length of l_0 to its final length of l, when its relative elongation amounts to $v = l/l_0$ and its specific elongation γ to $v - 1 = (l - l_0)/l_0$. In this book we shall call the quantity v the degree of elongation.

In the ideal case the final length would be reached very soon after application of the stress and when this is removed the rod would immediately spring back to its original length. Hooke's law states that the specific elongation is proportional to σ:

$$v - 1 = a \cdot \sigma \qquad (6.2)$$

If $\frac{1}{E}$ is substituted for the constant a, then E represents the modulus of elasticity, which is measured in g/cm² or in kg/cm², as

$$E = \frac{\sigma}{v - 1} \qquad (6.3)$$

and $v - 1$ is a number without dimensions.

E may be taken as a measure of the "strength" of the material, but to deduce it from extension experiments the case of elastic (fully reversible) extension has to be assumed. This ideal case, however, is never realized in fibrous materials. First of all, final elongation is never reached in a short space of time after application of constant tension, but, after fairly rapid extension at first, further elongation takes place at a gradually slower rate for some considerable time and the material tends asymptotically to reach a state of equilibrium. Secondly, the process is never reversible; true, when the tension is released, there is initially a rapid, then a gradual, ever slower retraction (elastic after-effect), but the material never reverts to its original length. This general behaviour of a fibre upon which tension is first brought to bear and then relaxed is represented diagrammatically in Fig. 91. (All organic fibrous substances behave roughly in this way [2]).

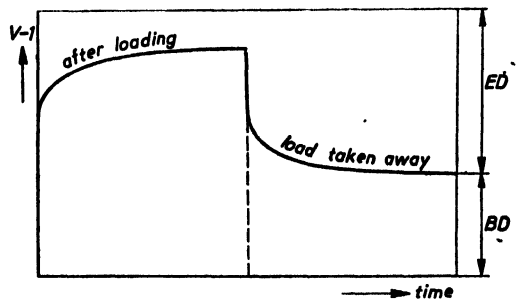


Fig. 91. Specific elongation ($v - 1$) of a cellulose fibre as a function of time in applying and releasing load. ED elastic portion of elongation and BD permanent portion of elongation.

[2] For this cf. *H. de Witt Smith* and *Eisenschitz*, J. Text. Inst., 22, (1931) T. 170.

The left part of the illustration shows the course of the specific elongation with time while under tension; the right part, the same function after release from tension.

It will be clear that the phenomena of extension always entail a time factor; nor can they be considered disassociated from that factor. Accordingly, it is not possible to deduce a modulus of elasticity from observations of this kind, except under extreme conditions wholly irrelevant to practical circumstances. *J. Karger* and *E. Schmid* [3] and also *E. Valkó* [4] discovered that cellulose fibres as well as natural silk behave like ideal bodies at the temperature of liquid air, and in this way they were able to determine the modulus of elasticity for a few fibrous materials [5]. *K. H. Meyer* and *W. Lotmar* [6] also succeeded in determining like moduli of elasticity by effecting extremely rapid deformations (acoustic vibrations).

Thus, leaving aside results such as these, obtained under very special conditions, remote from those prevailing in practice, we have no clear, unequivocal yardstick for the material strength of fibres in the above sense.

A practical expedient whereby the deformation of a fibre under stress may be approximately characterized is to make a stress-strain diagram on the basis of a breaking test and to determine the extension at break and the breaking strength, comparatively easy experiments to carry out. The extension at break is the elongation at which the fibre breaks under the breaking test, usually expressed as a percentage of the initial length. In this book we shall mostly use the relative degree of extension ε at break.

The breaking strength is derived from the tension at which the fibre breaks and must, of course, be properly related to the thickness of the object. Though it would be rational to refer the breaking force to the cross-section exhibited by the object at the moment of break (breaking tension), it is the custom in ordinary practice to refer it to the cross-section in its initial condition prior to its extension, from a desire to denote a material property of an object in its original form. E.g., if a fibre of $250\mu^2$ cross-section is torn by a 5 g load, its breaking strength is said to be

$$\frac{5}{250 \times 10^{-8}} \text{ g/cm}^2 = 20 \text{ kg/mm}^2.$$

Curiously enough, even in recording stress-strain diagrams, technical literature usually refers the tension associated with every degree of extension to the cross-section of the non-extended object.

Actually, this habit is misleading and irrational, for the recording of breaking strength or tensile stress related to the original cross-section, without due heed being paid to the preceding extension, expresses no material property at all.

[3] *J. Karger* and *E. Schmid*, Z. techn. Physik, 17, (1925) 42.
[4] *E. Valkó*, in *H. Mark*: Physik und Chemie der Cellulose, Berlin, 1932, p. 10.
[5] Extensibility is at the same time greatly reduced. Cellulose fibres in a very dry state exhibit the same phenomenon. In that state it would probably be possible to determine E, but no attemps to do so are known.
[6] *K. H. Meyer* and *W. Lotmar*, Helv. chim. acta, 19, (1936) 68.

At the moment of break after elongation v, the cross-section of the filament is smaller by $\frac{1}{v}$ than in its initial state, assuming always that the density of the material has remained unchanged during extension, which may be taken more or less for granted in the case of air-dried fibres. (For swollen objects see below). The effective breaking tension is, therefore, v times greater than the breaking strength customarily defined in practice.

Now, in the procedure just described, if fibres widely differing in elongation at break are being compared, then of two objects possessing the same tensile strength but different elongation at break, that having further extensibility will exhibit higher breaking tension.

For scientific purposes — especially in investigations concerned with regenerated model filaments which, as we shall see later, are prone to show up to two hundred per cent. elongation at break — it is positively misleading to correlate the breaking strength with the initial cross-section as this tends to produce unreliable data. The same may, of course, be said of the stress-strain diagrams, where the stress should always be related to the actual cross-section at the moment.

As the customary practical procedure is not likely to be abandoned, we propose in this book to term the number thus obtained the "b r e a k i n g l o a d", and that resulting from the rational procedure the "b r e a k i n g s t r e n g t h".

It is difficult with nearly all the fibres dealt with in actual practice to determine by direct experimental means the true cross-section in sq. mm. and data other than in kg/mm² are therefore usually given. The fineness of the filament is expressed as a weight measure per unit of length, which has the added advantage of disassociating the result from the density of packing of the fibre substance, so that the strength really is that of the actual fibre substance in hand. The fineness is then expressed in grams per denier, or in kilometres breaking length [7]. Admittedly, in all these cases the regain of the fibre is a factor to be reckoned with both in the cross-section and in the cm-weight. It must, however, be established besides, as it also affects the whole course of the deformation experiments.

The density d of the fibre has to be known to convert the other data to kg/mm², as follows:

$$1 \text{ g/denier} = 9 \text{ km breaking length} = 9d \text{ kg/mm}^2$$

[7] The fineness of the fibre D in deniers is given by the weight in g per 9000 metres of filament. The metrical number Nm is the lenghth of the filament in m per g. We therefore have the equation $D \cdot Nm = 9000$.
The breaking length R is the length of a filament in kilometres, the weight of which would be just enough to cause the filament in question to break. Let the breaking load be P, then:

$$R = \frac{9\,P}{D} = \frac{P.Nm}{1000}\,.$$

R can, of course, also be used as a measure of tension, but that would make "breaking length" a misnomer. In this book, therefore, we shall by preference express the tensions as g per denier or g per 100 deniers.

Accordingly, inserting the approximately correct value of d for air-dry cellulose fibres, viz., 1.50, the result is:

$$1 \text{ g/denier} = 9 \text{ km breaking length} = 13.5 \text{ kg/mm}^2$$

In the case of swollen objects the stress can more conveniently be related to the cross-section (or thickness) of an air-dry fibre which, per unit of length, contains just as much dry substance as the swollen filament under test[8]; for it is the strength of the cellulosic substance present in the fibre which one wishes to study and in this way the enlargement of the cross-section owing to swelling is avoided.

The stress-strain diagram is obtained by plotting the course of the degree of extension during the test as a function of the applied stress, when, as stated above, it is more consistent to relate the stress to the actual cross-section at the time.

We repeat with emphasis that, strictly speaking, all the data respecting elongation, breaking strength and breaking tension, as also the course of stress-strain diagrams, can only rightly be deemed correct if accompanied by complete time records of the extension experiment. For, according to Fig. 85, the degree of elongation is not established by a given stress, without a record of the time during which the load was applied. This circumstance is frequently overlooked, both in practice and in the literature.

Apparatus and procedures there are in abundance whereby stress-strain diagrams (or rather, force-extension diagrams) of fibres and filaments can be drawn, and the literature on the results thus obtained is voluminous but, for the reasons given, their common defect hampers in a number of ways both the interpretation of the observed facts and comparison of the results. The least that is required for exact measurements is a record of the velocity of extension which, according to *J. Kalff*[9], is most conveniently expressed as a percentage of the initial length per minute. Yet even this piece of information does not take us far enough, for, with the available apparatus, the velocity of elongation only remains constant during the whole process of extension if the stress is increased proportionally, which it very rarely is[10].

Hitherto, then, the data respecting stress-strain diagrams have provided a compromise with regard to the experimental difficulties, but they are not rational data. The three variables: stress elongation and time, are certainly indispensable to exact knowledge of the behaviour of a fibre subjected to deformation. The only known investigations of this nature are those carried out by *W. Wegener*[11] with artificial fibres. This author determined the elongation-time curves (cf. Fig. 91) for constant load of increasing size and

[8] *P. H. Hermans*, Kolloid-Z., 86, (1939) 107.
[9] *J. Kalff*, Rec. trav. chim., 48, (1929) 997.
[10] There is a small number of apparatuses in which the stress increases proportionally to the time. From the theoretical standpoint these are the best, but this is no place to go into details.
[11] *W. Wegener*, Zellwolle, Kunstseide, Seide, 46, (1941) 298, 342.

compiled with them a three-dimensional diagram of state. Figure 92 reproduces one of these diagrams, drawn for a viscose rayon. Unfortunately, however, the stress is here related to the original cross-section.

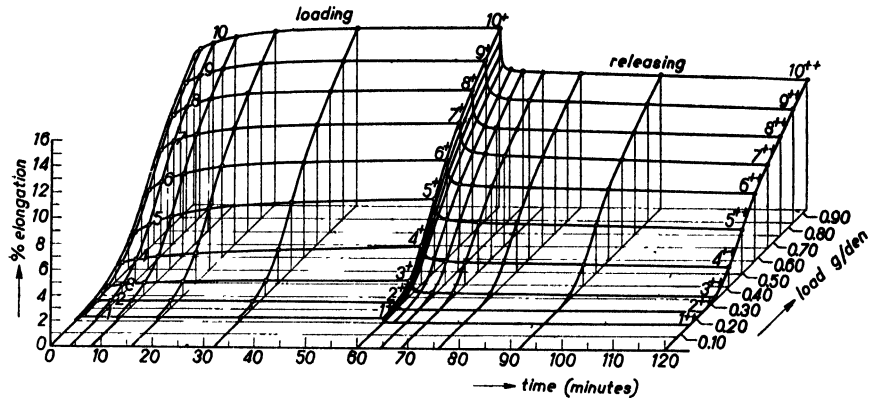


Fig. 92. Load-elongation-time diagram with adjacent release of load of a viscose rayon, after *W. Wegener*. (Elongation in per cent. of initial length; load in g per denier; time in min.).

Henceforth, rational stress-strain diagrams, connected with a given time of load, can be deduced from this spatial figure. These are the lines of intersection of the (vertical) planes parallel to the stress-strain axes with the curved surfaces of the diagram. *Wegener* calls them "Isochrones". Some of the isochrones corresponding to Fig. 92 are shown in Fig. 93.

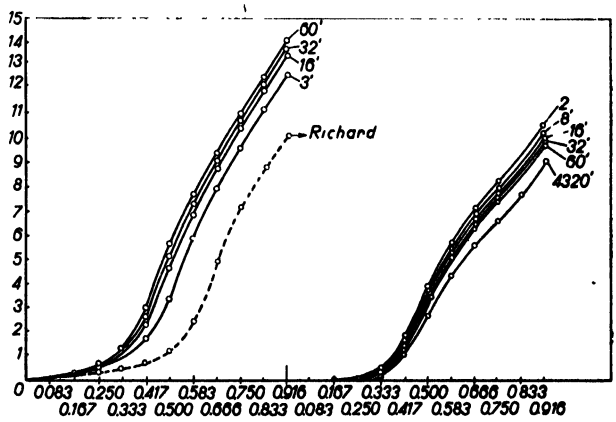


Fig. 93. Rational stress-strain diagram (isochrones) for a viscose rayon, after *W. Wegener*. For comparison a conventional SS curve taken direct from the apparatus designed by *Richard*.

The "elasticity" of the material — i.e., its recovery after the load has been lifted — can be assessed by constructing and comparing the isochrones for load and release. *Wegener* has demonstrated that the SS diagrams drawn up with the usual apparatus can never mount above the isochrones and will as a rule be below them (an example is given in Fig. 93). It will be observed that the breaking tension and the elongation at break given by the terminal points of the curves likewise depend upon the time.

It will now be clear that all the usual data given in the literature respecting

quantities of this kind are subject to the experimental conditions and that therefore no absolute value can be attached to them.

It is as well to remember that *J. Karger* and *E. Schmid* [12] state that the time factor is of very little account in native fibres, but in artificial cellulose fibres its influence under certain circumstances may be very considerable.

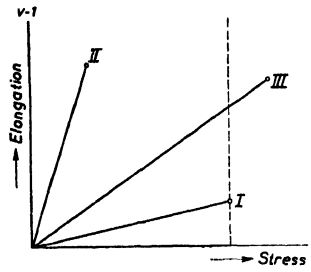


Fig. 94. Graph of stress-strain curves.

In conclusion we shall consider some special types of SS diagrams and see what interferences may be drawn from those curves as to the material properties. Figure 94 presents some SS curves in diagram as straight lines, for the sake of simplicity.

Relating the stress to the actual cross-section at the time, the breaking point is marked by a black dot. If we first compare materials I and II, we shall see that in two respects I is the stronger, because, besides showing less elongation at a given stress, it also exhibits a higher tension at break. There is the same qualitative difference in the former respect between I and III, but, against this, III has greater breaking strength than I. Hence there need be no parallelism between the "tensile resistance" (which is expressed by the modulus of elasticity in really elastic bodies, but which is in this case more difficult to seize quantitatively, but may nevertheless be assessed by the trend of the SS curves) and the breaking strength. Which of the two qualities is the more desirable will depend upon the demands made upon the material in actual use. Its elastic properties will also have some say in the matter, and some impression of these can be obtained by comparing the load and release curves.

The SS curve also enables one to judge of the effective energy required for the deformation, but then it is the actual, measured tensile force, instead of the stress, which has to be plotted against the extension, when this may be expressed, say, in grams and the extension in centimetres (Fig. 95). The area enclosed by the curve and the straight lines OA and AB indicates the w o r k o f e x t e n s i o n in g/cm up to breaking point B. By afterwards dividing by the original cross-section one finds the work per square millimetre cross-section of the material under test. The illustration shows how two materials with different diagrams I and II and with the same breaking strength and elongation may require different work of extension.

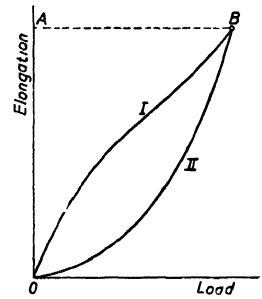


Fig. 95. Force-stram curves of two fibres of the same breaking strength and elongation at break, but displaying different energy of extension (diagram).

[12] *J. Karger* and *E. Schmid*, Z. techn. Physik, 17, (1925) 42.

With SS curves which are not straight lines, the material is said to be strengthened during extension if in its course the curve bends away towards the tension axis, and to be weakened if it inclines towards the extension axis. In Fig. 95 curve I first shows strengthening and then weakening; curve II shows weakening. It will be plain from an example we shall give that, if this phenomenon is to be properly understood, it is essential that the stress should refer to the effective cross-section. There are cases (e.g., with air-dry isotropic cellulose filaments) where the curve rises vertically from a given point (Fig. 96, curve A) when the stress is referred to the original cross-section. (Increase in extension without increase in tension). This apparent contradiction vanishes if the stress is then referred to the effective cross-section (Fig. 96, curve B). The latter procedure is, therefore, always to be preferred [13].

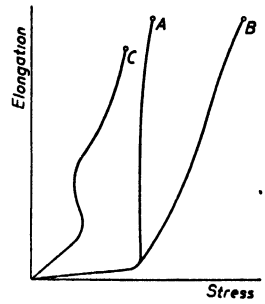


Fig. 96. Diagram of stress-strain curves.

§ 3. ON THE BREAKING STRENGTH

3.1. Some Data on the Breaking Strength of Various Fibres.

Native cellulose fibres used as the raw material for textiles are in many respects technologically superior to artificial fibres and in a sense, therefore, they may be regarded as an exemplary standard. In Table XXXV will be found the breaking strength and elongation at break of some native and artificial fibres, some dry and some swollen in water. The dry values hold good for an atmosphere with 65% relative humidity. As the numbers vary with the origin of the fibres, the approximate limiting values are given [14].

It will be seen that the breaking strength of native cellulose fibres has been observed to amount to as much as roughly 100 kg/mm², which may be esteemed high if it be considered that the strength of iron wire and steel wire ranges from about 30 to 160 kg/mm². Another striking point is the wet strength, which even surpasses the dry strength [15].

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[13] It has even been observed in artificial fibres, e.g., casein wool, (*G. Heim*, J. Text. Inst., 30, (1939) 213) that the SS curve becomes regressive towards the extension axis (curve C in Fig. 96), when elongation proceeds though the tension diminishes. This apparently paradoxical behaviour likewise disappears when the really prevailing stress is taken. The effect can only be manifested on the *Schopper* apparatus if the catches are removed from the weight lever.

[14] The figures given by various investigators also cover quite a wide range. We may here refer to compilations made by *J. Karger* and *E. Schmid*, Z. tech. Physik, 17, (1925) 42; *H. Mark*, Physik und Chemie der Cellulose, Berlin 1932; *O. Schmidhäuser*, Melliands Textilber., 17, (1936) 905; *K. Windeck—Schulze*, Faserstoffe, Frankfurt a.M., 1940; *P. A. Koch*, Klepzigs Textilzeitschr., 1941.

[15] The specimen of ramie which was the subject of *Karger* and *Schmid's* investigations (l.c.) proved to be an exception in this respect The same was found with ramie, investigated by the author (contrib. p. 8).

TABLE XXXV

Breaking Strength and Elongation at Break of some Fibres

MATERIAL	BREAKING STRENGTH		ELONGATION AT BREAK	
	Dry kg/mm²	Wet in % of dry strength	Dry	Wet
Cotton	30 — 80	100 — 120	1.06 — 1.12	1.07 — 1.13
Flax	up to 100	102 — 106	~1.02	~1.02
Ramie	85 — 95	116 — 125	1.02 — 1.03	1.02 — 1.03
Sheep's wool	15 — 23	76 — 97	1.28 — 1.48	1.29 — 1.61
Natural silk	60 — 70	87 — 94	1.14 — 1.17	1.17 — 1.30
Lignocellulose fibre	~50	—	—	—
Normal viscose fibres	20 — 35	45 — 60	1.15 — 1.25	1.20 — 1.35
Special viscose fibres	up to ~80	up to 75	~1.10	~1.10
Cuprammonium rayon fibres	20 — 35	50 — 70	1.11 — 1.25	1.17 — 1.30
Acetate artificial fibres	15 — 25	55 — 70	1.20 — 1.30	1.25 — 1.45
Ditto very strong	up to 60			
Casein fibre (Kasenka)	~10	~55	~1.60	~1.80
Nylon fibre	~70	~90	1.12	1.14

It will also be seen that technology is nowadays capable of producing artificial fibre of dry strength no longer inferior to that of native fibres. This, however, by no means signifies that the problem of manufacturing artificial fibres of the same quality as native fibres has been solved. The breaking strength is only a minor contributory factor in the technological value of a fibre; there are very many others playing a far more decisive part.

When cellulose artificial fibres are swollen in water, their tensile strength deteriorates appreciably. This deterioration amounts to as much as 40 to 50 per cent. in the still most current products, which are not intended to possess any specially pronounced tensile strength. This has all along been recognized as a distinct drawback. We shall revert directly to the supposed cause of this phenomenon [16].

3.2. The Theoretical Aspects of Tensile Strength

It was soon realized that great strength goes hand in hand with good orientation. Fibres which by X-ray and optical criteria are highly orientated commonly have the greatest strength (§ 3.4), though the two criteria are by no means always consonant as to orientation.

When it was still supposed that fibres were built up of oblong polymeric particles ("micels"), an attempt was made to associate the tensile strength with the lateral attractive forces of these particles orientated in parallel; it was thought that these somehow slid over each other in the process which ends in break [17]. The present theory that fibres are macromolecular systems has given rise to different notions.

The chain molecule itself, as primary valence chain, possesses very great

[16] A comprehensive investigation on the mechanical properties of native and artificial cellulose fibres has recently been published by *R. Meredith*, Shirley Inst. Mem., 19, (1944) 5, 29.

[17] E.g., *W. T. Astbury* and *Street*, Phil. Trans. Roy. Soc., H. 230, (1931) 75.

specific tensile strength. The question now is: To what extent will this affect the strength of the system?

If the molecules in an ideally orientated fibre are so anchored that they cannot slip off each other, the strength of the fibre should amount to the sum of the strength of the individual chains. Several investigators have attempted to calculate this strength from known molecular data. In this way *H. Mark* [18] found a breaking strength of 800 kg/mm² and *J. H. de Boer* [19], by an improved computation, reached as much as 2260 kg/mm². It is not surprising that these theoretical values exceed those actually observed by very orders of magnitude, for the same happens when the strength of a rock salt crystal computed from the lattice energy is compared with that actually observed.

In the above calculations it was assumed that all the molecules in the fibre cross-section are loaded equally and, therefore, break at the same time. This assumption, however, is highly improbable. The examination of other solid bodies has made it plain that break ordinarily starts from the smallest of flaws, or other defects in the structure, at the borders of which there is an accumulation of stress which may be as much as a multiple of the average stress, and thus accelerates rending. The actual strength is invariably far less than that which theory calculates [20].

P. H. Hermans [21] has moreover shown that the theory of a cellulose monocrystal, the molecules of which are evenly loaded during a tearing test, leads to absurdities, so that for this reason as well little value is to be attached to theoretically calculated strength values [22].

The chains in a real fibre, however highly orientated, will never be strained in an exactly uniform degree in the tearing test, but will reach the breaking tension more or less successively (also cf. *Y. Konisi* [23]); this may be plainly seen in the diagram after *K. H. Meyer* [24] presented in Fig. 97. This picture is, however, too primitive. Break does not necessarily result from a one-sided tear. If absolutely uniform strain is not brought to bear on all the chains, the stress at break depends on the statistical distribution of tension between the single chains which obtains in every cross-section in the process of rending. It will, however, always be less than that of the ideal monocrystal.

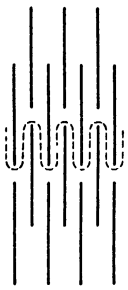


Fig. 97. Rent owing to breakage of chains.

It might also be asked whether it be not preferable to imagine that the molecules slide off each other. To withdraw a chain molecule embedded between others in the lattice frame by longitudinal displacement, a force would have to be

[18] *H. Mark*, Melliands Textilber., 10, (1929) 695.
[19] *J. H. de Boer*, Trans. Faraday Soc., 32, (1935) 10.
[20] See *R. Houwink's* book Elasticity, Plasticity and Structure of Matter, Cambridge, 1937, pp. 32, 105, 158.
[21] *P. H. Hermans*, Rec. trav. chim., 58, (1939) 63.
[22] The object would show 40 % extension at break and, on being torn, would explode!
[23] *Y. Konisi*, J. Soc. Chem. Ind. Japan, 41 . B, (1938) 439.
[24] *K. H. Meyer*, Hochpolymere Chemie, Leipzig, 1940. Vol. II, p. 310.

applied depending, not only on the size of the cohesive forces between neighbouring members of the chain, but also on the length of the molecule, that is on the number of its monomeric residues. Therefore, objects containing shorter chains might present the alternative mechanism in the rending process which is shown diagrammatically in Fig. 98. For an average degree of polymerization of about 300, *J. H. de Boer* (loc.cit.) calculated a tensile strength of 120 kg/mm² for the case in point. The longer the chains, the less likely does this kind of sliding become, of course. If we recall to our minds the picture of the microstructure of fibres as we have drawn it, then we must admit that there is no a priori argument against a contributory mechanism in the rending process such as that just mentioned. All the same, there is good reason to believe that chain break is primarily involved, especially in the case of native fibres.



----Area of rupture

Fig. 98. Plan showing process of rending resulting from sliding (..... = break surfaces).

I. Sakurada [25] states that the breaking load of ramie fibres does not change noticeably after careful nitration and acetylation in the fibrous form. He contends that the lateral cohesive forces of the esterified molecules must be considerably weaker than those of the unesterified ones. The fact that the breaking load nevertheless remains unchanged would tend to show that there is *no* "sliding off" at break. These experiments were later verified and confirmed by *G. Centola* [26]. *Sakurada* also found that the breaking load of rayon fibres converted to triacetyl cellulose remained practically unchanged.

The energy deployed does not conflict with these postulates. According to *P. H. Hermans* [27] the energy output in the rending test is amply sufficient to break down an even far greater number of primary valence bonds than that needed at least to produce break in a single cross-section.

Further corroboration of the statement that in native fibres the primary valence chains are themselves pre-eminently responsible for the strength of the fibre is afforded by investigations published by *K. H. Meyer* and *W. Lotmar* [28]. The moduli of elasticity of ramie, hemp and flax fibres determined by these investigators acoustically in the dry state (6000—11000 kg/mm²) are of the same order of magnitude as the values computed by them for an ideal fibre (12000 kg/mm²). This result merely signifies, however, that the primary valence chain actually is involved in very rapid, small deformations.

The moduli of elasticity of artificial fibres found by these authors were considerably lower (the highest value, viz., 4500 kg/mm², being found in

[25] *I. Sakurada*, Papierfabrikant, 36, (1938) 252; also cf. *I. Sakurada* and *S. Kawada*, J. Soc. Chem. Ind. Japan, 42, (1939) 225.
[26] *G. Centola*, Textilia (Milan), 17, (1941) 335; Bol. Sci. Fac. Chim. Bologna, 1941, 1.
[27] *P. H. Hermans*, Rec. trav. chim., 58, (1939) 63.
[28] *K. H. Meyer* and *W. Lotmar*, Helv. chim. acta, 19, (1936) 68.

Lilienfeld rayon, which is very well orientated). This does not, however, prove that the rending process is essentially different in this case; it merely shows that different linking mechanisms are involved here in small, rapid deformations. The breaking process is again more than probably connected, at all events partly, with the tearing apart of molecules. We shall be reverting to this directly. Nevertheless, the lower the average degree of polymerization of the raw material from which the fibres are produced, the more likely is it that the sliding mechanism plays a subsidiary part.

3.3. *The Effect of Swelling upon Breaking Strength*

The lateral cohesive forces of the chain molecules are liable to be weakened by swelling processes. With swelling agents operating only i n t e r micellarly, like water, this weakening may only affect the amorphous constituents. The view, expressed above, that "sliding off" is not a decisive factor in break, receives support from the fact that the strength of native cotton is not affected by swelling in water. It is obvious that the molecular chains are as a rule firmly anchored with their terminals in the crystalline regions and the weakening of the cohesion in the amorphous components cannot disrupt them. According to *Sakurada* and *Kawada* (loc.cit.), with swelling agents operating i n t r a micellarly, on the other hand, (as in the conversion in sodium hydroxide) the strength is adversely affected, and so here too sliding off seems to be a possibility.

As soon as they begin to swell, artificial fibres are known to lose much of their strength, but this does not give us the right to suppose that breaking strength has anything to do with a slidingoff mechanism. Freshly spun artificial filaments which have never been dried possess a considerably higher degree of swelling than re-swollen filaments, but their breaking strength is not less than that of the latter; indeed, freshly spun xanthate filaments with a degree of swelling exceeding 10 exhibit surprising strength (see p. 485). There does not appear to be any distinct connection between the degree of swelling and the tension at break, at any rate above a certain water content.

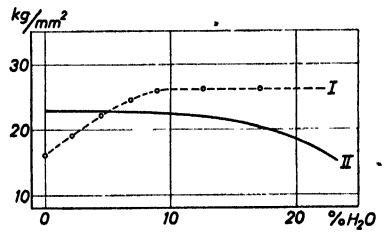


Fig. 99. Course of breaking strength of cotton fibre I and of a viscose rayon II, subject to the regain.

We see in Figure 99 how the breaking strength stands to the regain according to measurements made by *K. C. Brown, J. C. Mann,* and *F. R. Peirce* [29] for single fibres of cotton and by *K. Lauer* [30] for rayon. After vigorous drying, the strength of the cotton diminishes, but as from about 9% water content, it becomes constant. In regenerated fibres, conversely, it is in the dry state

[29] *K. C. Brown, J. C. Mann* and *F. T. Peirce,* J. Text. Inst., 21, (1930) 187.
[30] *K. Lauer,* J. makromol. Chem., I, (1943) 97.

that we get the most strength, which diminishes as from about 12% water content and finally falls to half its value in the dry state.

The probable explanation of this contradictory behaviour of native and regenerated fibres is the following[31]. The reason of the difference between theoretical and actual strength is that the chains within a cross-section of fibre are never equally loaded, but bear statistically uneven strain. Every factor which is affected by this distribution of tension will also affect the tension at break.

If n similar cords of exactly the same length are clamped in a rending apparatus, the stress at break of the system will be equal to n times the stress at break of a single cord. But if the cords are previously knotted to each other or tangled to some extent (Fig. 100 b); they will not all give way at the same moment. The system will have a lower tension at break. In swollen native fibres the molecules are naturally distributed very uniformly and it is easy to conceive that, thanks to the increased flexibility of the amorphous portions, the chains are more evenly strained than in the more brittle dry fibre. The reverse might easily be the case if, from the beginning, the molecular chains were less orderly in their arrangement, as they may be supposed to be in regenerated fibres. In the foregoing example the tension at break of n strands of unequal length (Fig. 100 c) will be far lower if they are clamped into the apparatus side by side and independently than if they had been previously knotted together as in Fig. 100 d, where now, in the beginning, two cords are under stress, whereas in 100 c only one is. A badly twisted cable made up of cords of unequal length, for instance, will easily have greater bearing strength than the original system. In the dry fibre the tension is more evenly divided in the disordered amorphous regions, owing to the lateral cohesive forces, than in the moist fibre, where the lack of uniformity comes into full play[32].

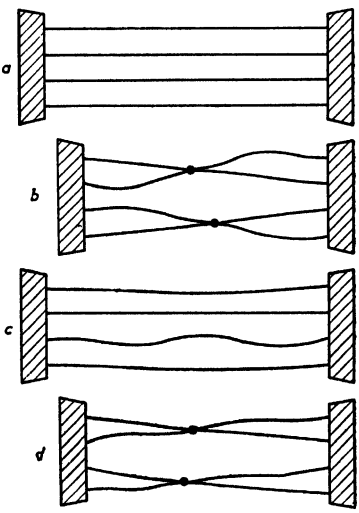


Fig. 100. Breaking strength.

It will be seen that the regain at which the strength of native fibres becomes constant and that of regenerated fibres begins to decrease appreciably, coincides approximately with the regain at which binding as water of hydration is completed (cf. p. 209) and, therefore, the strongest bonds between the chains in the amorphous portions are weakened. Any additional water there may be from now on

[31] *P. H. Hermans*, Kolloid-Z., 108, (1944) 177.
[32] *K. Lauer* has suggested another, less simple explanation of this phenomenon, Kolloid-Z., 107, (1944) 93.

becomes, as it were, a "lubricant" (p. 193). It is from this moment that the internal structure of the micellar system is clearly manifested, which is consonant with the above reasoning; nor is there any refutation of it in the fact that the degree of elongation at break increases, both in native and in artificial fibres, together with increasing moisture.

It is, we think, clear from the foregoing that, by representing the process of rending as closely connected with the break-down of molecular chains, it is possible to offer a ready explanation of the qualitative influence, at least, of swelling upon the strength of native and regenerated fibres, which no other representation has so far succeeded in doing. Yet it should not be supposed that the energy required to rend a fibre is utilized to any noticeable extent to break down the molecular chain, for this is certainly not so. *J. de Booys, H. L. Bredée* and *P. H. Hermans*[33] have proved that, if only the smallest conceivable fraction of the energy required to stretch isotropic (and other) filaments of regenerated cellulose to break were diverted to break down molecules, this would be amply sufficient to cause substantial depression of the average degree of polymerization, demonstrable by viscosity measurements. But they were unable to detect any change in viscosity of the rent material.

While a positive result would supply a plea in favour of the above representations, this negative result by no means refutes them. Compared to the number of breaches in the fibre, the number of impaired chains need only be minute, as may readily be realized by imagining the break of the chains in only one cross-sectional plane of the fibre, which would be quite enough to wrench the fibre in two. The energy brought to bear in extension to break is used chiefly to overcome the internal friction involved in the process of deformation (see section 4.4). The additional energy output required at the end of extension to tear the chain molecules apart contributes merely to the determination of the maximum value of the stress attained at breaking point.

In regard to the effect of liquids other than water upon the mechanical properties of cellulose fibres we have for reference only a few investigations, some of the results of which are contradictory. To these we shall revert in § 5.

3.4. The Influence of Orientation

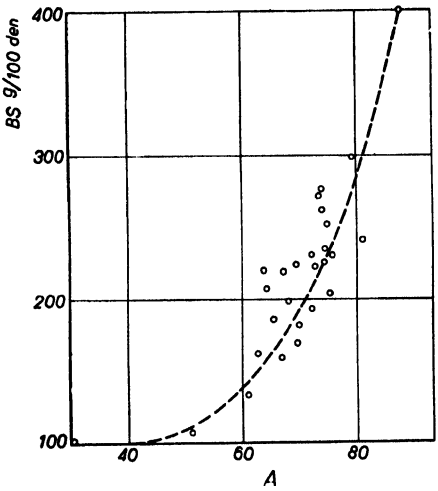
It has long been known that the breaking strength of cellulose fibres is closely associated with the degree of their orientation. *R. O. Herzog*[34] was the first to point this out as regards artificial fibres, but a similar dependence has also been observed in native fibres.

This is nowhere more clearly manifested than in cotton fibres in connection with their spiral structure, as may appear from the investigations reported by *D. R. Morey* (see p. 243) and later publications by *E. E. Berkley* and

[33] *J. de Booys, H. L. Bredée* and *P. H. Hermans*, Rec. trav. chim., 59, (1940) 73.
[34] *R. O. Herzog*, Naturwiss., 11, (1923) 172; Z. physik. Chem. A. 139, (1928) 235.

C. C. Woodyard [35] and *C. M. Conrad* with *E. E. Berkley* [36]. These investigators found the striking correlation of 0.954 between the directly measured breaking strength and that computed from the average pitch of the spiral structure. (The pitch was deduced from X-ray photographs and the strength varied in these investigations for the various cotton specimens from 40 to 80 kg/mm²)[37]. In America a radiographic cotton test for commercial purposes has even been developed from this finding, a test which is to take the place of the wearisome and much more laborious direct strength test applied to single fibres, or the equally troublesome *Lea* Test [38]. By them the highest values for the strength of native fibres were found to coincide with the highest parallel orientation of the fibrillæ (ramie and flax).

There have been many attempts to discover quantitative connecting links between the orientation and the strength of regenerated fibres as well. *C. Matano* and *M. Nakamoto* [39], as also the same with *T. Ozawa* [40], spun filaments from silk fibroin, which had been dispersed in conc. magnesium perchlorate solution, also from viscose variously stretched, analysed their X-ray diagrams and compared the results with the observed mechanical properties. In both cases the tensile strength steadily increased with the orientation, while extensibility decreased. It was only in the least orientated (almost isotropic) objects that the extension at break was also slight. *Y. Go* and *T. Kubo* [41] reached similar results. *I. Sakurada* [42] examined 25 different



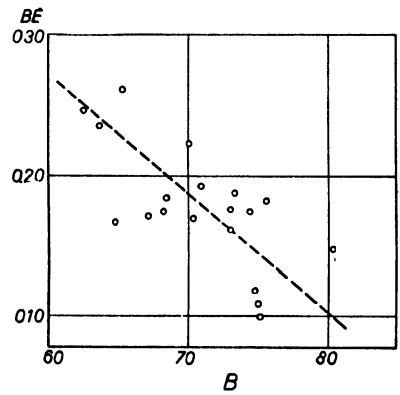


Fig. 101A, BS, and Fig. 101B, BE of 25 samples of rayon and staple fibre, plotted against the degree of orientation ascertained from X-ray data (after *Sakurada*).

[35] *E. E. Berkley* and *C. C. Woodyard*, Ind. Eng. Chem., 10, (1938) 451.
[36] *C. M. Conrad* and *E. E. Berkley*, Textile Research, 8, (1938) 341; cf. also *E. E. Berkley*, ibid., 9, (1939) 355.
[37] As *Conrad* and *Berkley* point out, the decrease in strength as a function of the pitch of the spirally wound fibrillae in the fibre is in quantitative analogy to the reduction in breaking strength of intertwined bunches of fibre as a function of the specific twist factor.
[38] Also see *W. A. Sisson*, Textile Research, 7, (1937) 435.
[39] *C. Matano* and *M. Nakamoto*, J. Soc. Chem. Ind. Japan, 39 B, (1936) 194, 406, 478.
[40] *T. Ozawa*, J. Soc. Chem. Ind. Japan, 40 B, (1937) 174.
[41] *Y. Go* and *T. Kubo*, J. Soc. Chem. Ind. Japan, 39 B, (1936) 458.
[42] *I. Sakurada*, Papierfabrikant, 36, (1938) 252.

rayons and commercial staple fibres and plotted their strength and elongation against a "Degree of Orientation" — suggested by *Go* and *Kubo* — derived from the X-ray diagram by measuring the distribution of the intensity of the interference (002) (cf. Chap. V, § 2). (This "Degree of Orientation" is derived in a physically obscure way from the width at half of maximum intensity; it is 100 for ideal orientation and 0 with isotropy). Figure 101 shows the result.

From it *Sakurada* concludes that there is obviously quite a clear relation between breaking strength and orientation. Closer investigation by the writer and his co-workers [43] has disclosed that this is only true of fibres manufactured by a similar process. They were able to show that the relation between the breaking strength and the orientation factor f, derived from optical data (see Chapter IV, § 6), of rayons spun by the ordinary viscose process, is entirely different from that obtaining in rayons spun by the *Lilienfeld* process. The relevant curves, which speak for themselves, are reproduced in Fig. 102.

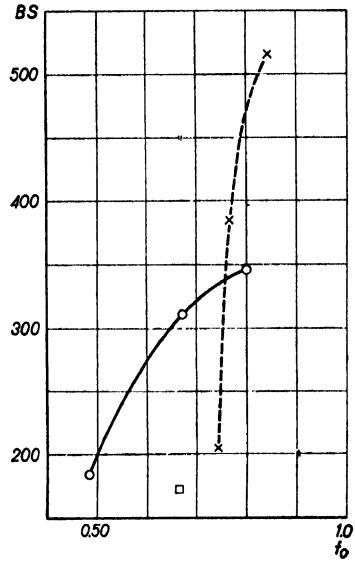


Fig. 102. Breaking strength in air-dry state of (0) ordinary viscose rayon and (x) *Lilienfeld* rayon spun with increasing stretch, plotted against the optical orientation factor f_o. The BS of a *Bemberg* rayon (□) is also given.

The result was similar when the breaking strength was plotted against the orientation factor f_X derived from X-ray data; also when the wet strength was considered. The figure also reproduces the data respecting a cuprammonium rayon (Bemberg) spun by the funnel process. This curve seems to be more akin to the *Lilienfeld* rayon curve than to the viscose rayon. Such comparisons, however, still suffer from many defects, even when, as in the case just cited, the radiographic evaluation has been quite exact. Thus the X-ray photograph should, by rights, have been taken at breaking point, instead of in the initial condition. A combination of radiographic and optical observation of the orientation along the entire stress-strain curves of filaments pre-stretched and tested in various states of swelling, might be expected to produce more reliable evidence (cf. Part III, Chap. X).

§ 4. ON THE RELATION BETWEEN LOAD AND ELONGATION AND THE REVERSIBILITY OF DEFORMATION

4.1. Introductory Remarks

As a rule the relation between load and elongation, or extension, is given visual form in load, or stress-strain diagrams. The shortcomings of this

[43] Contrib. p. 125.

mode of representation have been discussed in § 2. Nevertheless, curves drawn up from the data obtained with a mechanically well-constructed extension apparatus provide some clue to the deformatory properties of a fibre. We shall here consider some of the general features of these diagrams, reserving the fundamentals of the phenomena for discussion in Part III.

The first thing to be noted is that the stress-strain curves (SS curves) of the fibres always vary with their regain. The usual practice is to trace them for fibres conditioned in standard atmosphere of 65% relative humidity and for fibres swollen in water. When not otherwise stated, the curves we shall deal with below are always related to the standard atmosphere.

It should also be borne in mind that the breaking point of a fibre (characterized by its breaking strength *(BS)* and its extension at break *(EB)* should be conceived as a singular point of the SS curve and that it always requires special consideration and explanation. The SS curve shows the path along which the breaking point is reached. Although they are intimately related the one by no means definitely determines the other. Identical breaking points are often reached by quite different ways, and, conversely, fibres with SS curves of the same shape are liable to exhibit different breaking points. Experimental examples of both cases are known.

When studying the relations between SS curves and orientation, it should always be remembered that orientation increases during the process of extension itself, so that the orientation at the breaking point is invariably higher than that of the fibre in its initial state. Consequently, the SS curves cannot usefully be studied apart from the orientation entailed in the process of extension. However, we shall deal only cursorily with this point here, as it will receive fuller attention in its proper place in Part III.

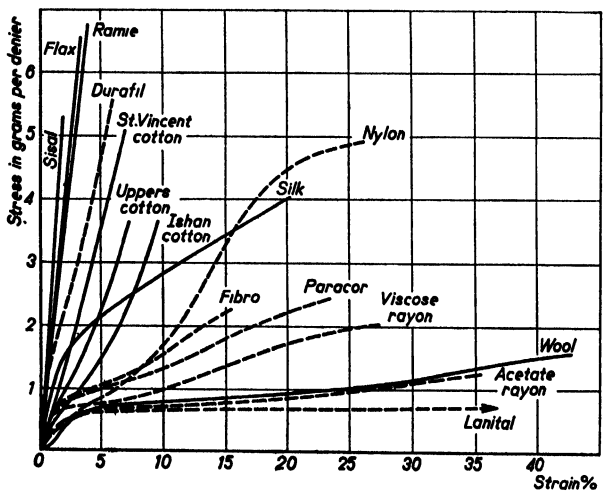


Fig. 103. Stress-strain curves of various natural fibres (full-line) and artificial fibres (broken lines) under comparable testing conditions, according to *R. Meredith*.

4.2 Stress-Strain Curves of Some Fibres

The stress-strain curves of fibres vary greatly with the nature of the sample, as is shown in Fig. 103 borrowed from *R. Meredith*[44]. The curves are taken under strictly comparable conditions at 65% rel. h. and 20° C., with a rate of

[44] *R. Meredith*, Shirley Inst. Mem., 19, (1944) 5.

loading of 10 g per denier per minute and a test length of 1 cm. It will be seen that both natural fibres (full-line curves) and artificial ones (broken-line curves) cover almost the entire diagram.

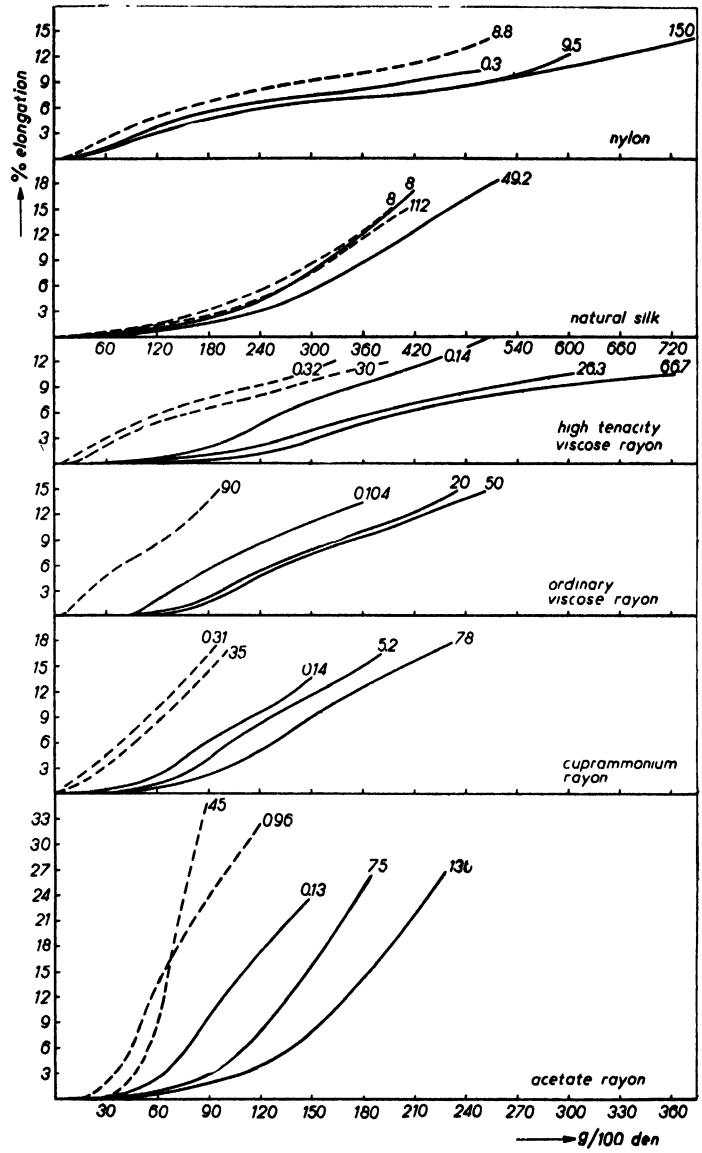


Fig. 104. Stress-strain diagrams of some fibre specimens, taken at various velocities and steady increase of load per unit of time. The numbers beside the curves represent the increase in load in g/100 denier per second. Full-line curves for 65 % rel. hum., broken curves for fibres swollen in water. (Stress for Nylon and natural silk drawn at reduced scale of 1 : 2). Stress referred to actual cross-section.

Figure 104 reproduces the SS curves of a few fibres, both in the air-dry and the wet state, and with different rates of elongation. They were traced from

data produced in the apparatus devised by *P. A. Schultz*, with which a constant increase in load per second is obtained [45]. The applied increase in load, expressed in grams per 100 denier per second, is indicated beside the curves. The indicated stresses relate to the actual fibre denier at the time.

For comparison come first the curves for Nylon, that very highly orientated and extremely strong American polyamide fibre, and for a degummed natural silk. Below come two samples of normal viscose rayon, I being better orientated than II. Finally we have a cuprammonium rayon (Bemberg), the orientation of which was between I and II, and a less orientated acetate rayon. (The stress curve for Nylon and natural silk was drawn to half the scale of the other curves). The picture we have before us induces the following comments.

The shape of the curves shows a continuous transition from Nylon, via natural silk, to the cellulose artificial fibres, roughly in the sequence of their orientation. Where the air-dry fibres are concerned, we see an ever more distinct *"yield point"* where elongation with increasing load all at once begins to increase with greater rapidity, which results in a "weakening" (cf. § 1) followed, in the case of cellulose fibres, by more or less distinct "strengthening". The yield point of wet fibres is at far lower stresses.

It is only with Nylon fibres that the rate of loading has little effect upon the course of the curves (though it was varied in the proportion of 1 : 500); yet the *BS* varies from 480 to 645 g/100 denier. The rate of loading affects the curves of the other fibres far more, the *BS* of all the fibres increasing with increasing rate of loading. The yield point also rises to higher stresses as the rate of loading increases.

It can be clearly seen that moistening with water has but little effect upon Nylon and natural silk, whereas its effect upon the other fibres is very considerable. This fact was discussed from other points of view in § 3.3.

The SS curves of highly orientated artificial filaments spun by the *Lilienfeld* process have not been included. Their shape is similar to that of natural silk. Breaking strengths up to more than 550 g/100 denier are attained, but the elongation at break is lower. In this case too the effect of moistening is far greater than in that of natural silk [46].

The altered position and shape of the curves and the shifting, or diminishing clarity, of the yield point with increasing orientation are salient features of Fig. 105, representing the SS curves of a number of model filaments manufactured in an identical manner from viscose. The filaments differ only in their degree of orientation (attained through different preliminary elongation in the swollen xanthate state).

[45] The experiments were carried out in the laboratory of N.V. Research, Arnhem. The *Schultz* apparatus is of the inclined plane tester type; see *V. E. Gonsalves*, Chem. Weekblad, 35, (1938) No. 34.

[46] E.g., see *H. D. W. Smith*, J. Text. Inst., 22, (1931) T. 158; Contrib. p. 8.

The yield point of the dry isotropic filaments is particularly marked. As orientation increases, it shifts towards greater stresses and becomes less distinct. It will also be noted (broken lines) how the *BS* and *EB* change as orientation changes, the former increasing and the latter decreasing [47]. The dotted lines represent the SS curves of any random viscose silk in the same category.

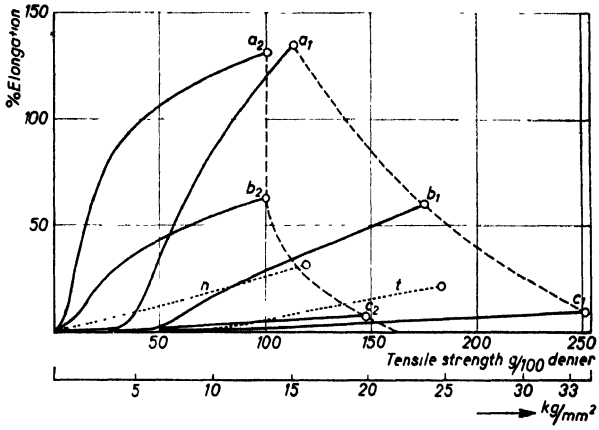


Fig. 105. Stress-strain curves of a number of model filaments of increasing orientation in the air-dry state (a_1 b_1 c_1) and in the wet state (a_2 b_2 c_2); a = isotropic. Preliminary elongation in the xanthate state for b = 1.5, for c = 2.0. Dotted-line curves represent the SS curves for an ordinary viscose rayon.

The picture presented by Figure 105 shows in rough outline how the mechanical properties of an artificial fibre change with its orientation at the beginning of the elongation test. The general picture resulting from an examination made by *R. Stoll* and *E. Rall* [48] of technical viscose rayons spun with increasing stretch is a similar one.

It has long been known in practice that the *BS* and *EB* change in an opposite sense as orientation increases. This phenomenon may be roughly explained by the fact that further orientation of the fibrous substance takes place during the elongation test. As a rule, an already extensively pre-orientated fibre cannot be elongated as far as one less pre-orientated; yet it must not be imagined that a number of differently pre-orientated, but otherwise similar, fibres will all break after reaching a given orientation. The matter is by no means as simple as that. Such will only be the case if the pre-orientation of the fibres has taken place under exactly the same conditions as those prevailing during the breaking test. Then the *BS* of all the fibres with different pre-orientation remains constant and only their EB varies. The author (loc. cit.) has published examples and illustrations of this fact and he gave the name of "homologous series" to such a collection of fibres.

If, however, pre-orientation and the elongation test take place under different conditions, the factors determining the *BS* and *EB* as well as the orientation are far more complicated and are not apparent at a first glance (see page 488). The broken lines in Fig. 105 represent the geometrical locus of the breaking point of a collection of filaments increasingly pre-elongated in the swollen xanthate state, and tested at 65% r.hum., or in the wet

[47] Cf. for this *P. H. Hermans*, Kolloid-Z., 86, (1939) 107; Proc. Acad. Sci. Amsterdam, 42, (1939) 478; Kolloid-Z., 89 (1939) 344.
[48] *R. Stoll* and *E. Rall*, Melliands Textilber., 20, (1939) 783.

state. A collection of this kind was designated as a "pseudohomologous series". This kind of series is always referred to two states of swelling, viz., that at pre-orientation and that in the test. As technical filaments are also previously stretched in the xanthate state, *Stoll* and *Rall* naturally arrived at a representation similar to that shown in Fig. 105.

The foregoing points the way to rational treatment of the SS curves and the breaking data of artificial fibres, whereby their history must always be taken into account and their isotropic fundamental state referred to. This will be our main theme in the third part of this book.

Figure 106 illustrates the influence of the regain upon the SS curve of cotton, which has been borrowed from *K. C. Brown, J. C. Mann* and *F. T. Peirce* [49].

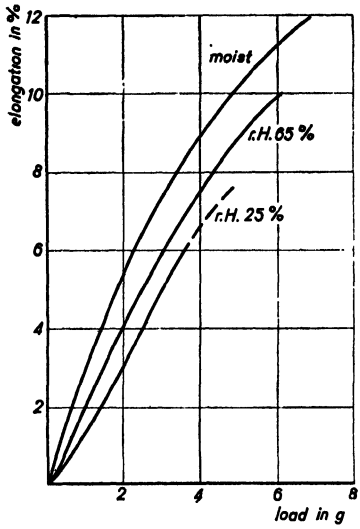


Fig. 106. Stress-strain diagram of cotton fibres with various regains according to *Brown, Mann* and *Peirce* (stress referred to original cross-section).

We have also borrowed from *C. S. Venable* [50] and from *S. E. Sheppard* and *E. K. Carver* [51], also from *H. R. Bellinson* [52] for SS curves of viscose rayon of several moisture contents. Figure 107 reproduces the observations of the first-named, where it can be very clearly seen how the yield point and the breaking point shift according to the moisture content.

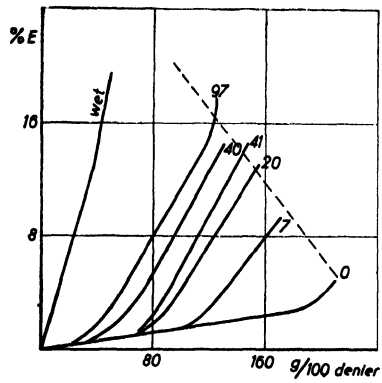


Fig. 107. SS curves of a viscose rayon at rel. hum. of the atmosphere changing from 0 to 100 %; stress referred to original cross section (after *C. S. Venable*).

Finally, in Fig. 108 we give the SS curves of isotropic model filaments of viscose at different degrees of swelling [53]. Here again we have the diagrams, already appearing in Fig. 105, of the air-dry and of the re-swollen isotropic filament. We see that isotropic filaments are exceedingly extensible (elongations up to $v > 3$ have been observed in isotropic filaments, which is more than 200% [54]). The figure at the same time affords an illustration of the fact mentioned in § 1, viz., that a certain point of state in the SS diagrams

[49] *K. C. Brown, J. C. Mann* and *F. T. Peirce*, J. Text. Inst., 21, (1930) 187.
[50] *C. S. Venable*, J. Physic. Chem., 29, (1925) 1237.
[51] *S. E. Sheppard and E. K. Carver*, J. Physic. Chem., 29, (1925) 1244.
[52] *H. R. Bellinson*, Textile Research, 10, (1940) 372.

may be reached in totally different ways. It furthermore shows that isotropic filaments do not obey the rule commonly applicable to ordinary artificial fibres, by virtue of which the BS is higher in the dry state than in the wet; indeed, in this case we have the reverse, for the filament with the highest degree of swelling also has the highest *BS*.

We shall see presently that the relatively low BS of air-dry filaments is due to the fact that these filaments break at a lower degree of orientation than the highly swollen specimens. Fundamentally, this again results from the fact that far greater resistance is opposed to the internal displacements of the fibrous substance necessary to the process of orientation, in the dry state, and the stresses required to overcome it there upon exceed the bearing strength of the filament. In a manner of speaking, the process of orientation consequently comes to an "untimely end". Were it not for this „complication", theoretically the curve of the airdry filament should also reach much farther and finally bend so far to the right as to surpass the *BS* of the swollen fibre. Yet, with filaments preliminarily elongated in the highly swollen xanthate state, and then dried, the dry *BS* is always greater than the wet *BS*, just as it is with the corresponding technical filaments (cf. Fig. 105).

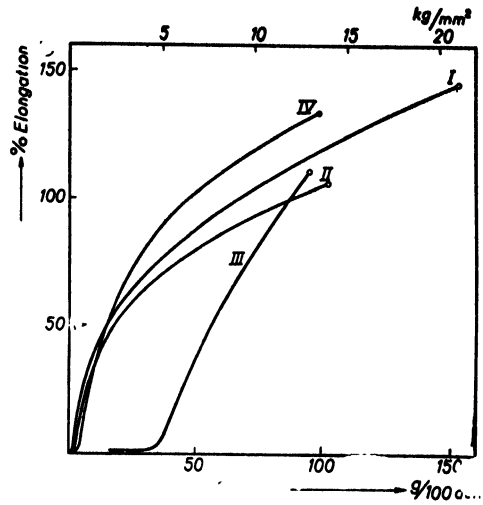


Fig. 108. SS curves of isotropic model filaments at various degrees of swelling q. I xanthate filaments (q = 13); II fresh cellulose filaments (q = 6.0); III air-dry filaments (q = 1.17); IV filaments re-swollen after drying (q = 2.4). (Stress referred to filament-denier at the time.) 0 = breaking point. (Degree of swelling q referred to the absolutely dry state).

P. H. Hermans [55] claimed some time ago that the SS curves of the swollen filaments in Fig. 108 can be represented at a first approximation by hyperbolas and that with respect to them the stress (according to an obvious mathematical assumption) runs roughly in inverse ratio to the square of the sinus of the mean angle of orientation α_m (Chap. IV, § 6.4) [56].

The use of a more reasonable measure of extension does away with the peculiar crossing of the curves in Fig. 108 (*P. H. Hermans*, loc. cit.) [57].

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[53] The degree of swelling = ratio of volume of swollen, to that of absolutely dry filament.
[54] *P. H. Hermans* and *P. Platzek*, Kolloid-Z., 97, (1941) 329.
[55] *P. H. Hermans*, Kolloid-Z., 86, (1939) 107; Proc. Acad. Sci. Amsterdam, 42, (1939) 478; Kolloid-Z., 89, (1939) 344.
[56] There is more about this in Part III. *Y. Konisi*, J. Soc. Chem. Ind. Japan, 41 B, (1938) 439 arrived at a similar result.
[57] Further details on this too will be found in Part III. Chap. XIII.

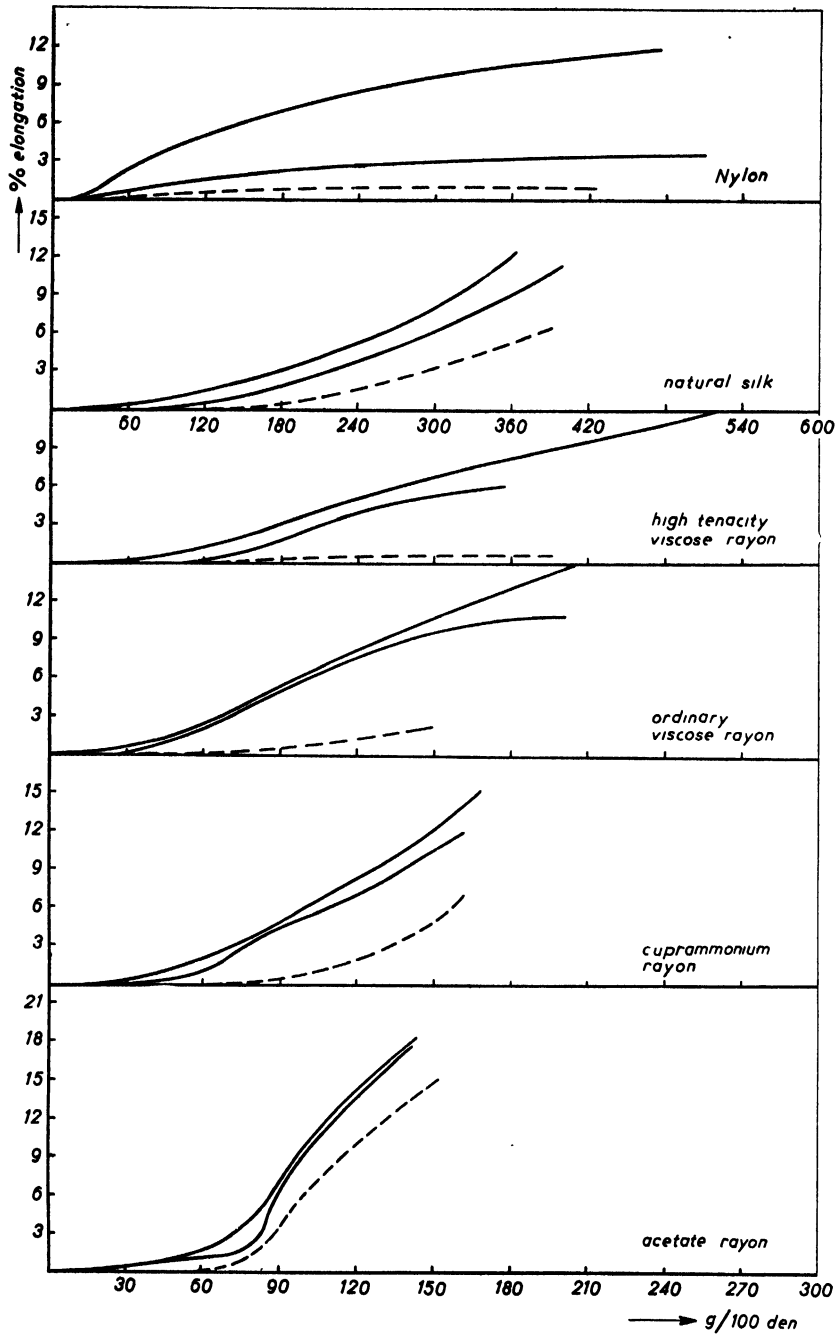


Fig. 109. **Recovery after load lifted and retraction after swelling** in water for the fibre specimens represented in Fig. 104. Upper full-line curves: stress-strain relation taken as in Fig. 104; lower full-line curves: recovery after load lifted; .... retraction after swelling and drying at 65% r.h. (Stress for Nylon and natural silk drawn to reduced scale of 1 : 2). Stress referred to actual cross-section.

4.3. *Recovery and Retraction*

The reaction of the fibres to loading followed by release was described in the first section. Sometimes the shortening which takes place when the load is lifted, or tension relaxed, is called the "elasticity" of the fibre; but, as the extent of such shortening depends very much upon the duration both of loading and relaxation, and is not, therefore, a true material constant, we prefer to call it "recovery". Figure 109 gives the amount of this recovery of a number of fibres after varying preliminary elongations at 65% rel. hum. and at a rate of release equal to the rate of loading. (The length of the filaments was measured at what was tantamount to an endless lapse of time).

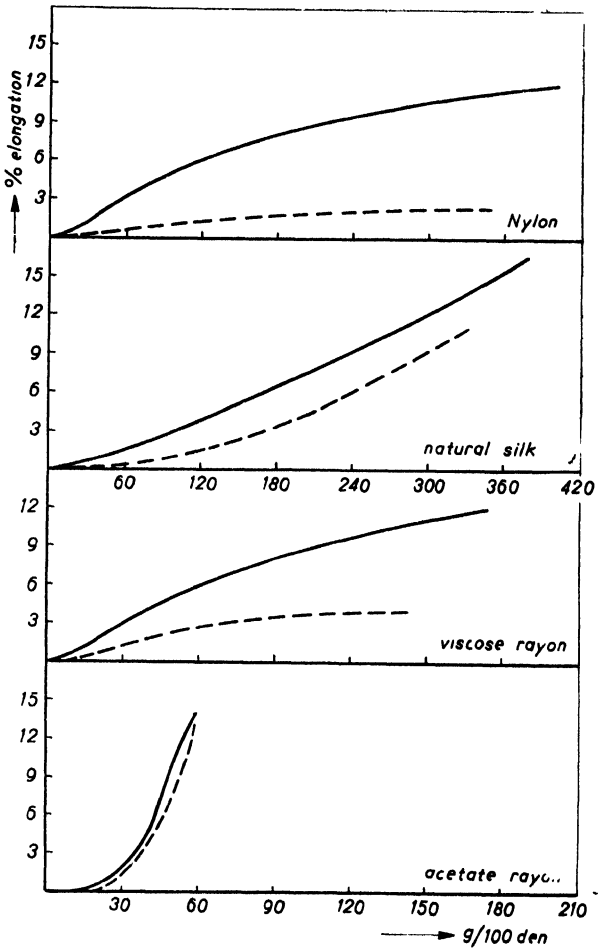


Fig. 110. Recovery of some fibre specimens after elongation in the wet state. Full curves: stress-strain relation; broken curves: recovery after lifting load. Stress given as previously (Stress for Nylon and natural silk drawn to reduced scale of 1 : 2).

It will be seen that the behaviour in this respect of the most divergent specimens is very similar. With elongations not exceeding the yield point, the recovery of silk and rayon is practically complete. Then the amount of nonreversible elongation keeps step with increasing preliminary elongation. *Frenzel* and *Hahn* constructed an apparatus designed to determine continuously this portion of irreversible elongation in rayon filaments.

Figure 110 gives us the recovery of a few specimens after elongation in the wet state, which is relatively much greater than in the dry.

In the foregoing experiments a fresh sample was taken at every degree of extension applied.

R. Meredith [58], in a recent attempt to investigate the "elastic" behaviour of fibres, followed a somewhat different procedure, which consisted in loading one given sample in successive cycles to 0.5, 1, 2, 3, 4 g per denier with total duration of stress equal to half a minute and time of recovery from the start of relaxation to reloading of 1 minute. A survey of some of his results is shown graphically in Fig. 111, where the fractional recovery from strain is plotted against the load and against the strain applied. This figure serves to illustrate the fact that no general statement as to the relative elasticity of natural and artificial fibres can be made. It will be seen that, with regard to recovery from strain, the "elasticity" of rayons surpasses that of cotton and ramie fibres, contrary to the opposite statement often met with in literature.

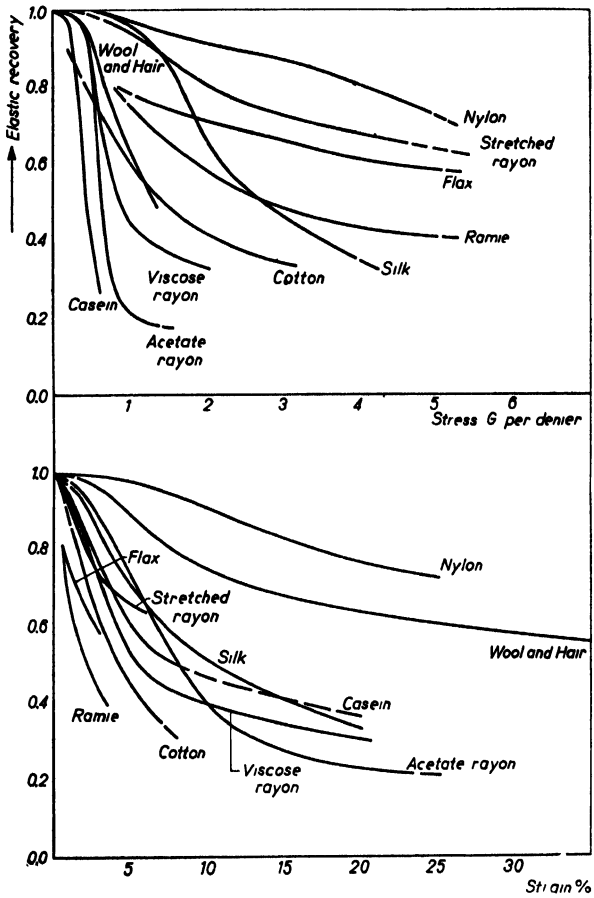


Fig. 111. Fractional recovery-stress and fractional recovery-strain curves of various fibres according to *R. Meredith.*

There is a fact, recently dwelt on by *A. Leadermann* [59], but hitherto neglected, which is very important for the light it may throw on the mechanism of deformation. It is that if Nylon, natural silk or viscose fibres are first subjected several times to strain under a weight insufficient to break them, with intervals until no further changes in length take place after loading and relaxing, it will be found that these fibres, which *Leadermann* describes as "mechanically pre-conditioned", behave like ideal elastic objects when subjected to renewed loading and relaxation tests with smaller weights than those previously used. Provided the times of test last long enough, from now on all the deformations are reversible.

The time-load diagrams now follow the size of the load in a perfectly straight

[58] *R. Meredith*, Shirley Inst. Mem., 19, (1944) 29.
[59] *A. Leadermann*, Textile Research, 11, (1941) 171.

forward way and are characteristic of the particular material concerned. In the light of these diagrams it is possible to predict the temporary behaviour of the material exactly, however complicated the sequence of loading and release. (With material of this kind, *Boltzmann's* classical principle of superposition proves to hold good to perfection).

The deformation of a filament thus mechanically conditioned is entirely comparable — even formally — with that of rubber at room temperature, there being a difference in magnitude only in the measure of time on the extension-time curve.

Leadermann calls the prolonged, but completely reversible change in shape under constant load: "primary creep", in contradistinction to the non-reversible portion of elongation of the "unconditioned" filament, which he terms "secondary creep".

Another important fact is that fibres pre-conditioned in the air-dry state having attained lasting elongation, will retract to a considerable extent if allowed to swell in water, after which they are again measured in the dry state. The broken curves in Fig. 109 show the lengths of these fibres after this passing swelling. We see that the further retraction is very substantial, only relatively slight permanent elongation remaining in the case of the higher preliminary extensions. This phenomenon is common to all the fibres (very differently constituted) shown in Fig. 109.

In practice — especially before the handling of rayon was properly understood — this property had unpleasant consequences, for if during manufacture (say, on the loom) the filament was exposed to excessive and unequal stresses, then later on, when the finished product was moistened, the filaments would shrink unevenly, thus causing unevenness of texture.

The author suggests distinguishing this shrinking after temporary swelling as s w e l l i n g r e t r a c t i o n. It is quite a common occurrence, which is bound to supervene when a fibre is raised to a higher degree of swelling than that at which the preceding deformation has taken place. It will, for instance, also be observed when highly swollen xanthate filaments, which are in equilibrium with a ten per cent. solution of ammonium sulphate, are elongated in this liquid and then, after the spontaneous recovery, are placed in a more dilute solution of salt (e.g., a 0.5 *N* sodium sulphate solution) in which they swell a little. They then shrink very considerably.

The shrinking of rayon filaments in water and caustic solution, comprehensively investigated by *W. Weltzien* [60], may be interpreted in the same way [61].

As the swelling retraction entails retrograde orientation of the fibres, it may be considered as a partial reversal of the previous process of orientation. This retrogression in orientation corresponds exactly to the retraction of the fibre (see *P. H. Hermans,* loc. cit. and Part III, Chapter VIII, § 5).

[60] *W. Weltzien,* Melliands Textilber., 7, (1926) 338.
[61] *P. H. Hermans,* Cellulosechemie, 19, (1942) 117 (also see Part III, Chap. XVII).

All these facts go to show that, *for the most part, the processes of extension and orientation in cellulose fibres are, in principle, reversible,* a circumstance which, though not directly apparent from their behaviour in loading tests, it is essential to recognise if the internal processes engaged in deformation are to be properly understood. Obviously, however, the reversal of these processes is impeded by internal resistances. These can be overcome to a greater or less degree, all according to the conditions, by allowing the deformed fibres subsequently to swell.

It should be stated in advance that the yield point also in a sense expresses the neutralization or overcoming of similar internal resistances to the mutual displacement of the elementary particles in the fibre necessary to orientation (cf. next section). Orientation does not set in until the yield point has been passed and at the same time an irreversible portion of the deformation begins to become noticeable, as the return of the particles to their original positions is likewise hampered (Fig. 109). We have already seen how the yield point is also shifted to appreciably lower stresses by swelling. Part III, Chapter VIII, § 5 and Chapter XV deal more fully with retraction and yield point.

4.4. Attempted Explanation and Mechanical Deformation Models

Many research workers have tried to find an explanation of the foregoing facts and also of the mechanical behaviour of elasto-plastic materials in general. There have been two distinctive methods of approach, viz., that by which direct correlation between the phenomena and molecular-mechanical theories has been attempted, and that resting on the representation of the perceptible behaviour of the objects by coarse mechanical models. Though the former is more compatible with the ultimate aim, the second is no less indispensable and instructive, since it is more conducive to a quantitative, mathematical description of the phenomena than the former.

We shall reserve a fuller treatment of the attempts at molecular-mechanical interpretations to the third part of this book, here only lightly touching on some of the more general points of view, after which we shall turn our attention to the deformation models.

The deformation of a body necessarily entails a change in the relative positions of its elementary particles. This even applies to the purely elastic extension of a piece of steel wire, when the particles return to their original position after the load is lifted. The same occurs when fibres are strained for not too long below the yield point. Elongation is then still slight; the shifting may then be explained as being the result of a lengthening of the distances between, or some other distortion of, the equilibrium of the molecules attracted by secondary valencies, or as the result of the distortion of main valency bonds. With recovery the accumulated potential energy is driven back to its initial state. This type of elasticity is similar to that of substances such as glass and metals. A co-determinant in the rate at which retraction takes place is the internal friction involved.

More extensive displacements and changes in position take place if the deformation is more prolonged or greater extension effected. They may be called internal processes of flow. We have seen that the greater deformations are also in part spontaneously reversible. Entirely different elastic elements from those previously mentioned must here come into play. As with rubber, they may conveniently be connected in thought with the changes in shape of chain molecules [62]. (Deformation reactions of this kind only take place with macromolecular substances; only in them will such changes in the shape of the molecules display striking effects).

An irreversible portion remains, however, after relaxation in deformations above the yield point. This means that a permanent rearrangement has taken place, in which the elementary particles have taken up new positions of equilibrium, very different from the original ones. These phenomena, which are characteristic of deformation above the yield point, in fibres always go hand in hand with a change in orientation, so that in this case deformation and orientation are always closely interconnected. A "memory", however, of the original condition persists, which, again, can be explained as the result of the changes that have taken place in the shape of the chain molecules and an effort to regain the original shape. Owing to weakening of the cohesive forces, like that which occurs during swelling, partial resumption of the original pattern of equilibrium can take place. Therefore, from the very beginning retraction is far greater when the fibre is elongated in the wet state (Fig. 110).

The "plastic flow" connected with orientation processes does not set in until a certain stress, which the yield point expresses, is exceeded. This stress depends, of course, upon the strength of the available cohesive forces; that is why it is also lowered by swelling. With a given load, the rate of flow depends, again, upon the internal friction. Flowing goes no further, but gradually dies away (Fig. 91), as it is in the nature of the concomitant processes of orientation that the stress necessary to attain ever further readjustments shall steadily increase and thus eventually hold the load in equilibrium. That is why ever bigger loads are needed to obtain further elongation. (Section of the SS curves after the yield point, where "strengthening" becomes apparent). In point of fact, upon repeated elongation of a fibre previously stretched beyond the yield point, the second yield point always falls at a higher stress than the first.

Several investigators have interpreted the various sections of the SS curves in much the same way. Suggestions were offered as far back as 1925 by *S. E. Sheppard* and *E. K. Carver* [63], *S. L. Bass* and *T. A. Kaupi* [64] express

[62] This does not mean to say that, as in the ideal case of rubber, the recovery here depends only on changes in entropy. The investigations of *Meyer* and *Lotmar*, cited earlier (§ 3 . 2) go to show that this is not so. Factors of energy will also be involved which, with chain molecules as cohesive as those of cellulose, are usually to be foreseen.

[63] *S. E. Sheppard* and *E. K. Carver*, J. Physic. Chem., 29, (1925) 1244.

[64] *S. L. Bass* and *T. A. Kaupi*, Ind. Eng. Chem., 29, (1937) 679.

entirely comparable views regarding cellulose derivatives. Here the so-called softeners play a similar part to that of water in cellulose: they lower the yield value and facilitate flow. *Sheppard* and *Carver* describe strengthening as "the formation with time while under stress of a metastable phase, due to the altered orientation of molecules composing the complexes which have aggregated to form the gel structure".

Recourse has been had with good effect to coarse mechanical models, consisting of suitable combinations of elastic and viscous elements, to illustrate the behaviour of plasto-elastic materials, using, for instance, springs and pistons hampered by a viscous liquid in their movements (so called spring and dashpot models). The former represent the elastic properties and the potential energies, the latter the internal frictional resistances. The deformation of these systems subject to load and time can then be described mathematically. The first to use models of the kind to describe the behaviour of textile fibres was *S. A. Shorter* [65].

Here we shall briefly discuss only the essential aspects of the conclusions drawn, leaving aside the mathematical treatment [66]. The two basic arrangements are shown in Figs. 112 A and 115 A. In the former case an elastic element (spring) and frictional resistance (piston with a leak in a cylinder imagined to be filled with a viscous liquid) are arranged in series; in the second case they are placed parallel. The springs should be made so that, under a load K, they undergo a relative elongation

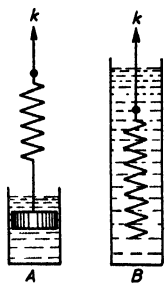


Fig. 112. Elastic and viscous element arranged in series.

$$x = aK \qquad (6.4)$$

where a is a constant characteristic of the spring (reciprocal modulus of elasticity). Let the pistons move, impelled by a force K, at a constant velocity

$$\frac{dx}{dt} = K/b \qquad (6.5)$$

where b represents a constant of friction (which might be termed the "modulus of plasticity").

Under load, the system obviously has the following properties:

1°. With loads of very short duration, only the spring comes into action and the system will therefore behave as one consisting of entirely elastic bodies. Its alteration in length is then reversible.

2°. With loads of longer duration, the piston also begins to move and in time t travels the distance $t\,K/b$ under the effect of the load. Figure 113 shows how elongation x (upper part of the illustration) proceeds under the influence of a loading K lasting from time 0 to t (lower part of figure).

[65] *S. A. Shorter*, J. Text. Inst., 15, (1924) T 215.

[66] For comprehensive mathematical treatment see *J. M. Burgers*, (1939): First Report on Viscosity and Plasticity, publisheid by the Acad. of Sci. Amsterdam, 1939.

3°. After the load has been lifted at time t, the system immediately retracts across distance aK and has therefore undergone a permanent extension tK/b.

4°. Under continuing strain deformation is unending and "flow" proceeds without let or hindrance.

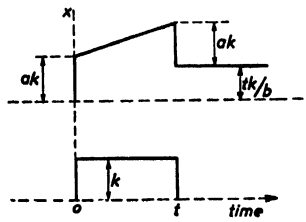


Fig. 113. Elongation x under constant load K for time t of model shown in Fig. 112.

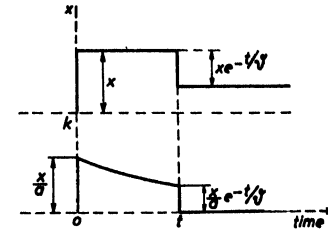


Fig. 114. Temporary tension K with elongation kept constant for model of Fig. 112 (relaxation).

It is interesting to note what happens when an elongation x is imparted rapidly to the system and kept constant for a time t. In the first instant the tension is then, of course x/a again; but then the piston begins to move, as a result of which the spring steadily retracts and the tension gradually diminishes (relaxation). It is easy to demonstrate mathematically that the tension diminishes according to the equation

$$K = \frac{x}{a}\, e^{-t/\Theta} \qquad (6.6)$$

where $\Theta = ab$, representing the time after which the tension has dropped to an e-part of the initial value. It is called the relaxation time of the system, which, as we observe, is a function of the modulus of elasticity of the elastic element, and the modulus of plasticity of the plastic element.

Theoretically, the system represented in Fig. 112A may be replaced by that of Fig. 112B, where the two elements are united into one, the spring itself being imagined as embedded in a viscous fluid. If a force K acts upon the spring, it is dragged through the viscous fluid and, as a result, of course, is drawn out. Though this picture more truly corresponds to the actual state of things in elasto-plastic materials, it involves some, not very serious, complications for quantitative treatment of the data.

The illustration in Fig. 112 cannot be applied to cellulose fibres, as here we do not observe any lasting flow with constant strain, but the behaviour represented in Fig. 91. The deformation of certain viscous plastic materials, like pitch, for example, is, however, in principle much on the lines of the model in Fig. 112. Another characteristic of this behaviour is that anisotropy disappears after the deformation.

Let us now consider the second, parallel arrangement of the two elements

as shown in Fig. 115A and B. The difference between Fig. 112B and Fig. 115B is that in the latter the spring is firmly attached to the bottom of the cylinder. This system obviously has the following properties.

1°. Nothing happens with strain of very short duration, as the inert piston must begin to move before the system can undergo any extension.

2°. With strain of longer duration the following takes place. The piston begins to move, but its speed gradually decreases as the spring absorbs a progressively larger part of the force bearing on the piston. Calculation shows that the elongation of the system in t time amounts to

$$x = aK\,(1 - e^{-t/\Theta}) \qquad (6.7)$$

After infinite time the system comes to rest and becomes $x = aK$ (for which see Fig. 116, which is arranged in the same way as Figs. 113 and 114). Here Θ is again the relaxation time of the system.

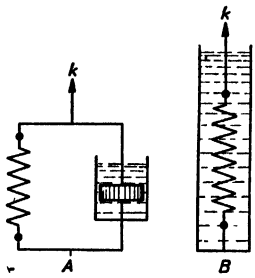


Fig. 115. Elastic and viscous element arranged parallel.

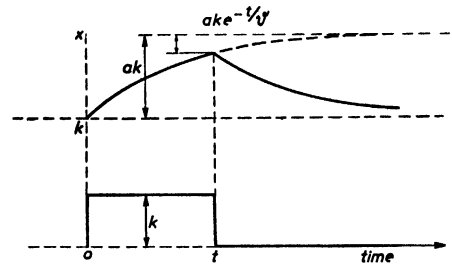


Fig. 116. Elongation x with constant load K for time t of model represented in Fig. 115.

3°. If the load is lifted at time t, the system slowly retracts, and again with diminishing rapidity. After an infinite time the initial state is re-established (Fig. 116), the spring is no longer stretched, but has returned to its original length. Hence the deformations are completely reversible; they are merely delayed by internal friction.

4°. With unending strain, elongation, which is approached asymptotically, is always limited.

It will be seen that the system we have just reviewed already shows more resemblance to the behaviour observed in textile fibres. Indeed, a fibre "mechanically pre-conditioned" as described by *A. Leadermann* [67] (cf. §4.3) comes very close to it. The behaviour of ordinary fibres, however, differs from it in many respects, viz.,

1°. Even with strain of very short duration a certain amount of elongation takes place. It is not till later that further elongation of the type shown in the upper part of Fig. 116 proceeds.

[67] *A. Leadermann*, Textile Research, 11, (1941) 171.

2°. The elongation-time curves with constant load (as shown in Fig. 91) cannot be exactly represented by formula (6.7); that is to say, we are not dealing with such simple systems with only one relaxation time, or with only one kind of plastic elements. *H. Holzmüller* and *E. Jenckel* [68] have shown that analysis of the elongation-time curves will reveal whether one, two or more relaxation times are proper to the system, and by such analysis it has been found that the true behaviour of cellulose fibres can be represented satisfactorily with two independent relaxation times.

3°. We have a yield point in cellulose fibres. Flow (the shifting of the piston) comes into the picture only as from a certain minimum load).

4°. The retraction when the load has been lifted is not complete. There remains a lasting elongation (which, however, can for the most part be made to retract by swelling).

It is quite feasible to build up a model taking these four points into account, by combining several springs and pistons and other elements, of which we shall speak directly. This is not just an entertaining pastime, but it helps us to form a better quantitative idea of the mechanical behaviour of fibres. Then the molecular mechanical theory of structure to be developed later will have to take this behaviour, so difficult to describe or to survey into account.

We already know that we must not have in our better adapted model a piston arranged in series to which a spring is not parallel, as there is no unlimited flow. The above four points can be allowed for as follows, for which see Fig. 117 where the definitive system is reproduced [69].

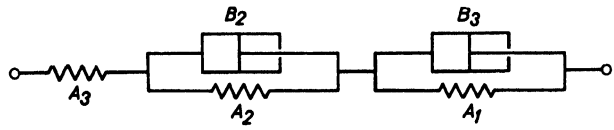


Fig. 117. Model designed to illustrate the elasto-plastic behaviour of rayon fibres (see text).

Re Point 1. A "free" spring A3 is arranged in series. It accounts for the immediate, almost unretarded extension brought about by short strain.

Re Point 2. Instead of a system of the type represented by Fig. 115 two are arranged in series (A_2B_2 and A_1B_1), each with different constants a and b, i.e., with different relaxation times Θ_2 and Θ_1.

[68] *H. Holzmüller* and *E. Jenckel*, Z. angew. Chem., 53, (1940) 214; Z. phys. Chem., A. 186, (1940) 359.

[69] The author is indebted to extensive theoretical and practical research by *Dr. Vreedenberg* (N.V. Research, Arnhem), which greatly stimulated the execution of this plan. *H. A. Vreedenberg*, J. Polymer Sci., 1, (1946) 329.

Re Point 3. With suitable constants, the system as depicted in Fig. 117 can correctly represent at a first approximation the SS curves as from the yield point. To represent the behaviour before the yield point, it has to be assumed that, at the very beginning of the test, spring A_2 was stretched a certain amount, but that its spontaneous recovery was prevented by some obstruction. This spring does not come into action until tension brought to bear upon it exceeds that at which the spring remained stationary before. As we shall see later (Part III, Ch. XV), this assumption is closely associated with the pre-orientation of the fibre at the beginning of the extension test.

Re Point 4. Here another assumption with respect to system 2 of Fig. 117 comes to our aid, viz., that spring A_2 only party retracts after the load has been lifted and that it is again brought to a standstill (is obstructed) when reaching a certain tension on its way back[69a].

A fibre mechanically preconditioned in the *Leadermann* sense exemplifies the system of Fig. 117, where deformation is confined to the area between the obstruction limits of system 2. For this reason the reaction of such fibres to deformation is a good deal simpler. In form it is wholly comparable to that of vulcanized rubber at room temperature, there being only a difference in magnitude where the measure of time is concerned on the elongation-time curve with constant load (and after lift of load).

The lasting elongation of an ordinary cellulose fibre is of a radically different nature from that proper to the system represented in Fig. 112. Whereas here there is some elongation at the end, though no residual anisotropy (the spring in the model no longer being stretched), in the other case the anistropy imparted to the system during the process of extension partly persists (a stretched, but obstructed, spring remains). There is an undoubted connection between this residual anisotropy and the permanent elongation, both in the model and in reality.

If the obstruction is removed from the spring, there will be further retraction of the system as time goes on. We see this effect in the form of swelling retraction and this also shows us that the states and conditions of obstruction of the springs must stand in close relation to the intermolecular forces of cohesion.

We shall reconsider this matter when we come to discuss molecular mechanical models (Part III, Chap. XV). All we shall say here is that the analysis of air-dry cellulose fibres gives us for system 2 with obstruction a relaxation time of the order of only a few (1 — 2) seconds, and for that without obstruction, of the order of about 4 to 5 minutes. Thus system 2 deals principally with

[69a] *(Note added in proof)* Also see the recent paper by *Vreedenberg*, cited on p. 297.

relatively rapid deformations and system 1 accounts for the likewise noted, far more protracted after-effects [70].

Finally, we may here introduce some ideas which have some bearing on the molecular mechanical theory. There are two kinds of "flow" in an elasto-plastic substance. When elements of the nature of Fig. 112 form constituent parts of the system, we shall refer to m a c r o f l o w. Such systems no longer contain stretched elastic elements after deformation and after a sufficient lapse of time; nor does their elongation definitely go hand in hand with the elongation of the elastic elements.

We shall speak of m i c r o f l o w when no elements of the kind represented in Fig. 112 occur (as, for example, in Fig. 117). Some "flow" admittedly takes place during the deformation, but it is limited to certain structural elements, in the main, the original coherence perseveres, even if permanent elongation has taken place. In this case there will always be deformed elastic elements present and the elongation is clearly interrelated with the elongation of these elastic elements.

Liquids and many so-called plastic materials, such as pitch, invariably display macroflow, while vulcanized rubber is a typical example of pure microflow. As we have seen, the behaviour of artificial cellulose fibres also points in the first place to microflow. There might conceivably also be combinations of the two kinds of flow.

The "sliding-off mechanism" in the deformation of fibres, as discussed in section 3.2, would correspond to macroflow. A substance which at first exhibits only microflow might quite possibly also give signs of macroflow after very heavy deformation.

§ 5. THE EFFECT OF LIQUIDS OTHER THAN WATER

We have only two publications on this subject; one, Japanese, by *S. Iwasaki* and T. *Miyamoto* [71], and one by *K. Lauer* [72]. It is the more difficult to assess these investigations, in that the reactions liable to result from the immersion of cellulose fibres in non-aqueous liquids are not easily followed, especially if, as in this case, exact details of experimental procedure are lacking. When air-dry fibres are immersed in dry organic liquids, the water content of the former is apt to change, particularly if they are dehydrating liquids. That alone would distinctly affect their mechanical behaviour. Operating with dry fibres, it is exceedingly difficult to guard against the effects of the unintentional importation of small amounts of water. Judging by measurements of the heat of sorption, only the lower alcohols, up to propyl alcohol, and

[70] For another recent approach introducing spring and dashpot models having less simple properties, see *G. Halsey, H. J. White* and *H. Eyring*, Textile Research J., 15, (1945) 295, and later papers in that journal by *Eyring* et al.
[71] *S. Iwasaki* and *T. Mijamoto*, J. Soc. Chem. Ind. Japan, 41 B, (1938) 222.
[72] *K. Lauer*, Kolloid-Z., 107, (1944) 93.

possibly also the lower fatty acids, may be expected to penetrate into the dry fibres. Moreover, the author's study of the penetration of water and glycerol into cellulose fibres (literature cf. Chap. II, p. 186) inclines him to foresee all manner of complications (time effects).

Lauer states that glacial acetic acid, pyridine and benzene reduce the breaking strength of cotton fibres and at the same time the elongation at break; artificial cellulose fibres, on the other hand, become stronger in glacial acetic acid and elongation also diminishes. *Lauer* develops a theory on fibre structure from these observations. He does not say, however, how the experiments were carried out and it would seem as if the effects observed were due merely to the withdrawal of water from the fibres; for exactly the same effects can be induced — even quantitatively — by reducing the water content (cf. § 3.3) [72a].

The Japanese publication referred to above, which was evidently overlooked by *Lauer*, provides fuller details. *Iwasaki* and *Miyamoto* after dipping air-dry and fully dried rayon into various organic liquids, determined a complete SS curve. It is not clear, however, whether effective precautions were taken against the admission of moisture during the determination and also against the condensation of water vapour when volatile substances, such as petroleum ether, were used. The lower alcohols, up to n-propanol (n-propyl alcohol), affect the SS curve in the same sense as water, which accords with the fact that, like water, these liquids are able to penetrate into the amorphous components of the fibre, except that the effect is less marked, n-butanol and n-pentanol involving only insignificant changes. Formic acid and acetic acid act like the lower alcohols. Propionic acid and butyric acid are indifferent, or else strengthen to some extent (possibly by withdrawing water). The difference between air-dry and fully dried immersed fibres comes out clearly with the higher petroleum fractions. In the former case the shape of the SS curve is scarcely altered at all, except that it becomes a little shorter (therefore strength and elongation are lower). In the second case the oils have obviously protected the dry fibres, in the sense of having prevented water adsorption. The SS curves are like those of dried-out fibres. Deviations found in the fractions of quite low boiling point are probably due to the absorption of moisture resulting from cooling during evaporation.

Thus little more emerges from the experiments than that the lower alcohols and fatty acids serve to some extent the purpose of "softeners" and that the others, which do not penetrate into the fibres, are either indifferent or, at the most, slightly impede the process of elongation, causing it to break down sooner. (Shorter SS curve, but otherwise of the same shape).

72a *(Note added in proof).* Recently this was confirmed by *G. Centola*, Ann. chim. appl., 36, (1946) 82 who repeated *Lauer's* experiments with acetic acid of 93, 96 and 100 % strength. The considerable drop in strength as obtained by *Lauer* in cotton was, however, not confirmed.

§ 6. BENDING RESISTANCE

He who grapples with the "lateral strength" of the fibres — under which head their bending strength may be said to fall — will be confronted by an even more formidable problem than that presented by their "tensile strength". Experimentally, too, it is far more difficult to handle quantitatively.

There are various types of apparatus for the determination of the "lasting bending strength" of fibres, by means of which the slightly loaded fibres are moved continuously to and fro until they break, the number of times they are bent being registered. Only relative measurements can be made with this kind of apparatus, of course, upon the construction of which the result depends.



Fig. 118. Plan for the determination of the "Loop strength"

An expedient is resorted to for rayon filaments and for staple fibre fibrillae by which the "knotting strength" — i.e., the *BS* after the thread has been knotted — is determined and expressed (in the normal *BS* as unit) as the relative knotting strength (rel. *KS*). The looping strength is similarly determined by joining two filaments as illustrated in Fig. 118. It need hardly be said that devices of this kind are only roughly informative.

It has been discovered that highly orientated fibres do not, on the whole, possess very satisfactory "lateral strength", a property, none the less, very essential to textile fibres. A first-hand example is afforded by ramie fibres, known to be very well orientated and to possess eminent tensile strength. They display a certain brittleness and a tendency to split up into fibrillæ, which constitute serious impediments to their use in the textile industry. Their lasting bending strength, or crack- and bending strength, judged as relative knotting strength, is not encouraging [73]. Cotton fibre, on the other hand, exhibits very good lasting bending strength. *H. Staudinger* and co-workers [74] report that it lies within 12000 and 20.000 complete bends (i.e., to and fro), while that of ramie is between 3000 and 4000. The average orientation of cotton fibres is known to be considerably inferior to that of ramie fibres. True, the individual fibrillæ of cotton fibres are themselves excellently orientated longitudinally, but they are arranged spirally in the fibres with a pitch in the neighbourhood of 30°.

Artificial fibres have far less bending resistance, tested by the same standards. With one exception, where 1000 to-and-fro movements were registered, the numbers recorded by *Staudinger* and co-workers for these range from roughly 30 to 200. *H. Böhringer* [75], testing single fibres of wool fibre, found

[73] See *J. M. Mathews*, Die Textilfasern, Berlin, 1928.
[74] *H. Staudinger* and co-workers, Ber., 70, (1937) 1565; Melliands Textilber., 18 (1937) 681; Ber., 72, (1939) 1709; Naturw. 27, (1939) 548; Melliands Textilber., 20, (1939) 693; Papierfabrikant, 36, (1939) 373, 481; Kunstseide und Zellwolle, 21 (1939) 288; Zellwolle, Kunstseide, Seide 45, (1940) 2.
[75] *H. Böhringer*, Z.f.ges. Text. Ind., 41, (1938) 218.

about 1500, as against 20000 for cotton. The values also depend, of course, upon the fibre thickness. *E. Franz* and *H. J. Heiming* give the following figures:

Polyamide fibres	> 250 000
Wool	150 000
Silk	76 000
Cotton	64 000
Staple fibre	6 800

(Experimental conditions: Angle of bend 180°, 200 bend phases/min. loading weight 1.5 kg/mm. Free length of insertion 10 mm.).

It has also been observed unfailingly in artificial fibres that first-rate orientation and tensile strength are not necessary concomitants of optimum technological serviceability. With regard to this matter we refer to the publications of *W. Schieber*[76], *R. Stoll* and *E. Rall*[77] and *H. Lohmann*[78].

We must not forget that the apparatus used for the determination of bending strength are as yet by no means perfect and that the reproducibility of the results often leaves much to be desired.

It is very tempting, of course, to probe the reason for the exemplary resistance of cotton fibre to bending. This may conceivably have something to do with the spiral arrangement of the fibrillæ. Experimenting with model filaments twisted when swollen and then dried, *P. H. Hermans*[79] was able to show that the knotting strength of artificial filaments can be greatly improved by a spiral arrangement of the textural orientation. The production, however, of this kind of texture on an industrial scale would not be an economical proposition since it would require the twisting of the single filaments on the spinning machine individually.

Torsion, in a variety of ways, provides another means of testing lateral strength, the aim being to determine the modulus of torsion and allied quantities. These tests constitute, in a way, a measure of the forces of cohesion perpendicular to the fibre axis. But the available material on this subject is very scanty.

From measurements made by *F. H. Clayton* and *F. T. Peirce*[80] it appears that the modulus of torsion for cotton fibres at 65% rel. regain is only roughly 200 kg/mm², which means to say one third to one quarter of the modulus of elasticity. It varies very much with the moisture content, being 450 kg/mm² for perfectly dry fibres and about one tenth of this value for those saturated with water. These authors also measured the modulus of bending, which again corresponds with the cohesive forces *in* the direction of the fibre, and found it to be about six times higher than the modulus of

[76] *W. Schieber*, Zellwolle 5, (1939) 266.
[77] *E. Stoll* and *E. Rall*, Melliands Textilber., 20, (1939) 783.
[78] *H. Lohmann*, Z. angew. Chem., 53, (1940) 107.
[79] *P. H. Hermans*, Kolloid-Z., 108, (1944) 180.
[80] *F. H. Clayton* and *F. T. Peirce*, T. Text. Inst., 20, (1929) T 315.

torsion. Whereas the modulus of elasticity from 25% to 100% rel. regain falls to only about 45% of its value, the modulus of torsion drops to 10%. All these observations underline the immense difference between the cohesive forces along with, and lateral to, the fibre axis and the difference in their sensitiveness to swelling, and lend added verisimilitude to our picture of the microstructure of fibres.

W. Jancke [81] applied similar tests to viscose rayon at temperatures ranging from 100° to 185°. Measurements made by *R. Auerbach* [82] suffer from the defect of an error of calculation amounting to several orders of magnitude.

We have as yet no knowledge of the interrelationship between bending resistance, knotting strength, modulus of torsion and modulus of bending, nor as between these and the microstructure of the fibre. Further exploration of this field is urgently called for, especially in view of the numerous problems besetting the study of artificial fibres.

§ 7. MECHANICAL PROPERTIES AND BREAKDOWN

It is clear that cellulose fibres must lose some of their strength after being subjected to chemical treatment which results in breaking down the molecules to shorter chains. True, not every shortening of the chain need immediately lead to measurable changes in mechanical properties; in this respect it is rather the degree of break down, and also the distribution of broken-down places (voids) within the micellar frame which will tell. If, for instance, a few chains are split up at even distances within the whole fibrous mass, or even if all the chains are broken down from 3000 to 1500 DP., this need not yet affect the strength of the fibre (cf. page 305). But considerable damage to the strength of the fibre might ensue if, in a structure as represented by Fig. 17, there were a concentration of the same amount of break-down places in the ultrafibrillar regions so easily accessible to the chemical reagent, and those critical amorphous regions which are decisive for the cohesion of the fibre.

English research workers were the first to investigate systematically the relation between fibre strength and hydrolytic acid break down. *C. Birtwell, D. A. Clibbens* and *A. Geake* [83] detected a certain relation in fibres pretreated with acid between breaking strength and viscosity in cuprammonium solution, which was to a very large extent independent of the conditions under which the acid reaction had taken place. *D. A. Clibbens* and *B. P. Ridge* [84] report that, after the action of oxidizing reagents, which in themselves caused only slight loss of strength, if any, there may be a falling off in strength in the treatment with alkaline reagents, because it is not till then that any further

[81] *W. Jancke*, Melliands Textilber., 11, (1930) 359.
[82] *R. Auerbach*, Kolloid-Z., 32, (1923) 369.
[83] *C. Birtwell, D. A. Clibbens* and *A. Geake*, J. Text. Inst., 17, (1926) T 145.
[84] *D. A. Clibbens* and *B. P. Ridge*, J. Text. Inst., 18, (1927) T 135; 19, (1928) T 389.

decrease in the DP takes place (cf. page 138). Hence the viscosity in cuprammonium solution is then indicative, not of the strength after oxidation, but of that found after treatment with alkali. *B. P. Ridge* and *H. Bowden* [85] have much the same to say about artificial fibres, but, with the same viscosity, the strength of a degraded native fibre is not the same as that of an artificial fibre.

At a later date *H. Staudinger* and co-workers [86] reported on extensive investigations into the same subject. They broke down cotton and ramie fibres in stages by acid hydrolysis or by oxidation, following as they did so the DP and the mechanical properties of their objects. It transpired that breaking strength, extension at break and bending resistance change but little so long as the DP falls no lower than to about 700-800; but below 700 these qualities deteriorate rapidly, and when the DP is less than 200 the objects are apt to crumble to powder and no longer possess the specific properties of fibre. Figure 119 presents the course of the breaking strength of degraded ramie and cotton as a function of the D.P. *Staudinger* found that, after their conversion to nitrocellulose, degraded fibrous objects likewise retain practically the same breaking strength and bending resistance, which corroborates the finding of *I Sakurada* [87] already cited.

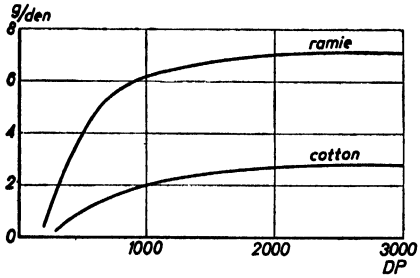


Fig. 119. Breaking strength of degraded ramie and cotton fibres subject to the average degree of polymerization (according to *E. Plötze* and *H. Person*, 1940).

Following these investigations made by *Staudinger* and co-workers, *E. Plötze* and *H. Person* [88] showed that the X-ray data of the fibrous objects are not noticeably altered by the break down in the fibre form and, therefore, that the orientation and lattice structure remain unaffected, an observation which, as a matter of fact, had already been reported earlier by *K. Hess*.

Like *Ridge* and *Bowden* [89], *Staudinger* points out that artificial cellulose fibres with a DP of between 200 and 500 possess as a rule far better mechanical properties than degraded native fibres of the same DP. An example of this is provided by Table XXXVI, borrowed from *H. Staudinger* and *J. Jurisch* [90]. *Staudinger* ascribes the inferior strength of degraded native fibres to that of artificial fibres of the same degree of polymerization to a more unfavourable distribution of the "voids" caused by the chemical action. According to this

[85] *B. P. Ridge* and *H. Bowden*, J. Text. Inst., 23, (1932) T 319.
[86] *H. Staudinger* and co-workers, Ber., 70, (1937) 1565; Melliand Textilber., 18, (1937) 681; Ber., 72, (1939) 1709; Naturwiss., 27, (1939) 548; Melliand Textilber., 20, (1939) 693; Papierfabrikant, 36, (1939) 373, 481; Kunstseide und Zellwolle, 21, (1939) 288.
[87] *I. Sakurada*, Papierfabrikant, 36, (1939) 252.
[88] *E. Plötze* and *H. Person*, Z. physik. Chem., B. 45, (1940) 193.
[89] *B. P. Ridge* and *H. Bowden*, J. Text. Inst., 23, (1932) T 319.
[90] *H. Staudinger* and *J. Jurisch*, Melliand Textilber., 20, (1939) 693.

hypothesis, once a void has been formed somewhere, it is to be assumed that any further break down will preferably proceed from that starting point. These results are shown diagrammatically in Figure 120.

TABLE XXXVI

DP, Breaking Strength (BS), Elongation at Break (EB) in Air-Dry State and Bending Resistance (BR) of some Cellulose Objects

Fibre	DP	BS g/den	EB in %	BR
Cotton (oxidized)	340	0.7	5.8	100
„ „	290	0.8	5.4	60
„ (treated with HCl)	260	0.5	2.3	30
Viscose staple fibre	520	2.2	20.7	340
Ditto oxidized	290	1.1	11.1	30
Viscose staple fibre	370	1.9	28.4	100
Viscose staple fibre	250	2.0	8.0	65
Viscose rayon	280	1.9	10.3	35
Cuprammonium rayon	440	2.1	14.3	270

Though we have the same number of "voids" in an artificial fibre of the same DP, they are more evenly distributed.



Fig. 120. Arrangement of voids produced by chemical attack in a decomposed fibre (diagram), after *H. Staudinger* and *J. Jürisch.*

Investigations by *G. V. Schulz* and *E Husemann*[91] published not long ago, and to which we have had occasion to refer more than once, may possibly help to explain why break-down seems to take place in layers, as it were. These investigators state that alien groups, with bonds very much more readily split up hydrolytically, are embedded at regular intervals in the molecule of native cellulose fibres. They then further assume that these bonds are arranged side by side in certain long-period lattice planes (cf. pages 20 and 84).

An interesting paper by *O. A. Wuorinen*[92] supports the view that, when cellulose fibres are treated with acids of a concentration which, though inducing imbibition, does not yet lead to appreciable swelling, the chain first begins to break down at certain given places. It was shown that in this case only very low-molecular products of hydrolysis (chiefly monosaccharides) are extracted, and the inference from that was that local break-down of the chains takes place, probably in the non-crystalline regions (which are the most accessible to, and the first to be reached by, the reacting liquid). As we have already seen, break-down proceeds quite differently as the result of hydrolysis in the homogeneous state (in solution), as no preference for terminal bonds is exhibited. *Wuorinen's* research nevertheless needs to be extended so as to include the distribution of chain length in the solid phase.

[91] *G. V. Schulz* and *E. Husemann*, Z. physik. Chem., B 52, (1942) 23.
[92] *O. A. Wuorinen*. Papier J., 27, (1939) 307, 322, (Norwegian); Finnish Paper Timber J., 21, (1939) 298, 329.

There is, however, another noteworthy fact — likewise observed by *Staudinger* and *Jurisch* [93] — which the above scheme of things does not directly make plain, and it is that, after the extraction of hydrolytically decomposed fibrous objects with sodium hydroxide, which is supposed to dissolve out a certain amount of the low-molecular components, the mechanical properties improve again very noticeably. As this fact might be revealing where artificial fibres are concerned, verification is called for.

H. Staudinger, M. Staudinger and H. Schmidt [94] published a short time ago some interesting discoveries respecting the decomposition of cellulose fibres by micro-organisms. Fibres taken from fishing nets which had been used for a long time and had become fragile, were found to have deteriorated very considerably in breaking strength and, when examined under a microscope, were seen to have been corroded in places. On the other hand, the degree of polymerization was still, surprisingly enough, very high (above 2000) and their bending resistance was also satisfactory. Artificial fibres exposed to the action of boggy water behaved in a similar way. Thus here again it is safe to assume that break-down of the chain preferably starts at the end groups. It looks as though these observations might also prove useful to the disintegration on a large scale of cellulose fibres preparatory to dissolving processes. *K. Schönleber* [95] has written on the morphological phenomena produced by the decomposition of cellulose fibres by bacteria and fungi.

[93] *H. Staudinger* and *J. Jurisch*, Melliand Textilber., 20, (1939) 693.
[94] *H. Staudinger, M. Staudinger, H. Schmidt*, Zellwolle, Kunstseide, Seide 45, (1940) 2.
[95] *K. Schönleber*, Zellwolle, Kunstseide, Seide 46, (1941) 336.

CHAPTER VII

CHEMICAL REACTIONS IN FIBRES

The micellar microstructure of fibres becomes noticeable in the course of chemical reactions and gives rise to a great variety of phenomena which cannot here be discussed in extenso. Roughly speaking, the following are discernible:

§ 1. MICROSCOPICALLY HETEROGENEOUS REACTIONS

These are perceptible when the fibres enter into a reaction which brings about only slight swelling, or none at all. In that case the reagent does not at first penetrate into the micellar system and the fibre is gradually attacked from outside and is converted (see the example portrayed in Fig. 43, p. 167)

§ 2. MICROSCOPICALLY HOMOGENEOUS REACTIONS

In this case the primary process is always one of swelling, which makes the interior of the fibre accessible to the reagent. This penetrates into the micellar system almost in its entirety and the reaction therefore proceeds from within. This is the commonest type of chemical reactions in the fibre form. If we consider the submicroscopic processes, we can foresee many different cases liable to be met with, all according to the conditions of reaction, all of which have been demonstrated fairly convincingly.

If pervading intramicellar swelling takes place, the reaction may seem to be homogeneous because it takes place in a one-phase system (cf. page 36). If, for instance, hydroxyl groups are being substituted, this may in that case be equally effected in all the chain molecules present so that at any moment any random section of the chain, if not too small, will exhibit the same degree of substitution. (P e r m u t o i d r e a c t i o n). Yet even here it is to be foreseen that sections of the chain bordering the larger micellar capillaries, which are therefore more easily accessible to the incoming reagent may display a higher degree of conversion than those in other places. In any case they will reach a given degree of conversion sooner.

If there is no intramicellar swelling and the reagent, though between the beams of the micellar systems, is not within them, then it will be the most exposed sections of the chains on the outside of the beams that will react (topochemical, or micellar heterogeneous reaction). In that event there are various ways in which the substituted hydroxyl groups may be distributed among the chain molecules in a given stage of reaction. The amorphous regions, or the marginal

portions of the micellar system, will be the first to react, while the reaction in the crystalline regions will at first only affect their surfaces and then gradually work inwards.

The prevailing conditions or course of the reaction can be analysed by combining stoichiometry with X-ray photographs or solution and extraction experiments. Test cases of such reactions are contained in some excellent papers published by *G. Centola*[1], who points out that often fibres incompletely esterified in the reaction as a whole are to be considered — all according to the conditions of manufacture — as mixtures of unesterified cellulose (in the crystalline regions) and triesters (in the amorphous marginal chains), though sometimes, again, they may be regarded as homogeneous. In the former case they exhibit the X-ray diagram of unesterified cellulose; in the second, either a new, characteristic diagram, or merely diffuse interferences. According to *Centola,* if native or mercerized ramie fibres are suitably acetylated so that they gradually become microscopically homogeneous, the cellulose interferences of native fibres may remain almost unchanged up to about 35% acetic acid content and those of the mercerized fibres up to as much as roughly 50%. Only after further acetylation - and then rather suddenly — do the interferences typical of triacetyl cellulose appear. The explanation which *Centola* suggests is that at first only the intercrystalline marginal chains are converted to triesters. Since the percentage of amorphous regions in the mercerized fibres is larger and the crystalline regions are, moreover, smaller, the reaction can in this case proceed much further, until the lattice structure is also altered. This view is corroborated by the fact that *Centola,* by subsequently treating the fibres which still produced the cellulose diagram with hot methanol under tension, succeeded in partially crystallizing the acetylated amorphous regions. There then appeared a mixed diagram of cellulose and triesters.

Similar phenomena had been noted before by *K. Hess* and co-workers, but a different less appropriate interpretation was put upon them.

Centola[2] affirms that, also in the xanthation of alkali cellulose (which is of such special interest to us in this book), at first only the amorphous regions react, the reaction of the crystalline regions being deferred till later (see page 336).

It will be clear from *Centola's* investigations, which we have cited here as an example, that what has been observed to happen during reactions in the fibrous form fits in excellently with current ideas respecting the structure of fibres.

For a general, fairly up-to-date survey of the X-ray data respecting reactions in the fibrous form, we refer to an article by *W. A. Sisson*[3 4], in which he also makes mention of the further comprehensive writings.

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[1] *G. Centola*, Gazz. chim. Ital., 65, (1935) 1015; Atti X Congr. intern. Chim. Roma, 1938, Vol. IV, (1938) 123, 139. Also see *D. Vermaas* and *P. H. Hermans*, J. Polymer Sci., 2, (1947) 397.

[2] *G. Centola*. Atti X Congr. intern. Chim. Roma, Vol. IV, (1938) 722, 728.

[3] *W. A. Sisson*, Ind. Eng. Chem., 30, (1938) 530.

[4] Also cf. Part I, Chapter II, § 5.

The intrinsic structure of the fibre also makes itself felt in the break-down reactions that take place in the fibrous form. It is evident from investigations by *O. A. Wuorinen*[5] that, in hydrolytic acid decomposition, low-molecular sugars are formed as decomposition products from the very beginning of the reaction. The places of cleavage are not, as they are in the course of reaction during hydrolytic decomposition in solution, evenly distributed over the entire chain according to the rules of chance, but are accumulated in certain, obviously very exposed sections. As the acid reaction proceeds, the rate at which sugar is formed at first slows down considerably, until it finally reaches a constant value. This is the very opposite of what happens in homogeneous hydrolysis, when, of course, sugar formation steadily increases.

Recently it has been demonstrated by several American workers[5a] that in hydrolysis with hot aqueous solutions of strong mineral acids a very rapid decrease of the cuprammonium viscosity sets in in the first few minutes, followed by a long period during which the viscosity remains constant or diminishes only slightly.

Nickerson and *Habrle* (cf. also below) conclude that an increase in crystallinity occurs in the first few minutes of hydrolysis, which the author could confirm by X-ray investigation (unpublished work). *Pacsu* based a rather revolutionary theory on the constitution of cellulose on similar findings.

In line with this, *O. Eisenhuth* and *E. Schwartz*[6] were able to show that the rate at which the DP diminishes at the beginning of the acid reaction increases in the following order: native fibres, mercerized native fibres, regenerated fibres; which means to say that the looser the structure and the larger the portion of amorphous substance, the greater will be this rate. In time this velocity will be observed to slow down; but, if treatment of the fibres with strong sodium hydroxide is interposed, it increases again to the original rate, the reason for this being that the caustic solution has further loosened and disengaged "inner surfaces".

The heterogeneous character of many reactions which, at a first glance, are homogeneous microscopically, is nevertheless often disclosed under the microscope by the peculiar way in which the fibre disintegrates (a way, moreover, which is conditioned by the morphological fibre structure), when lateral and longitudinal fissures may produce microscopic fragments of the utmost variety. (See p. 168).

Many attempts have been made to utilize the easier accessibility of the non-crystalline portion of the fibres to chemical reactions for a quantitative computation of the amount of amorphous substance. Thus *R. F. Nickerson*[7], for example, has suggested a method by which the fibres are boiled with

[5] *O. A. Wuorinen*, Papier J., 27, (1939) 307, 322, (Norwegian); Finnish Paper Timber J. 21, (1939) 298, 329.

[5a] *E. Pacsu* (paper cited on p. 142). *R. F. Nickerson* and *J. A. Habrle*, Ind. Eng. Chem. 39, (1947) 1507.

[6] *O. Eisenhuth* and *E. Schwartz*, Die Chemie, 55, (1942) 380.

[7] *R. F. Nickerson* et al, Ind. Eng. Chem., 34, (1942) 85, 1480; 37, (1945) 592: 38, (1946) 299; 39, (1947) 1507; cf. also *H. J. Philips*, Text. Res. J., 18, (1947) 585.

hydrochloric acid, the evolution of carbonic acid being measured as a function of the time. This method is based on the fact that the impaired cellulose is speedily hydrolysed to glucose and that, under similar circumstances, glucose likewise evolves carbonic acid. *C. M. Conrad* and *A. G. Scroggie* [8] have devised an improved version of this method. *C. B. Purves* [9] and co-workers suggest a reaction involving treatment of the cellulose with thallous ethylate followed by methylation, when the quantity of bound methyl groups would provide a measure of the accessibility of the fibre.

Although methods of this kind offer a relative yardstick by which to measure the vulnerability of various fibres to certain reagents, and though it is invariably found that native fibres (with little amorphous substance) are less vulnerable in this respect than regenerated fibres (with much amorphous substance), such chemical methods cannot be expected to furnish exact information as to the crystalline-amorphous ratio. The extent to which a given chemical reaction takes place will depend, not only on the quantity of amorphous substance, but also upon the conditions of affinity of that particular reaction and upon the size of the molecules of the reagent and of the solvent [10]. It is to be expected that the figure obtained from one given reaction will be different from that obtained from another.

The divergent percentages of amorphous substance computed by the investigators mentioned are very much smaller than those derived from physical methods (see next Chapter). The latter are to be preferred, because actually the concepts "amorphous" and "crystalline" cannot be satisfactorily defined by any but physical means.

An exceptionally favourable case of a micro-heterogeneous chemical reaction in fibres, however, seems to be the exchange reaction with heavy water D_2O. According to a very recent communication by *H. Mark* et al [11], regenerated cellulose fibres exhibit a very rapid exchange reaction within a few minutes, followed by an extremely slow reaction. In native cellulose samples there is only a rapid exchange and no slow reaction could be detected.

If it is assumed that the rapid reaction takes place in the amorphous regions easily accessible to water, the exchange curves permit computation of the fraction of the accessible fibre portion in various samples. The results agree reasonably well with the figures derived by the author from other physical data (cf. next chapter). The slow after-reaction in samples consisting of cellulose II may be considered as an exchange taking place inside the crystalline regions, which is in conformity with previous findings that a small amount of water can penetrate into the lattice of cellulose II (see chapter II, § 5).

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[8] *C. M. Conrad* and *H. G. Scroggie*, Ind. Eng. Chem., 37, (1945) 572.
[9] *C. B. Purves* et al, J. Amer. Chem. Soc., 66, (1944) 59.
[10] Indeed *Purves* did find that the molecular weight of the solvent was a determining factor and tried by a method of extrapolation to obtain a result independent of it.
[11] *V. J. Frilette, J. Hanle* and *H. Mark*, Communicated at the XIth Int. Congress of Pure and Appl. Chemistry, London 1947.

CHAPTER VIII

THE CRYSTALLINE-AMORPHOUS RATIO IN CELLULOSE FIBRES

§ 1. GENERAL REMARKS

Frequent references under various headings have been made in this book to the differences between the crystalline and non-crystalline components of the fibres, as also to their quantitative ratio[1]. In this Chapter we shall briefly consider the matter on its own merits.

To begin with, it should be pointed out that there is in reality no sharply defined borderline between the crystalline and the amorphous portions of a macromolecular system and that the distinction hitherto made between these two states of the substance should be understood as being merely approximately descriptive.

A system like cellulose will probably contain every gradation between the state of perfect, three-dimensional order, which may justly be termed crystalline, and the other extreme of chains of quite random orientation in no order at all, possibly convoluted and kinked.

What is to be included in crystalline is a matter of definition and, even if we succeed in giving a good definition, we shall yet have to bear in mind that the non-crystalline components may nevertheless comprise a variety of structures. It is therefore by no means a foregone conclusion that the non-crystalline portion of various fibres represents an identical state. Nevertheless, this assumption has been implicit hitherto in all references to the "amorphous component", and there is no gainsaying that this may quite conceivably be an unwarranted supposition in the comparison of such divergent objects as native and artificial fibres, which may give rise to false conclusions.

For this reason, some investigators, among whom *Baker, Fuller* and *Pape*[2] deserve special mention, prefer to speak of "various degrees of lateral order".

If the terms "crystalline" and "amorphous" are to be retained, an unequivocal definition will have to be formulated of what is understood by crystalline and, if it is to be of any value, this definition will have to answer to an experimental criterion. In that case, the best definition will probably be that which is based on X-ray investigation, when the formulation would be that the crystalline

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[1] See p. 21, 148, 152, 188, 205, 237, 265.

[2] *W. O. Baker, C. S. Fuller* and *N. R. Pape*, J. Amer. Chem. Soc., 54, (1942) 776. *W. O. Baker*, Ind. Eng. Chem., 37, (1945) 246.

portion is that part of the fibre substance which gives rise to selective diffraction of X-rays. Even this, however, is not quite satisfactory, since with diminishing size of the crystallites the selective diffraction (which produces sharp diffraction maxima) gradually passes over into a more diffuse scattering. In any event it shows that minute regions of perfect order would escape this definition, despite the fact the local density of packing and the cohesive energy between the chains may be of exactly the same value in these minute regions of, say, three or four chains thick and only a few glucose residues in length, as they are in a larger crystal. If, therefore, the standard is the density, or the penetrative power of a swelling agent, the result need not necessarily tally exactly with that of the X-ray if chemical methods are employed (see final paragraph of preceding Chapter). If the inter-chain cohesive energy exhibits gradual transitions, the degree of penetration of a swelling agent, or the degree of conversion in a "micellarly heterogeneous reaction", will likewise depend upon the nature of the swelling agent or the reagent.

It will be evident from all this that as a rule physical criteria are to be preferred and that more confidence can be placed in experimental methods which are not liable to change the structure of the fibre itself.

The standard based on the sorption of water vapour, to which we appealed in Chapter II, is a border case in point which, for the reasons given above, is open to criticism, though the smallness of the water molecule and the comparatively slight swelling in the region used for this test, which is restricted to monolayers of water molecules, may be regarded as extenuating circumstances, particularly since the method is merely used for a relative computation and no attempt to deduce absolute values from it is made.

The reasonable agreement between the computation of the crystalline fractions from experiments on the exchange of D_2O in cellulose (mentioned at the end of the preceding chapter) and those deduced from various physical data also encourages belief in the reliability of sorption evidence in this regard.

§ 2. REVIEW OF THE RESULTS SO FAR OBTAINED

For reasons already given, we shall here ignore estimates of the crystalline-amorphous ratio based on chemical reactions and shall consider only the results of physical methods.

Apart from some earlier attempts, which we shall disregard, since they do not seem to have a reliable basis, the first possibly significant results are from very recent data. They represent a further development of the work by the author in collaboration with *A. Weidinger* on the contribution of the disordered fibre portion to the "diffuse background" in X-ray exposures.

A comprehensive description of the new methods of investigation would lead us too far afield and we shall confine ourselves to summing up some of the principal features[3]:

1. Radiation strictly monochromatized by reflexion was used.

[3] *P. H. Hermans* and *A. Weidinger*, J. Appl. Phys. 19, (1948) 491.

2. The total amount of incident radiation during exposure was measured with the aid of a device first introduced by *J. M. Goppel* in an investigation on the crystallinity of rubber[4]. It consists of a small miniature camera, located at the centre of the film, containing an inorganic substance irradiated by the pencil of X-rays transmitted by the cellulose and yielding a comparison interference near the centre of the film. This device provides a measure of total incident intensity.
3. The fibres were exposed to the radiation in the form of pellets of constant dimension and density, consisting of single fibres randomly orientated. This permitted control of radiation absorbed and elimination of all orientation effects.
4. Radiation scattered by air was quantitatively accounted for and the background intensity was also corrected for the components not specifically belonging to the disordered portion. (Compton radiation and radiation due to the thermal agitation of the atoms).

The Goppel device permitted reduction of the intensity measurements to equal intensity of incident radiation.

The exposures obtained consisted of a number of interference rings exhibiting uniform intensity and width over 360° and superimposed on a diffuse background.

A typical photograph is shown in Fig. 120 A.

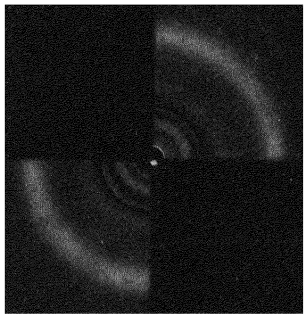


Fig. 120. A. X-ray photograph of a "randomized" rayon pellet as used for quantitative computation.

Two quadrants of the film were covered by lead sector plates and were not exposed. They show, by contrast, the existence of a diffuse background in the exposed quadrants. The

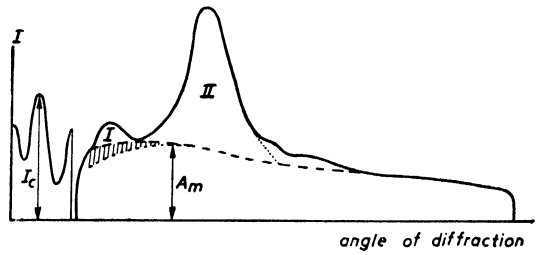


Fig. 120 B. Radial photometer curve corresponding to Fig. 120 A. Left-hand part refers to comparison substance; right-hand part to cellulose.

interference seen inside the small central ring is the Goppel-comparison interference of the inorganic substance in the auxiliary miniature camera.

Fig. 120 B shows a radial photometer trace taken from one of the exposed quadrants.

At the left is seen the comparison interference I_c from the miniature camera. It serves as a measure of absolute intensity. The right-hand part of the curve refers to the cellulose. It consists of two peaks I and II corresponding to the 101 and the (101) + (002) + (021) interferences respectively (cf. chapter V p. 253), superimposed on the diffuse background (indicated by a broken line). After subtraction of radiation scattered by the air in the camera (hatched area) the background, associated with the disordered or amorphous fibre portion, is seen to exhibit a flat maximum.

The height A_m of this maximum (corrected for *Compton* and thermal scattering) is considered as a measure of the fraction of disordered cellulose,

[4] *J. M. Goppel*, Thesis Delft 1946; Appl. Sci. Res. A 1 (1947) 1, 18.

whereas the integrated intensity (total surface) of the crystalline interferences above the background, designated as I_{cr}, is considered as a measure of the crystalline fraction.

It was found that the total integrated intensity of all scattered radiation (total surface under the photometer curve minus hatched area) was constant within the experimental error (10—15%) for all kinds of cellulose, as it should be on theoretical grounds [5].

In table XXXVII the values found for I_{cr} and I_m are listed for a number of fibres. All the figures are reduced to an equal value of I_c and expressed in arbitrary, but, for each single quantity, mutually comparable units.

TABLE XXXVII

Relative X-ray intensity of the crystalline peaks and the amorphous background observed in various cellulose samples, expressed in arbitrary units.

Sample		I_{cr}	I_m
A.	*Native cellulose*		
	Standard cotton	1.95	0.28
	Native ramie	2.07	0.27
	Purified flax	2.03	0.28[5]
	Bleached linters	1.80	0.28
	Average	1.98	0.28
	Sulphite pulp	1.88	0.34
	Bacterial cellulose	1.19	0.58[5]
B.	*Mercerized or regenerated cellulose*		
	Viscose staple	1.10	0.58
	Rayon (low orientation)	1.11	0.56[5]
	Rayon (high orientaion)	1.05	0.54
	Tyre cord rayon	1.15	0.57[5]
	Cellophane	1.21	0.54
	Lilienfeld rayon	1.08	0.58
	Cuprammon. rayon	0.97	0.54
	Average	1.10	0.56
	Fortisan rayon	1.08	0.49
	Mercer. ramie	1.25	0.47

The data from some native and regenerated samples which may be considered

[5] Cf. *A. H. Compton* and *S. K. Allison*, X-rays in theory and experiment, v. Nostrand, New York 1935, p. 189, 190.

as constant within the experimental error (samples which, moreover, exhibit almost equal sorption of water vapour) have been averaged in the table.

In the series of regenerated celluloses all rayon samples (including Lilienfeld and Cuprammonium yarn) have practically equal values of A_m as well as of I_{cr}, no matter what their degree of orientation. The only exception is Fortisan (a yarn produced by saponification of highly stretched cellulose acetate fibre). It exhibits a somewhat lower A_m value (though I_{cr} is not correspondingly higher).

In the native fibres I_{cr} is considerably higher and A_m lower than in rayon. Sulphite pulp from wood is sligthly less crystalline. Bacterial cellulose falls well within the range of rayon, this being the first example of a cellulose with the spectrum of cellulose I having so large an amorphous fraction.

These results are in general conformity with expectations based on other physical data. In other work (see Chapter II § 5) it has been postulated that the sorption ratio is proportional to the percentage of amorphous substance. It is of interest that the sorption ratios calculated from the X-ray data by taking the ratios of the A_m-values tally well with those actually observed. This is demonstrated in Table XXXVIII A.

TABLE XXXVIII A

Sorption ratios calculated from the height of the amorphous maximum and those observed experimentally

	Calc.	Obs.
Woodpulp	1.2	1.2 —1.3
Rayon (viscose)	2.0	1.95—2.02
Fortisan	1.75	1.64
Mercerized ramie	1.68	1.60

From the figures tabulated in Table XXXVII it is also possible to compute the absolute crystallinity figures. Let the fraction of crystalline substance in native and regenerated cellulose be x and y respectively, then it follows from I_{cr} that $x/y = 1.98/1.10 = 1.80$. This figure requires correction for a necessary integration along the Debye-Scherrer circles and then becomes 1.88. Another correction necessary owing to the different water content of the specimens during exposure reduces this to 1.78.

From the ratio between the A_m values (28/56) we find $(1-x)/(1-y)$. Hence we have:

$$x/y = 1.78 \qquad (1-x)/(1-y) = 0.50$$

Assuming a probable error of plus or minus 3% in both ratios, we obtain from these equations

$$x = 0.69^5 \pm 0.02 \qquad y = 0.39 \pm 0.03$$

These figures are in satisfactory agreement with previous estimations from other physical data. (See Table XXXVIII B).

TABLE XXXVIII B

Crystalline fraction in native cellulose and rayon derived from various physical data

	native fibres	rayon
a. Sorption isotherms [6]	0.68	0.35
b. Density determinations [7]	0.60	0.25
c. Optical and X-ray orientation.factor [8]	——	0.40
d. Recrystallization of amorphous cellulose [9]	——	0.35
e. X-ray data	0.70	0.39

[6] According to a recent paper by *A. J. Hailwood* and *S. Horrobin* and a comment upon it by *D. Vermaas*, Trans. Faraday Soc. Gen. Discussion on Swelling and Shrinking, London 1946 (in the press). cf. Chap. II § 5.
[7] Cf. This Part Chapter III § 2.
[8] Cf. Part III Chapter XI § 3.4.
[9] P. *H. Hermans* and *A. Weidinger*, J. Amer. Chem. Soc., *68*, (1946) 2547).

All the physical methods listed seem to give the correct order of magnitude. The figures arrived at by means of chemical methods (see Chap. VII § 2), on the contrary, vary considerably.

The figure listed under d) in Table XXXVIII B followed from experiments on the heat of recrystallisation of a 100% amorphous cellulose powder obtained by dry grinding of woodpulp and rayon. This quantity was deduced from the difference between the heat of wetting of the amorphous powder and that of the product recrystallized in hot water. (cf. p. 190 and 517).

Some further interesting deductions were made from the relative intensities of the two main crystalline peaks (see Fig. 120 B). In native cellulose the experimentally determined intensity ratio of the two peaks is close to that following from *Andress'* theoretical calculations based on the accepted cellulose I lattice. In rayon the averaged ratio is about three times higher than the theoretical one and, moreover, varies from sample to sample.

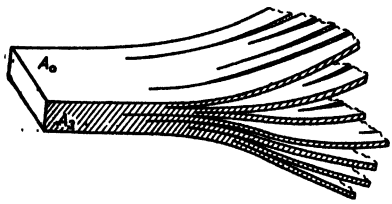


Fig. 120 C. Diagram of cellulose crystallite and its gradual transition into disordered regions.

The cellulose II crystallite (Fig. 77 and Fig. 120 C) is shaped like a flat ribbon (see p. 252) and with some degree of approximation the first peak corresponds to the "top planes" (A_o) and the second peak to the "side planes" (A_s) of the ribbon.

The top plane is the one carrying the densest population of hydroxyl groups and it represents a preferential cleavage plane. It is also the plane whose lattice constant and sharpness of line is always first affected when cellulose is exposed, either to intramicellar swelling agents, or to chemical substitution reactions in fibre form. Shift of position, line broadening or decrease in total

intensity of the first peak almost invariably precedes changes of the second peak.

On the other hand, if we consider the gradual transition of a crystalline region into the molecular fringes constituting the disordered regions (see the right-hand part of the diagram shown in Fig. 120 C), there is no necessity to assume that the disturbances of lateral order in the A_0 and A_3 directions run exactly parallel. On the contrary, it seems reasonable to assume that order in the A_0 direction is sooner destroyed than that in the A_3 direction. (In Fig. 120 C this has been expressed by drawing more horizontal than vertical fissures).

Since the integrated interference intensity at random orientation is primarily a function of the fraction of relevant spacings having the correct value, it will be clear that in such a structure the relative A_3 intensity may be enhanced as compared to the A_0 intensity. States of two dimensional lateral order may thus bring about a shift of the normal intensity ratio of two interferences holding for one large, three-dimensional crystallite.

These considerations may serve to broaden our concept of "crystallinity" in macromolecular systems and to support the point of view recently expressed by *Baker, Fuller* and *Pape*[2], in particular, who prefer to speak of degree of lateral order rather than of degree of crystallinity.

Obviously, when considering the total integrated intensity of the crystalline peaks a measure of the crystallinity, what we actually measure is the fraction exhibiting lateral order, either in three or in two dimensions. It is in this broader sense that we should think of crystallinity in fibres. It is not surprising that the fraction so computed is not very different from that derived from sorption data, though exact equality is by no means a necessary condition.

Finally, we wish to stress once more the particularly striking fact that *all physical evidence indicates equal degree of total lateral order in all rayons thus far investigated,* including highly orientated tyre cord yarns, Lilienfeld and cuprammonium rayons, with possibly the single exception of Fortisan[10]. Between "crystallinity" and orientation there seems to be little, if any, correlation. This fact seems to be significant, though difficult to explain[11].

[10] It should be added that the conclusions arrived at by chemical standards, though leading to different absolute figures, may appear to be no different, as, for instance, in the investigations recently published by *E. L. Lovell* and *O. Goldschmid*, Ind. Eng. Chem., *38*, (1946) 811.

[11] Note added in proof. For an appendix to this chapter dealing with some further data obtained during the printing of this book, see p. 517.

PART III

ARTIFICIAL CELLULOSE FIBRES

INTRODUCTION

The manufacture of artificial fibres — a task tackled at first empirically and perfected step by step — involves the conversion of the raw, organized material, as supplied by Nature, to a liquid that can be spun and then regenerated to a fibre possessing those qualities which the textile industry requires. Notwithstanding the enormous amount of work, both practical and research, spent on the successful development of technical processes since the birth of the rayon industry, it was not until a short while ago that a plausible scientific explanation was suggested of some of the many fundamental reactions which take place in the process.

The raw material used for the manufacture of artificial fibres is either dissolved direct by the action of a dispersing liquid (cuprammonium process), or else is first converted by chemical treatment to a cellulose derivative and then dissolved (viscose, nitro and acetate processes). Even if it may be said that the purely chemical reactions which then take place are fairly well understood in the rough at this time, yet formidable difficulties arise the moment an attempt is made to formulate the physical state of the concentrated technical spinning solutions. There is no doubt that the fibrous structure of the raw material in these dispersions is extensively degraded, but the very reverse of unanimity of opinion prevails as to the condition of the dispersed particles, their shape, their mobility and their interactions; in other words, as to the "structure" of the solution. It is scarcely surprising, then, that there should be equal uncertainty as to the fundamental processes which take place during spinning, i.e., while particles intermingled at random in the solution are re-uniting into a reconstituted, thread-like system of fibrous structure.

The structure of the spun fibres is reminiscent of that of the native fibres in many ways. They are anisotropic micellar systems in the sense defined on page 36 and the evidence of X-ray investigations is that regions of chain molecules in lattice order occur in them. We have acquired the means of controlling, within certain limits, the orientation of this micellar system and we have discovered that there is some connection between the orientation and the technologically important properties of the fibres. There nevertheless remained many elementary questions unanswered respecting the microstructure of the artificial fibres, the distinguishing features between it and that of naturally grown cellulose fibres and its relation to the technical

properties which count in textiles. Nor have we as yet by any means conclusive evidence of the processes set in motion by the dissolution of the structure of the raw material, and not completed until the structure of the regenerated fibre has been definitely formed. It was not until the last few years that a basis was found for a fairly effective scientific treatment of subjects of this class, and it is of this we shall treat in the present volume.

Although it is, unfortunately, impossible to present a rounded-off theoretical exposition of the whole field of research, for there is much that has scarcely come to fruition and a great deal more which is not yet understood, we now have some fairly well grounded connecting links and, in addition, an abundance of fresh incitements to further scientific exploration of this field of research.

In the following pages we shall not be specially concerned with the chemistry and technological aspects of the various methods by which spinning solutions are made, assuming the subject to be known, since it has already been dealt with comprehensively in several publications [1]. Instead of these, we shall bring forward other fundamental problems and results. To this one exception has been made in Chapter II, where the principles upon which the manufacture of viscose is based are briefly particularized.

The matter will furthermore be dealt with chiefly in the light of the viscose process, because it is that most commonly used in practice and also most thoroughly investigated. This entails a rather one-sided presentation which the author regrets but could not avoid, the more so because he is not qualified to deal in like manner with the cuprammonium and acetate processes.

[1] See, for instance, *W. Weltzien* and *K. Götze*, Chemische under physikalische Technologie der Kunstseiden, Leipzig 1930; *O. Faust*, Kunstseide, Dresden and Leipzig, 1931; *K. Götze*, Kunstseide und Zellwolle, Berlin 1940.

CHAPTER I

ON THE CHARACTERIZATION OF CELLULOSE AS A RAW MATERIAL FOR THE PRODUCTION OF ARTIFICIAL FIBRES

The cellulosic raw materials from which artificial fibres are produced are always preliminarily purified or subjected to a disintegrating process, whereby they are to some extent degraded. They consist of mixtures of polymerhomologous celluloses and, moreover, are contaminated by organic impurities allied to cellulose [1].

With time, a number of standards and testing methods have been evolved in actual practice, which the celluloses used as raw material for the production of artificial fibres are required to pass. We shall not discuss them in this book, but refer the interested reader to the comprehensive surveys given by *L. Hebbs* [2] and *H. Müller—Clemm* [3], where the historical development is also presented. A chart will be found in the latter, giving the recent minimum demands made upon cellulose for artificial fibres. *K. Götze* reviews the matter in his book [4] and describes in detail some of the methods of test. It need only be added that the important tests whereby the practical suitability of a cellulose is judged are not confined to physical and chemical procedures, but that often the morphology of the fibres (uniformity of fibre dimensions, presence of certain kinds of cells or fragments of cells) has also to be taken into account.

Many of the present customary tests were evolved empirically at a time when scientific knowledge of cellulose was still very scanty and the constitution of cellulose was completely shrouded in mystery. The connecting links were only gradually discovered and new tests, based on scientific discoveries, were adopted. The artificial fibre industry, however, has not as yet issued any uniform, precise specifications for the required properties of wood pulp [5]. *G. Jayme* and *Kuo-fu Chen* [6] have recently published a very interesting report on new methods of testing wood pulp for its suitability for the viscose

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1 *H. Lachs, J. Kronman* and *J. Wajs,* Kolloid-Z., 79, (1937) 91.
2 *L. Hebbs,* J. Text. Inst., 27, (1936) 169.
3 *H. Müller-Clemm,* Papierfabrikant 38, (1940) 309; Zellwolle, Kunstseide, Seide 45, (1940) 359; Z. angew. Chem. 54, (1941) 113.
4 *K. Gotze,* Kunstseide und Zellwolle nach dem Viskosenverfahren, Berlin 1940, p. 132 ff. Also see *E. E. Dorr,* Z. angew. Chem., 53, (1940) 13, 292; Kunstseide und Zellwolle 23, (1940) 93.
5 Cf. also *J. Löbering,* Kolloid-Z., 98, (1942) 186; *K. Lauer,* Papierfabrikant 40, (1942) 180.
6 *G. Jayme* and *Kuo-fu Chen,* Zellwolle, Kunstseide, Seide 48, (1943) 47.

process, in which many other new points of view on this subject are dealt with.

One of the oldest standard tests for wood pulp is the determination of its α-cellulose content, whereby is ascertained the insoluble constituent in caustic soda solution of 18 per cent. at room temperature. In practice, the soluble organic constituents thus likewise found are given the collective name "Hemicelluloses" and these, again, can be subdivided into a β- and a γ-fraction (cf. page 91). This test is a rough fractionation of the polymer-homologous mixture. The α-fraction contains the cellulose components of polymerization above approximately 150 to 200, the average degree of polymerization *(DP)* generally being somewhere between 600 and 1000. In addition to the low members of the polymerhomologous celluloses, the "hemicellulose" fraction also contains other polymeric carbohydrates and other contaminations of cellulose, such as polyuronides and pectins, also ligneous and resinous contaminations. All according to origin and preliminary treatment of the raw material the polymeric carbohydrates consist of xylans (chiefly), mannans, glucosans and galactans in varying proportions. Nor is the α-fraction always free from these accompanying substances [7].

Formerly, only cotton linters of high alpha content (97—99%) were accepted for the cuprammonium process and acetate cellulose artificial fibres; the viscose industry was satisfied with wood pulp containing 86—90% of α-cellulose.

The knowledge that the low fractions were not only valueless, but sometimes even injurious in the manufacture of artificial fibres has tended in course of time to increase the required α-cellulose content progressively. In the last few years so-called "purified wood pulps" of higher alpha content have been developed, which now satisfy the requirements of the cuprammonium and acetate manufacturers. Yet the alpha content is not the only criterion for the degree of purification [8]. Viscosity tests are, of course, applied to the suitably dissolved material to assess the average degree of polymerization, and a more exact test is the determination of the chain length distribution by some or other process of fractionation (Part I, Chapter III, § 3).

Recently, fractionation tests have become more and more customary in actual practice for characterizing pulps and for uniformity control.

Latterly more attention has also been paid to the effect of the chain length distribution upon the properties and utility of the regenerated fibres. Although the degradation, which the preparation of the spinning liquor still entails, considerably alters the chain length distribution, the latter naturally also depends upon the raw material used.

[7] For this compare, for instance, *E. E. Dörr*, Z. angew. Chem., 53, (1940) 13, 292; Kunstseide und Zellwolle 23, (1940) 93; *A. Meller*, Paper Trade J., 124, (1947) 104 (here also further literature).

[8] E.g., see *N. A. Rosenberg*, Zellstoff u. Papier 21, (1941) 184.

According to *Götze* [8] good rayon pulp should be as even as possible with respect to molecular size. Neither very long nor very short chains should occur in large numbers.

Apart from the characterization of the raw material as connected with the chain lengths, it might be interesting, from the theoretical standpoint, to know the nature of the existing end groups, or the alien groups built into the cellulose chain. The methods, however, by which these may be identified are still in the initial stages of development; nor are the technical implications as yet fully understood. The presence of carboxyl as a foreign group, for which there is now available a practicable method of identification, deserves special mention in this context. (Cf. Part I, Chapter III § 1).

Quite recently, the part played by impurities such as pentosans and hexosans in artificial fibre manufacture has been receiving increasing attention and at the same time progress has been made in the application of appropriate methods for their determination, while experience is also accumulating. Total hydrolysis of the substance and determination of the other sugars, besides glucose, present in the product of hydrolysis (xyloses from the xylans, mannoses from the mannans, etc.) facilitate a quantitative computation of the accompanying substances. In regard to this matter reference may be made to an article by *H. Koch* [9].

The chemistry of the impurities in cellulose, together with what we know of their genesis and existence in plants, is an intricate subject with as yet many open questions, into which we cannot enter here. A survey of it is to be found in a treatise by *A. G. Norman* [10]. We can do no more than mention that, according to *H. Koch,* the hexosans (glucosans, mannosans, galactosans) predominate in the hemicelluloses of conifer wood pulp, which also contain substantial amounts of pentosans (xylans), while the hemicelluloses in the pulp of deciduous trees, cereal straw and potato tops consist mainly of pentosans. The latter are known to be the easiest to identify and determine approximately because, when heated with hydrochloric acid, they produce furfural. In an article published not long ago, *P. Marpillero* [11] pointed out that a fairly high pentosan content appears to be a feature common to the starting materials for cellulose production available in those countries which have a moderate climate; it is found both in hardwoods and in straw, stems, annuals, etc., whereas it is the hexosans which predominate in Scandinavian conifers. New pulping methods will have to be evolved to turn the former to good account and the progress made in the last few years is very encouraging (see the article just mentioned by *Marpillero*).

Although some of the xylans of the ready pulp are easy to extract with the hemicellulose fraction, a portion of them often remains behind in the alpha

[9] *H. Koch,* Zellwolle, Kunstseide, Seide 45, (1940) 358.
[10] *A. G. Norman,* The Biochemistry of Cellulose, the Polyuronides, Lignin, etc. Oxford 1937. Also see: *L. E. Wise,* Wood Chemistry, Reinold, New York 1946.
[11] *P. Marpillero,* Papierfabrikant 40, (1942) 9.

cellulose fraction. Thus *E. Correns*[12] reports on a beech pulp with 90% alpha cellulose which still contained 20 to 30% of pentosan. *E. Schmidt* and his collaborators[13] are of opinion that in beechwood pulp the xylan is built into the cellulose chains. They suggest that there are alternate rows of glucose residues and xylose residues at regular intervals. The configuration of the xylose residue is very similar to that of the glucose residue, from which it differs only in that the CH_2OH group at the fifth C atom is replaced by hydrogen. It may be supposed to be formed by oxidation of the former to a carboxyl group, followed by decarboxylation while splitting off CO_2 and might easily fit into the cellulose lattice. Other investigators favour the theory of short xylan chains which, by some process of mixed crystallization, are built into the cellulose lattice and are therefore difficult to extract[14].

There is as yet no unanimity as to the part played by the substances accompanying cellulose upon the properties of the artificial fibres, this question having only recently been raised and being therefore still in the melting pot, as it were. To put it in a nutshell, we may perhaps be allowed to say to-day that there is no necessity for the complete elimination of the substances collected under the name of "hemicelluloses", however exacting the claims made upon the manufactured artificial fibres, and that it is only above a given percentage that these substances may be troublesome. We must qualify this statement by adding that the admissible percentage of pentosans is materially lower than that of hexosans.

According to *H. Lindpainter*[14a] pulps containing over 8 per cent. pentosans are unsuitable for the manufacture of viscose rayon. Normal figures in ordinary rayon pulp are 3—4.5 per cent. (of which one third to one half is in the α-cellulose fraction) and it seems to be impossible thus far to remove the pentosanes completely in processing pulp. Pulps with high pentosan content generally, cause difficulties in viscose filtration. It is, however, by no means certain that the pentosans as such affect filtration. *G. Jayme* asserts that the pentosan content is only a figure indicative of the efficiency with which the pulp was processed. The deleterious effect of poor processing is poor reactivity of the fiber in the viscose process (cf. Chap. II § 1.5).

There remains the revolutionary theory propounded by the American *W. K. Farr* respecting the structure of fibres, to which reference was made on page 28. In recent years she and her co-workers have published numerous articles on the subject. According to this theory, pectins play a very important part as an essential binder (interlinking substance) for the fibrous property between crystalline cellulose particles of microscopic size. This theory may be regarded as having been refuted by recently published articles from the

[12] *E. Correns*, Z. angew. Chem., 54, (1941) 363.
[13] *E. Schmidt* and co-workers, Cellulosechemie, 13, (1932) 129; Papierfabrikant, 31, (1932) 138.
[14] *W. T. Astbury, J. M. Preston* and *A. G. Norman*, Nature, 136, (1935) 391.
[14a] *H. Lindpainter*, Melliands Textilber., 23 (1942) 229.

pens of *R. L. Whistler, A. R. Martin* and *M. Harris*[15] and also of *C. W. Hock* and *M. Harris*[16]. These were able to prove that the elimination of the pectin substance from cotton fibres does not noticeably alter either the strength or the viscosity of their solution in cuprammonium. They were moreover able to show that *Farr's* "cellulose particles" are artefacts which are liable to be formed from the cuprammonium solution itself, even in the absence of cellulose.

As to the theory respecting the processes which go to the formation of artificial cellulose fibres, it is important to note that, whereas the possible adverse effect of cellulosic impurities is discussed, their presence is by no means considered in any way essential to the production of good fibres. For, under proper conditions, good fibres can be successfully spun from entirely pure cellulose objects. Hence, taking the fundamentals, and, above all, resisting all technical bias, we may look upon the *raw material in question as a mixture of polymerhomologous celluloses distinguishable by its chain length distribution, having a given, though admittedly not fully known and exactly definable, supermolecular structure.* Uncertainty still prevails as to the function of the end groups, or other alien groups, and as to whether chemical cross links do or do not exist between the individual chains.

[15] *R. L. Whistler, A. R. Martin* and *M. Harris*, J. of Research Nat. Bur. of Standards (Washington) 24, (1940) 555; Textile Research, 10, (1940) 269.
[16] *C. W. Hock* and *M. Harris*, J. Res. Nat. Bur. Standards (Washington) 24, (1940) 743.

CHAPTER II

VISCOSE

§ 1. BRIEF ACCOUNT OF THE PROCESS OF VISCOSE PRODUCTION

1.1. *Introduction*

Viscose production comprises, essentially, three stages, viz., the conversion of the initial cellulose to alkali cellulose (sodium cellulose) by the action of sodium hydroxide, the conversion of the alkali cellulose to cellulose xanthate by the action of carbon bisulphide (sulphidation) and, finally, the solution of the xanthate in water, or dilute sodium hydroxide, to viscose. Intervals are allowed between mercerization and sulphidation, as also after solution and before spinning the viscose, such being known in practice as alkali cellulose ageing and viscose ripening.

There is extensive literature on the processes underlying viscose production, but it is not within the scope of this book to present this matter in all its details; we shall therefore merely pass its main features in brief review. A list of selected publications dealing more comprehensively with the subject is appended to this Chapter [1].

1.2. *Mercerization and Ageing*

The reactions between cellulose and alkali hydroxides cover a wide and, in many respects, highly complicated range of phenomena which, because of their practical importance, have been subjected to very searching enquiry.

Cellulose absorbs sodium hydroxide solutions, swelling as it does so. As the concentration of the sodium hydroxide increases, the degree of swelling (the proportion of the volume of swollen to that of the unswollen substance) passes through a maximum at 2—3 molar solutions. The level and exact position of the swelling maximum depend upon the nature and quality of the object and also upon the temperature. These conditions have recently again been carefully investigated by *G. Saito* [2]. Regenerated and modified celluloses swell more than do native celluloses.

Owing to partial solubility, the treatment of cellulose objects with caustic soda solutions always involves loss of weight, a fact which is closely associated

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[1] The nature of the present description calls for the citation of only a few original publications in the text.

[2] *G. Saito*, Kolloidchem. Beih. 49, (1939) 365; J. Soc. Chem. Ind. Japan, 43, (1940), 126, 170, 227.

with the chain length distribution in the object. The dissolved components are fractions of short chains, their quantity depending upon the concentration and temperature of the swelling agent. Solubility increases as the temperature drops and the optimum solubility coincides approximately with the swelling maximum.

As was stated in Part I, Chapter V, there is a very real difference between native and regenerated cellulose of the same average chain length, where solubility in alkalis is concerned, in that regenerated objects can be dissolved completely if the caustic solution is of the right concentration and temperature.

Above a given concentration of sodium hydroxide, which at 20° is in the neighbourhood of 13% NaOH for native cellulose, X-ray data show that intramicellar swelling sets in and the lattice of a compound is formed which in the literature, is described as Sodium Cellulose I (page 24). Apart from this compound, a number of other sodium celluloses have been described, which are formed under different conditions of concentration and temperature, each of which produces a different X-ray diagram. Borrowing from *H. Sobue, H. Kiessig* and *K. Hess* [3], we show the zone of existence of these compounds in Fig. 121 [4]. It must be admitted that the boundaries indicated are not always equally reproducible, as the equilibria are often retarded. Table XXXIX comprises some further details respecting these compounds.

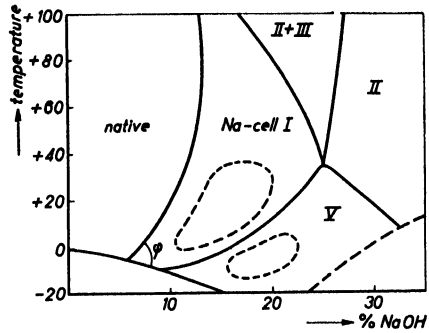


Fig. 121. Zone of existence of various sodium celluloses according to *H. Sobue, H. Kiessig* and *K. Hess*. (The areas bounded by broken lines are those where the optimum formative conditions prevail).

TABLE XXXIX

Probable Stoichiometrical Composition and Length of Fibre Period of Sodium Celluloses [5]

Sodium Cellulose	Composition	Fibre Period.
I	$C_6H_{10}O_5 . NaOH . 3H_2O$	20.5 Å
II	$C_6H_{10}O_5 . NaOH . H_2O$	15.4 Å
III	$C_6H_{10}O_5 . NaOH . 3H_2O$	20.5 Å
(IV)	$C_6H_{10}O_5 . H_2O$	10.3 Å
V	$C_6H_{10}O_5 . NaOH . 5H_2O$	15.3 Å

[3] *H. Sobue, H. Kiessig* and *K. Hess*, Z. physik. Chem., B. 43, (1939) 312.
[4] Cf. against this *G. Champetier*, Ann. de Chim. (X) 20, (1933) 5 who, by other means, reaches totally different results.
[5] After *H. Sobue, H. Kiessig* and *K. Hess*, Z. physik. Chem., B. 43, (1939) 312.

The compound originally designated as Sodium Cellulose IV turned out later to be free from alkali. It is identical to *Sakurada's* cellulose hydrate (page 25). It results from washing out Sodium Cellulose I or III with water in the cold and also from the regeneration of cellulose from viscose in the cold.

Practical experience has made it clear that only in the Sodium Cellulose I region are the initial conditions suitable to the production of viscose. This in no way implies, however, that every sodium cellulose exhibiting the X-ray diagram of Sodium Cellulose I is necessarily suitable; on the contrary, practice has narrowed down the limits very considerably.

In the viscose factory the cellulose is as a rule steeped in caustic soda solution of 18 to 20 per cent. concentration at 18° to 22° C., a concentration above the swelling maximum. A small fraction, depending upon the hemicellulose content of the starting material, thereby goes into solution, while the bulk is converted to sodium cellulose.

After the steeping process, the sodium cellulose is freed by mechanical means from excess, adhering caustic soda solution, being pressed to a specified weight proportionate to the dry initial cellulose, which is called the "press factor".

The stoichiometrical composition of the sodium cellulose indicated above only refers, of course, to the quantity of sodium hydroxide and water absorbed by the crystalline regions and tells us nothing about the total quantity of these components absorbed by the swollen cellulose, for this also contains the constituents bound in, and capillarily absorbed by, the intermicellar spaces, or amorphous regions. Probably *Donnan* equilibria [6] are also involved in this absorption of NaOH.

In actual practice the main concern is the total composition of the sodium cellulose after steeping until equilibrium is reached in caustic soda solutions of different concentrations and after being squeezed out to a given press factor. As a good guide, *G. Champetier's* work [7] may be mentioned.

According to *Champetier,* the following conditions are found if a cellulose object, fully distributed to a fibre suspension up to establishment of equilibrium, is steeped in a relatively very large quantity of sodium hydroxide of a given concentration and the sodium celluloses subsequently separated off and subjected to varying degrees of pressing, are analysed (cf. Fig. 122). A straight line is produced if the NaOH content ascertained for each object in moles per monomeric residue $C_6H_{10}O_5$ is plotted against the water content in moles per monomeric residue. A different straight line is found for each equilibrium concentration of the steeping liquor, but all the straight lines intersect at one point. Whatever the criticisms may be of the conclusions *Champetier* draws from the position of this point of intersection — which we

[6] *S. M. Neale,* J. Text. Inst., 20, (1929) 373; 21, (1930) 225; 22, (1931) 328, 399.
[7] *G. Champetier,* Ann. de Chim., (X) 20, (1933) 5.

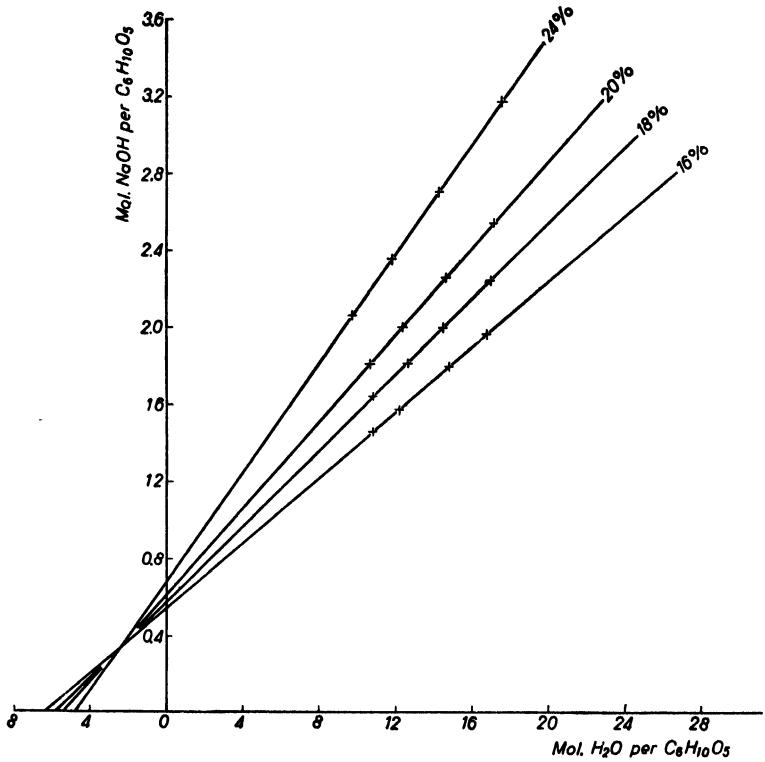


Fig. 122. Relation between total sodium hydroxide content and water content of sodium cellulose. The crosses stand for objects squeezed in varying degrees. Every straight line refers to a given concentration of steeping equilibrium-liquor.

shall not enter into here – it is a fact that, on the whole, his asseverations are borne out by what actually happens. A natural deduction is that then the equation

$$c = \frac{NaOH - 10\ k.\ cell.}{1 - k.\ cell.}$$

must hold good, where c = concentration of the steeping liquor in per cent. by weight of NaOH, NaOH = sodium hydroxide content of the sodium cellulose in per cent. by weight and cell. = cellulose content of the sodium cellulose in per cent. by weight, while k is a constant amounting to approximately 0.00823 for sulphite pulp at 20°. To give an example: it shows that a sodium cellulose with 32% by wt. of cellulose (press factor 3.13) which has been steeped in liquor of 18% by wt. strength, contains 15.9 per cent. of NaOH. This equation is only valid if equilibrium has been established between the cellulose and the steeping liquor. Under practical conditions this proviso is only met when the cellulose, in the form of a mash, comes into contact with an excess quantity of steeping liquor, as it does in the very latest processes. If, however, the cellulose is in sheets and is mercerized in so-called steeping presses, equilibrium is never reached and the sodium

content is lower. The customary composition of the sodium cellulose in viscose manufacture is somewhere between the limits of 15—16% by weight of NaOH and 30—34% by wt. of cellulose.

We shall leave aside, as having no practical relevance, the question as to the amount of the sodium hydroxide which is bound intramicellarly and that bound in some other way, since the matter is in any case beyond any real practical control.

After passing through the presses, the sodium cellulose is changed in shredding machines into a flocculent mass of looser consistency. Oxygen is absorbed from the air and an oxidative decomposition process sets in with generation of heat. This process is then allowed to proceed to whatever degree is desired by storing the shredded mass for a given time at a properly adjusted temperature. It is this process which is known as "ageing". It is precisely because of this reaction induced by a g a s that the sodium cellulose needs to be flaky; that is to say, so that the reaction may take place evenly throughout. The subsequent sulphidation is likewise a reaction with carbon bisulphide vapor and for the same reason the fibrous mass must be of this loose consistency. Inadequately pressed sodium cellulose ages slowly and unequally. The higher the pressfactor has been, the more rapid is the absorption of oxygen.

As, at the practical temperatures, the rate of oxygen consumption by the whole mass is far slower than the diffusion of the atmospheric oxigen to the place of reaction, the velocity of reaction is governed entirely by the speed of the oxidation reaction itself. Accordingly, in this range of temperature ageing displays a high (chemical) temperature coefficient. It is not until the temperature is above roughly 60° that oxygen is consumed so rapidly that the position is reversed and the rate of reaction then depends only upon the velocity of diffusion, when the coefficient of temperature also drops to a fraction of the original value.

The oxidative decomposition during ageing decreases the average length of the chains, the size of which, again, determines the viscosity of the subsequent spinning liquor. Ageing allows of regulation of the viscosity and indeed the very purpose of this process is to force this viscosity into practicable limits. The classical processes aim at attaining an average degree of polymerization of usually between 200 and 400, all acccording to the required concentration of the viscose and the upper viscosity limit set. Without ageing, the viscose obtained from the usual raw materials would be far too viscous to manipulate. Lately, however, it has been found possible to operate successfully with considerably higher *DP*.

In many respects a fairly high *DP* is an advantage and there is an expedient by which viscoses possessing this advantage can be obtained, that being to reduce to a certain extent the concentration of the cellulose in the viscose. As we shall see, however, on the one hand the direct effect of this expedient is

very restricted and, on the other, serious economic and also technical considerations set a limit to the lowering of the concentration of viscose, which at best is about 5—6% cellulose. Against this, the usual concentration of cellulose in practice is 7.5—8.5 per cent. In every special case a compromise will be sought between the desire to attain the highest possible *DP* and the choice of a dilution which is both technically and economically permissible.

The mechanism of ageing is not yet fully understood, there being still some lack of agreement in the statements of various investigators; we would here refer to those already cited on p. 140. As the mathematic and methodic groundwork has now been laid, the subject might well prove a fruitful field of research. The presence of certain heavy metal salts, such as relatively small amounts of iron salts, accelerates ageing, and oxidizing agents like hydrogen peroxide have a similar effect. The presence of alkali sulphides produces very considerable acceleration, when probably induced oxidation of sulphide and cellulose takes place. Alkali sulphite slows down ageing velocity.

1.3. Xanthation Reaction

As has been stated, in sulphidation carbon bisulphide vapour is allowed to act upon the slack sodium cellulose, when the main reaction is comparable to the effect of carbon bisulphide upon sodium alcoholate:

$$C_2H_5ONa + CS_2 \longrightarrow C\begin{matrix}\diagup OC_2H_5 \\ = S \\ \diagdown SNa\end{matrix}$$

Sodium ethyl xanthate.

The reaction can be generally formulated as follows:

$$ROH + NaOH + CS_2 \longrightarrow RO.CS.SNa + H_2O \qquad (1)$$

and this formulation also holds good for sodium cellulose. The xanthation of alkali cellulose was discovered in 1892 by the Englishmen *C. F. Cross* and *E. J. Bevan*[8], since when the technical repercussions have been enormous.

The xanthate residue is evidently a highly hydrophilic group and the xanthates of even the higher alcohols therefore dissolve readily in water. If a cellulose molecule is charged with a sufficient number of xanthate groups, it likewise becomes soluble in water.

Practical experience has shown that 32—36 kg of carbon bisulphide to 100 kg of cellulose in the sodium cellulose suffices to produce a satisfactorily soluble xanthate, which means to say that per monomeric residue $C_6H_{10}O_5$ 0.68 to 0.75 mole of CS_2 enters into reaction, nevertheless, only 0.50 to 0.55 mole of this quantity is actually bound as cellulose xanthate. The remainder is used up in an unavoidable secondary reaction, in which carbon bisulphide and

[8] *C. F. Cross* and *E. J. Bevan*, D.R.P. 92520.

sodium hydroxide react together directly, in accordance with the equation:

$$3\ CS_2 + 6\ NaOH \longrightarrow Na_2CO_3 + 2\ Na_2CS_3 + 3\ H_2O \qquad (2)$$

Thus technical xanthate always contains just so much of the salts sodium carbonate and sodium trithiocarbonate as corresponds stoichiometrically to the quantity of carbon bisulphide not bound as xanthate according to formula (1).

The coloured trithiocarbonate is responsible for the orange tint of the xanthate and the brown colour of the viscose, the xanthate itself being almost colourless or faintly yellow.

In practice the term "xanthate ratio" (*XR*), or "γ-number" [9] is applied to the number of moles of CS_2 which are bound as xanthate per 100 moles of $C_6H_{10}O_5$.

Much investigation has been devoted to the xanthation reaction and its mechanism has been the subject of much contention. We shall discuss it later, but shall first consider a few more experimental facts.

Whereas it used to be a fairly common assumption that, even after the action of an excess quantity of carbon bisulphide, products are formed containing at most 0.5 mole of CS_2 bound as xanthate per mole of $C_6H_{10}O_5$ (*XR* = 50), *H. L. Bredée* [10] has now made it absolutely clear that this view is due, either to misleading methods of analysis, or else to inappropriate experimental conditions. In ordinary technical sodium cellulose a xanthate ratio of roughly 100 (i.e., 1 CS_2 : 1 $C_6H_{10}O_5$) can easily be obtained by using an excess of carbon bisulphide. *Bredée* also describes a perfectly reliable analytical method for the determination of the *XR* in the sulphidation product. After exhaustive sulphidation he obtained from a sodium cellulose with 15.0% NaOH and 29.6% cellulose (in which, therefore, there was 1 $C_6H_{10}O_5$ per 2 NaOH) a product containing per mole of $C_6H_{10}O_5$ exactly 1 mole of CS_2 in the form of xanthate and 0.4 mole CS_2 in the form of trithiocarbonate. Thus, according to formulas (1) and (2), 1.8 moles of the available 2 moles of NaOH were consumed, which is sufficient evidence that even in the presence of excess CS_2 the reaction must come to a standstill.

Although, theoretically, a trixanthate is a possibility, and, indeed, can actually be obtained under different conditions [11], there are no practical means of incorporating a large enough excess of NaOH in the sodium cellulose to sulphidize any further OH groups there may be in the cellulose. The only result of restraining pressing, with the object of obtaining a higher NaOH content, is a more pronounced side reaction according to formula (2).

All the same, in the dissolved state it is possible to attain a higher *XR* than 100 (see next section).

[9] According to *H. Fink, E. Stahn* and *A. Matthes*, Z. angew. Chem. 47, (1934) 1002.
[10] After *H. L. Bredée*, Kolloid-Z., 94, (1941) 81.
[11] *Th. Lieser* and *E. Leckzyck*, Ann. 511, (1934) 137; 522, (1936) 56.

The question of the mechanism of the xanthation reaction has been hotly debated, the crucial point being whether the reaction is permutoid or micellarly heterogeneous (cf. page 305). The supposed fact that an *XR* of only about 50 can be attained favoured the latter alternative, even now upheld by *Th. Lieser*, who contends that only the surfaces of the crystalline regions enter into reaction and that in the later dissolution of the xanthate supermolecular particles also go into solution (cf. also p. 48). The circumstance noted by *W. Schramek* and *F. Küttner* that, after sulphidation, a mercerized fibre still exhibits the X-ray diagram of sodium cellulose, at first seemed a weighty argument in support of this view, but the conclusiveness of the evidence has since been called in question by *H. L. Bredée's*[13] discussion of the problem[14]. For *Bredée* has been able to show that the quantity of NaOH used in *Schramek* and *Küttner's* experiments is insufficient to bring about complete xanthation of the fibres (see above).

Nor can *Lieser's* argument[15] be maintained that xanthation is limited to the surfaces of the crystallites. He succeeded in substituting methyl groups for the xanthate groups. The resulting methyl cellulose, with a mean degree of substitution of 0.5, was then subjected to acetolysis and he found about 10% of cellobiose octacetate in the reaction product, the former supposed to have come from the unchanged cellulose in the interior portion of the crystallites. But, looking at the problem statistically and considering the probability of an arbitrary distribution of one xanthate group per two glucose residues, it will be clear that there should even be more than 10% of cellobiose octacetate.

We must not lose sight of the fact, however, that the question is not merely whether the xanthate reaction (be it in industrial sulphidation, or with the use of excess CS_2) reaches only the intercrystalline amorphous fibre regions, or whether it may penetrate, in principle, also into the regions, of lattice order, but — and this is far more important — how the dispersion of the xanthate later takes place in the solution.

This is where *G. Centola's* important investigations[16], to which, unfortunately, too little attention has hitherto been paid, offer assistance (cf. page 308). From these it would appear that the matter is most probably as follows. At first sulphidation, also with excess CS_2, actually does take place topochemically, in so far as the reaction tends preferably to occur in the "fringe-like" intercrystalline regions, when maybe more than one xanthate group falls to one $C_6H_{10}O_5$. The X-ray diagram of Sodium Cellulose I then persists, but, while the xanthate is stored, the interferences of the Sodium Cellulose I become progressively fainter and wider, finally to disappear altogether.

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12 *W. Schramek* and *F. Küttner*, Kolloidchem. Beih., 42, (1935) 331.
13 *H. L. Bredée*, Kolloid-Z., 94, (1941) 81.
14 Also compare *Th. Lieser's* counter-arguments, Kolloid-Z., 94, (1941) 6 and *W. Schramek's*, Kolloid-Z., 94, (1941) 92.
15 *Th. Lieser*, Ann., 483, (1930) 132.
16 *G. Centola*, Atti X Congr. intern. chim. Roma. Vol., IV, 117, (1938), 129, 138, 722, 728.

Centola points out the analogy with the gradual process of mercerization (page 308) and assumes that there is gradual penetration of xanthation into the crystalline regions owing to retarded equilibrium between the richly xanthated intercrystalline chain sections and those which have not yet entered into reaction, this being due to some kind of interchange of ester radicals. There is proof that an adjustment of the kind actually does take place in the dissolved state. (See next section). Now if the xanthate is dissolved before reaction has taken place through and through, the process of adjustment continues during dispersion. Some polymolecular complexes should therefore go into solution at first and then disperse gradually into single chains or their association complexes [17].

At a later date *O. Kratky* and his collaborators [18] were able to confirm that this is actually what happens. One advance in method which stands to the credit of these investigators is their introduction of an absolute standard of intensity in their X-ray photographs. It was found that the alkali cellulose diagram becomes weaker as xanthation progresses without at first losing in distinctness to any serious extent. This would correspond to a reduction in the quantity of crystalline substance amounting to something more than 30%. With degrees of sulphidation of 40 to 50, the interference bands were found to widen and there was gradual transition to an amorphous diagram. These investigators state that technical sulphidation breaks off at a stage where the sodium cellulose still produces a moderately sharply defined diagram. A fresh 30 per cent. solution of the xanthate still showed faint alkali cellulose interferences, whereas these have certainly disappeared in a 20 per cent. solution [19]. Meanwhile counter-arguments have again been recently advanced by *W. Schramek* and *O. Succolawsky* [20] but the author believes that they are not significant.

It should be pointed out that the *DP* diminishes appreciably during sulphidation, a relatively short process (1½ — 3 hours). This is to be conceived of as a continuation of ageing, as some atmospheric oxygen is also always present during sulphidation. The oxidation side reaction is, moreover, probably accelerated by the sulphur compounds.

Finally it is interesting to note that a reaction similar to sulphidation can be induced, and a soluble product obtained with carbon oxysulphide (COS). The products, however, are far more unstable and liable to decompose than those resulting from sulphidation with CS_2.

1.4. Viscose and Viscose Ripening

The discussion of the processes involved in the solution of the xanthate in water or dilute sodium hydroxide may fittingly follow the views set forth

[17] For this compare also *J. J. Stöckly*, Kolloid-Z., 105, (1943) 190.
[18] *O. Kratky, B. Baule, A. Sekora* and *R. Treer*, Kolloid-Z., 96, (1941) 301; *O. Kratky, F. Schossberger* and *A. Sekora*, Z. Elektrochem., 48, (1942) 409.
[19] Attention is drawn to analogous conditions prevailing with other high-molecular substances (for which see pages 55 and 58).
[20] *W. Schramek* and *O. Succolowsky*, Kolloid-Z., 100, (1942) 299.

in the preceding section respecting the mechanism of xanthation. According to the latter, progressive dispersion of the xanthate continues to take place for a time after solution, owing to an interchange of ester radicals whereby xanthate groups deriving from chain sections (more abundantly occupied by xanthate residues) of the most accessible fibre regions are transferred to those sections which are as yet unengaged [21].

Recording the viscosity readings of a viscose produced under ordinary industrial conditions, it will be found that after solution they follow with time the course shown in the graph of Fig. 123.

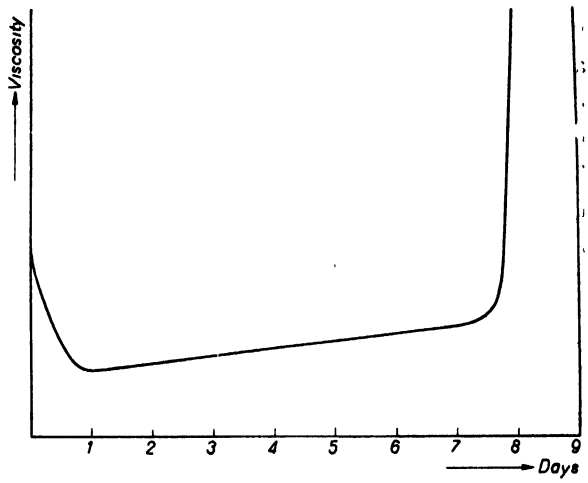


Fig. 123. Variation with time of the viscosity of a technical viscose.

At first (for about 24 hours at 15°) the viscosity drops, goes through a minimum and then slowly rises again. It is only natural to connect this drop in viscosity with the process of dispersion just mentioned, as *Centola* (loc.cit.) does. The descending section of the viscosity curve becomes smaller, or can be made to disappear altogether, if larger quantities of CS_2 are used for xanthation, or if a longer interval is allowed before dissolving.

The views set out here require that equilibria should be established in a viscose solution, permitting of an even distribution of the xanthate groups between all the cellulose chains and groups. Many observations have actually been reported which support this view. E.g., *Centola* has shown that unsulphidized alkali cellulose from regenerated fibres gradually dissolves when introduced into a viscose produced from a xanthate prepared with excess carbon bisulphide.

The xanthation reaction (1) is to be regarded as an equilibrium reaction pushed far to the right:

$$ROH + NaOH + CS_2 \rightleftarrows RO.CS.SNa + H_2O \qquad (3)$$

There is always a small amount of free CS_2 in every viscose, a fact which is demonstrable by passing an inert gas through it. That gas then invariably contains some CS_2. The CS_2 concentration in the viscose depends upon how the cellulose molecules are charged with xanthate groups. Heavily charged

[21] It should be noted that, the dissolving process being gradual, mechanical conditions (stirring) must be expected materially to affect it and the properties of the viscose shortly after its manufacture. Little serious study has as yet been given to this matter.

and less heavily charged chains side by side, therefore, are not stable, for in such cases a process of adjustment sets in.

The presence of a certain amount of free CS_2 in the xanthate equilibrium (3) is responsible for yet another process which is closely associated with the so-called ripening. The alkali cellulose and the free sodium hydroxide in the viscose compete for the CS_2 since reaction (2), which had already occurred as a side reaction in the sulphidation, also comes into operation. According to *J. G. Weeldenburg* [22], however, who has studied the reactions taking place in the viscose very thoroughly and in an exemplary fashion, reaction (2) is also an equilibrium, be it likewise one shifted very much to the right-hand part of the equation. It may, however, be assumed that, under the conditions prevailing in the viscose solution, the CS_2 tension in (2) is far lower than in equilibrium (3) [23]. Gradually, therefore, always more CS_2 is withdrawn from the xanthate equilibrium and converted to trithiocarbonate and sodium carbonate according to (2). As a result, the cellulose becomes progressively "more insoluble" and after some time there is spontaneous gelatination in the viscose. This process receives support from the consumption, during reaction (2), of "peptizing" sodium hydroxide and the formation of salts which reduce the solubility of the xanthate. As illustrated in Fig. 123, the viscosity increases slowly at first and then suddenly rises with extreme rapidity round about the coagulation point. As the xanthate groups are withdrawn and an increasing number of OH groups are thus vacated, the chain molecules will have a growing tendency to associate and a spreading "structuralization" of the solution will set in (see below), betrayed by gradual increase in viscosity. The very readable detailed statements of *J. J. Stöckly* [24] may here be usefully consulted. Junction points (points of interconnection) are now again gradually formed in the ripening viscose between the individual molecules and this eventually leads to the formation of a continuous gel frame (coagulation).

G. Centola [25] verified the increasing aggregation of the molecules during the process of ripening by some elegant experiments, in carrying out which he proved, by dilatometric measurements, that the volume of the viscose likewise passes through a minimum value during the process of ripening, though this minimum comes considerably later than the viscosity minimum. Judging by other dilatometric experience, it may be said that the initial increase in density is due to the larger number of dissolved molecules resulting from the dispersion of the xanthate. Finally, however, the desolvation inherent in increasing association gains the upper hand and the density again decreases.

[22] *J. G. Weeldenburg*, Thesis, Delft, 1927; Rec. trav. chim. 47, (1928) 496; 49, (1930) 1180.
[23] Weeldenburg states that CS_2 vapour can also be withdrawn by a stream of inert gas from an alkaline solution of Na_2CS_3.
[24] *J. J. Stöckly*, Kolloid-Z., 105, (1943) 190.
[25] *G. Centola*, Boll. Sci. Fac. Chim. ind. Bologna I, 1946 (1942); cf. also *E. Heymann*, Trans. Faraday Soc., 32, (1936) 467.

Increasing molecular aggregation during the ripening process was also deduced from experiments by *R. Signer* and *W. Meyer* [26] on the birefringence at flow of dilute viscose solutions.

The foregoing depicts the intrinsic nature of viscose ripening in broad outline. It is controlled, as we have seen, by the velocity of chemical reactions and therefore also exhibits an obviously chemical temperature coefficient, this being something between 2.6 and 2.8 per 10° [27]. The chemical reactions then release the so-called "colloid-chemical" processes of ripening. Borrowing a colloid-chemical term, these might be called a gradual "reduction of the degree of dispersion". Investigations by *R. Bernhardt* [28] deserve mention here, in the course of which he carried out ultrafiltration experiments with ripening viscose and produced evidence to show that the permeability of the ultrafilter used to the xanthate decreased as ripening progressed. The ripening of a viscose solution can also be made retrograde by stirring the viscose with carbon bisulphide. The *XR* then increases again, as part of the CS_2 is bound as xanthate, another portion being converted, in accordance with formula (2), to trithiocarbonate and soda.

The relation between the CS_2 reacting in this and the other way is a measure of the relation between the velocities of reaction of the two reactions (1) and (2). As *Weeldenburg* (loc.cit.) has shown, high concentrations of NaOH check reaction (2) and this is no doubt why the xanthation reaction is more favoured than reaction (2) in the sulphidation of alkali cellulose than in "re-sulphidation" in the viscose, where xanthation produces less yield.

Whereas the ratio of the *velocity constants* is the criterion for the competition between the two reactions during the sulfidation, the ratio of the *equilibrium constants* of the two reactions is decisive in the matter of viscose ripening, and it is here that reaction (2) therefore always gains the upper hand in the end.

It has been found that appreciably higher degrees of xanthation than those brought about by "dry" sulphidation can be obtained by the addition of larger quantities of CS_2 to the viscose, viz., up to approximately 170 *XR*.

In actual practice, a small amount of sodium sulphite (1.5 to 3% of the weight of cellulose) is often added to the viscose. This very considerably reduces the velocity of ripening. The mechanism by which the Na_2SO_3 retards reaction is not yet known, but it is certain that the Na_2SO_3 itself is not thereby consumed.

The addition of Na_2SO_3 may result in another side reaction, which induces the formation of sodium sulphide (Na_2S). In this case the CS_2 reacts with the caustic soda solution by yet a different reaction from that in equation (2), but not yet explained.

W. Klauditz [29] has a different view with regard to the formation of Na_2S, looking upon it as a "saponification" of the xanthate. One thing is certain, however, and that is that Na_2S occurs in the viscose only if Na_2SO_3 has been added.

If the last-mentioned secondary reaction is disregarded, the quantity of salts (Na_2CO_3 and Na_2CS_3) present in the viscose is always stoichiometrically

[26] *R. Signer* and *W. Meyer*, Helv. chim. acta, 28, (1945) 325; *W. Meyer*, Thesis Bern 1945
[27] This statement is based on the Hottenroth number, a ripening standard.
[28] *R. Bernhardt*, Kunstseide 7, (1925) 169.
[29] *W. Klauditz*, Papierfabrikant 37, (1939) 251.

equivalent to the quantity of CS_2 according to equation (2) no longer bound as xanthate, no matter whether the salts are formed direct from CS_2, or whether they have come into existence during ripening.

J. Sauvy has reported that ripening can be accelerated by the addition of hydrogen peroxide [30].

The chemical processes in the ripening of viscose are entirely similar to the reaction of the xanthate of low-molecular alcohols with alkali [31].

J. P. Hollihan and *S. A. Moss Jr.*[31a] have reported that the degree of xanthation of a ripened viscose can be made to rise considerably on reacting it with acrylonitrile. This substance decomposes the trithiocarbonate with formation of di-β-cyano-ethyl sulphide and liberation of CS_2. The latter then gives rise to rexanthation.

There is no more chain break-down during viscose ripening [32]. Viscose does, admittedly, absorb oxygen avidly, but the latter is used up in the oxidation of easily oxidized sulphur compounds and the cellulose is thus protected from oxidative decomposition [33]. This reaction with oxygen is responsible for a certain amount of thiosulphate in the viscose.

Ripening can be followed by watching the trend of the *XR* or γ number, the latter dropping steadily during ripening. The value of the number at the moment of coagulation depends upon a variety of factors, such as concentration and *DP* of the cellulose, percentage of free NaOH in the viscose, salt content.

The condition in which the viscose is spun by the ordinary spinning process (see next Chapter) in practice is represented by a γ number of about 35 to 40; in the funnel process, however, ripening proceeds much farther.

There are two ways of determining the xanthate ratio:

1. A weighed sample of viscose is spread to a thin film on a glass plate, where it is allowed to coagulate in ice-cold saturated ammonium chloride solution; all sulphurous salts are then washed out with the same liquid and the sulphur content of the xanthate retained in the film is determined, either by the *Carius* method, or, more conveniently iodometrically in accordance with directions published by *H. L. Bredée* [34].

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30 *J. Sauvy*, L'Ind. Textile, 63, (1946) 143.
31 Reference should be made to the publications already mentioned by *J. G. Weeldenburg* and *Klauditz*.
31a *J. P. Hollihan* and *S. A. Moss Jr.*, Ind. Eng. Chem., 39, (1947) 222.
32 *A. Lottermoser* and *F. Wultsch*, Kolloid-Z., 83 (1938) 189; *G. Centola*, Boll. Sci. Fac. Chim. ind. Bologna 1941, 7; Chem. Z., 1942 1, 1956.
33 In sulphidation by the emulsion process (reaction of carbon bisulphide upon the cellulose soaked in caustic soda solution), however, *G. Jayme* and *J. Wellm* recently observed degradation, Kolloid-Z., 107, (1944) 163. They succeeded in reducing it considerably by adding glucose. The degradation observed by *R. Signer* and *W. Meyer* (Helv. chim. acta, 28, (1945) 325) during ripening must be ascribed to the abnormal composition of their viscose solutions (low concentration and free admission of oxygen).
34 *H. L. Bredée*, Kolloid-Z., 94, (1941) 81.

2. The xanthate content of the viscose is determined by precipitation with diethyl chloracetamide, after *H. Fink, R. Stahn* and *A. Matthes*[35] (γ number).

Many methods of analysis formerly recommended produce unreliable results.

Under working conditions the "ripeness" of the viscose is determined for the current industrial control by a simpler and quicker method than these two, viz., one devised by *V. Hottenroth*[36]. This provides no data as to stoichiometrical proportions, but an empirical number running parallel to the *XR*. One measures the number of millilitres of ten per cent. ammonium chloride solution which it is necessary to add to a somewhat diluted viscose to induce incipient coagulation. The method rests on the neutralization of the free alkali by the ammonium salt and the insolubility of the xanthate in concentrated salt solutions. Given the same *XR*, therefore, the Hottenroth number also depends upon the concentration of free alkali and of cellulose in the viscose, amongst other things. As the velocity of precipitation of the viscose during spinning is influenced in the same way by like factors, the empirical "Hottenroth ripeness" has proved to be a very serviceable guide right up to the present day[37].

To characterize a viscose it is also the practice to determine the total alkali content and the cellulose content (percentage of "titerbildende Substanz"), these two quantities being expressed in per cent. by weight. The former, in particular, is of little value to scientific investigation; indeed, it may even be misleading; for the total alkali content comprises the total measurable sodium content of the compounds NaOH, Na_2CO_3, Na_2CS_3 (and possibly Na_2S), each of which is highly distinctive in its bearing upon the properties of the viscose.

For a comprehensive definition of a viscose it is best to express the concentration of all components in moles per litre, when it is necessary to establish the following:

1. The concentration of cellulose.
2. The *DP* and chain length distribution of the cellulose.
3. The xanthate ratio.
4. The concentration of actual free NaOH.
5. The concentration of "salts".

As proved above, apart from small amounts of Na_2CO_3, possibly deriving from the original soda content of the alkali cellulose or the solvent liquor, and the percentage, if any, of Na_2S in viscoses to which Na_2SO_3 has been added, the "salts" consist of a mixture of Na_2CO_3 and Na_2CS_3 in the molar ratio of 1 : 2. If *a* moles of CS_2 are used per monomeric residue $C_6H_{10}O_5$ present in

[35] *H. Fink, R. Stahn* and *A. Matthes*, Z. angew. Chem., 47, (1934) 602.
[36] *V. Hottenroth*, Chemiker Ztg., 39, (1915) 119.
[37] An instrumental improvement of *Hottenroth's* ripening determination, tested in practice, has recently been published by *Gernert*, Kunstseide und Zellwolle 23, (1941) 80.

the alkali cellulose and if the xanthate ratio XR is 100 x, then $a - x$ moles of CS_2 have contributed to the formation of salt and there will be present one-third $(a - x)$ moles of carbonate and two-thirds $(a - x)$ moles of trithiocarbonate.

We have finally to mention the reaction of xanthates with iodine in an alkaline solution, upon which also their iodometric determination rests. This generates in simple ethyl xanthate an insoluble compound known as dixanthogene, a yellow precipitate formed according to the following formula:

$$2C_2H_5\text{-}O\,.\,CS\,.\,SNa + 2\,I \longrightarrow 2NaI + C_2H_5O\,.\,CS\,.\,S\text{-}S\,.\,CS\,.\,OC_2H_5.$$

To all intents and purposes, the cellulose xanthate reacts in a similar manner. Yet it is by no means clear how the disulphide bridge always can come into existence between two xanthate groups. For stereochemical reasons, the most obvious assumption is that xanthate groups of adjacent chains react with each other. If this is true, the cellulose would in this reaction form a kind of network (interlinking of parallel adjacent chains by primary valencies). Observations made during the deformation of normal cellulose-xanthate filaments and those preliminarily treated with iodine would appear to support this view. This means to say that the cellulose underwent a kind of "vulcanization".

The following must be borne in mind when considering the practical significance of ripeness.

First and foremost, the ripeness of the viscose which is to be spun is required to remain constant. Then, subject to the other working conditions, everything is focused upon a given ripeness, which is considered the optimum. As a rule it is governed by a great variety of entirely different, empirically discovered factors, which we cannot discuss here. We have as yet no fundamental knowledge at our command respecting the influence of viscose ripening upon the internal structural conditions in the regenerated filament. Scientific investigation of this subject is still entirely lacking; nor can it be undertaken without emancipation from the special and very complicated conditions of the industrial spinning process. A limited way to it is opened up by model experiments with isotropic filaments, which will be discussed later.

1.5. Filterability of the Viscose

An exceedingly important property of viscose from the practical point of view, which has not been mentioned at all as yet, is its filterability. This is very sensitive to quite a number of circumstances, the discussion of which, however, is likewise outside the scope of this book [38]. Bad filterability is ordinarily the result of the presence of incompletely dissolved components of the fibre, which appear as highly swollen particles (barely perceptible

[38] For this see, e.g., *A. Marschall*, Supplements to "Die Chemie" No. 45, (1942) 65. (3. Forschungstagung Zellwolle und Kunstseide-Ring). *E. E. Dörr*, Z. angew. Chem., 53, (1940) 292; *Th. Kleinert, G. Hingst* and *I. Simmler*, Kolloid-Z., 108, (1944) 137.

under the microscope more often that not) in the viscose. Before the relevant phenomena could be controlled and rationally investigated, a well defined index had to be found by which to express filterability. *P. H. Hermans* and *H. L. Bredée* [39] pointed the way to this. *O. Samuelson* [40] has recently published extensive investigations into the filterability of viscose, showing, among other things, that the intensity of the mechanical treatment during solution is an important factor, being proportionally greater as less sodium hydroxide and carbon disulphide are used for the preparation of the viscose. He has experimental evidence (using the ultracentrifuge) that the filterability actually is affected by relatively large particles.

Not long ago *G. Jayme* and *Kuo-fu Chen* [41] proved that it is the primary wall of the fibres in particular which affects the filterability of dissolved cellulose xanthate. The primary wall is specially slow to react in xanthation and its preservation varies with the process of disintegration applied to the pulp. Many disturbing phenomena observed in practice and hitherto not understood have thereby become comprehensible and are now open to more exact analysis.

Quite recently the filtration problem has been comprehensively reviewed by *R. Vuori* [41a]. By his own work this author was led to the conclusion that the presence of long chain fractions diverging greatly from the general average chain length is responsible for filter clogging.

1.6. Chemical Processes in the Spinning of Viscose

When spun by the normal process, the viscose is brought into contact with a sulphuric acid solution in a spinning bath, which also contains a sulphate or several sulphates. The main thing is for the acid content to be adjusted to the alkali content of the viscose. One of the sulphates is invariably sodium sulphate, besides which generally either magnesium or ammonium sulphate and a small amount of zinc sulphate. The following are examples of some spinning baths used under working conditions:

9% H_2SO_4, 22% Na_2SO_4
8% H_2SO_4, 18% Na_2SO_4, 5% $MgSO_4$ 0.7% $ZnSO_4$
7% H_2SO_4, 16% Na_2SO_4, 8% $(NH_4)_2SO_4$, 0.8% $ZnSO_4$

Suitable filaments cannot be spun with sulphuric acid alone, for the viscose must first gelatinize to cellulose xanthate, after which the acids can react and decompose the xanthate. There are, therefore, two alternatives, viz., either to spin material in a bath containing only coagulating salts first and then to decompose the resultant xanthate filaments with acids; or else to adjust the acid and salt contents of the spinning liquor so that the two pro-

[39] *P. H. Hermans* and *H. L. Bredée*, Rec. trav. chim. 54, (1935) 680; J. Soc. Chem Ind., 55, (1936) 1.
[40] *O. Samuelson*, Svensk Papperstidning No. 21, (1945).
[41] *G. Jayme* and *Kuo-fu Chen*, Zellwolle, Kunstseide, Seide 48, (1943) 47.
[41a] *R. Vuori*, Thesis Helsinki, 1947 (in English).

cesses follow each other automatically. The acid, which at first penetrates into the material with the salts, is moreover neutralized right at the beginning by the alkaline components of the viscose, with the result that a neutral or alkaline salt zone actually does at first permeate the viscose and bring about gelatinization before the acid decomposes the xanthate[42]. This temporary successive operation of the coagulating salts followed by the acid p_H limit is assisted by the greatly retarding effect of the salts upon the diffusion of the H ions in the sulphuric acid. This is easily demonstrable by diffusion experiments in which first pure sulphuric acid and then mixtures of sulphuric acid and sulphate are made to diffuse into alkaline gel particles (stained by an indicator) from coagulated viscose. It will then be found that sodium, ammonium and magnesium sulphate, in the usual concentrations for spinning solutions, delay the penetration of the acid p_H limit in a marked degree. (In concentrations of less than 1%, zinc sulphate does not have this effect). The reduction of the diffusion velocity of the H-ion is probably due to the formation of HSO_4-ions[43]).

The common practice is to use the combined sulphuric acid and sulphate baths for large-scale work, but in the laboratory there is nothing against first spinning in a salt bath and subsequently decomposing, or "fixing". A concentrated solution of ammonium sulphate is specially recommended for the salt bath, as this not only performs the duty of a salt, but also neutralizes the anti-gelatinizing effect of free NaOH.

The decomposition of the xanthate may be represented by the following equations:

$$RO.CS.SNa + H' \longrightarrow RO.CS.SH + Na'$$
$$RO.CS.SH \longrightarrow ROH + CS_2$$

The first ionic reaction takes place with immeasurable rapidity, but the velocity of the second reaction, i.e., the dissociation of the unstable xanthogenic acid, is measurable. (With alkyl xanthates, the acids, which are stable for only a short while, can be isolated at low temperature)[44].

The constant of dissociation of the free xanthogenic acids is somewhere between that of acetic acid and that of formic acid; consequently, acetic acid

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[42] It is evident from the following that the viscose extruded from the nozzle and passing as a filament into the strongly acid salt bath retains a pH above 7 (i.e., remains *alkaline*) for a considerable distance right up to its surface. The decomposition of the salt solution in the viscose by acid is accompanied by turbidity, caused by the separation of drops of CS_2 (in which sulphur in dissolved when the viscose contains sulphite). It can be shown that this cloudiness does not begin until the pH has dropped to below 7. Now, close to the nozzle it may be observed that this turbidity starts to form at some distance from the spinning filament, so in the spinning bath. The filament lying within this zone of turbidity, therefore, still has everywhere a pH of > 7.

[43] In experiments of this kind sodium chloride has no delaying effect upon the diffusion of hydrochloric acid. This harmonizes with the known fact that good filaments cannot be spun in baths composed of hydrochloric acid and chlorides. In this case the zone of turbidity outside the spinning filament, which was mentioned in Note [42]), does not occur!

[44] Although the filament emerging from the spinning bath has an acid reaction right to the core, it still contains a good deal of undecomposed xanthate in the form of xanthogenic acid, which only gradually decomposes.

causes only slow decomposition of the xanthate and this is not accelerated until the p_H values are comparatively low.

If highly dilute solutions of viscose (containing roughly 0.04% of cellulose) are mixed with very dilute equimolecular solutions of various acids and a note is made of the time which elapses until flocculation of separated cellulose becomes visible, the effect of the ionic strength of the acids chosen will be found to be most pronounced. Moreover, variation of the temperature of reaction will make it plain that there is a decisive chemical coefficient of temperature for the time of reaction, which, therefore, depends upon a chemical reaction. The latter is undoubtedly the decomposition reaction of the free xanthogenic acid (according to unpublished experiments by *H. G. Bungenberg de Jong).*

This is where the intrinsic action of that favourite additional component of the spinning bath, zinc sulphate, may be seen to operate, for, whereas Na_2SO_4, $MgSO_4$, etc., barely affect the time of reaction at all, small amounts of zinc sulphate retard it very materially. What is formed is primarily zinc xanthate, a salt which, compared to the alkali xanthates, excels in stability, both towards hydrogen ions and towards spontaneous decomposition ("ripening"), which can also be demonstrated by other means [45].

Another manifestation of the effect of small amounts of zinc sulphate in industrial spinning baths is the formation of a relatively stable film containing zinc xanthate on the spinning filament. This has a specific effect upon the process of spinning, into which, however, we cannot enter here.

The other components of viscose exposed to the action of the acids in the spinning solution are also decomposed very quickly; in fact, before the xanthate. This liberates more carbon bisulphide, besides which hydrogen sulphide and carbon dioxide are formed:

$$Na_2CS_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S + CS_2$$
$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + CO_2 + H_2O$$
$$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S$$

It is the practice of late to recover most of the liberated CS_2 and use it afresh.

If the viscose also contains sodium sulphite, SO_2 will be liberated as well, which is known to enter into a complicated reaction with the hydrogen sulphide, when elementary sulphur likewise separates off. The thiosulphate formed in the viscose by the action of atmospheric oxygen is also liable to yield some sulphur as decomposition proceeds.

§ 2. THE VISCOSITY OF VISCOSE

2.1 *General Remarks*

The literature on the viscosity of solutions of high-molecular substances is exceedingly copious. The experimental conditions have been pretty thoroughly

[45] For this cf. *S. Poznanski*, ref. Z. angew. Chem., 51, (1938) 768; and *Z. Kawata*, J. Cellulose Inst. (Japan), 17, (1941) 27.

investigated and, on the whole, are fairly clear. But, notwithstanding all that has been done, the theoretical side of the matter can by no means be regarded as satisfactorily settled. *W. Philippoff's* monograph[46] is an up-to-date presentation of the subject. Here we shall only consider some fundamental points which are particularly interesting from the practical point of view, leaving aside all details as to apparatus and technical quantitative estimations.

The definition of the viscosity η as the quotient of shearing strength τ and velocity gradient $\frac{dv}{dx} = D$:

$$\tau = \eta \frac{dv}{dx} = \eta D \qquad (1)$$

is assumed to be known. In the c-g-s system of units, the unit of $\tau = 1$ dyne/cm² and the unit of the viscosity is 1 poise. (The viscosity of water at 20° is 0.01 poise).

If τ changes proportionally with the velocity of flow (that is to say, if η remains constant at every velocity gradient), we have the ideal condition of a pure *Newtonian* flow, which many low-molecular liquids fulfil. It is n o t as a rule met, however, in solutions of high-molecular substances, when η is n o t a constant and is therefore dependent upon the velocity of flow. This being due to a change wrought by the flow itself within the inner structure of the liquid, we speak in such cases of "structural viscosity". For particulars as to the viscosity to reveal anything typical of the solution in question, it is then necessary that they should be supplemented by pertinent data respecting the recorded condition of flow.

Nevertheless, with extreme dilution most of these solutions approximate the ideal condition and it is therefore appropriate that we should begin our discussion of viscosity phenomena by considering very dilute solutions of this kind.

2.2. *Extremely Diluted Solutions*

It has transpired that sufficiently dilute solutions of high polymers obey the *Einstein* viscosity law. This equation, originally deduced theoretically for certain suspensions of coagulated globular particles, is as follows:

$$\frac{\eta}{\eta_0} = \eta_r = 1 + kc_v \qquad (2)$$

where η is the viscosity of the solution, η_0 that of the pure solvent, η_r the relative viscosity of the solution and c_v the concentration by volume of the solution in millilitres per millilitre; k is a constant which has the value of 2.5 in the Einstein formula, but in the case now in question of solutions of high-molecular substances, it generally has some other value. We can also write formula (2) thus:

$$\eta_r - 1 = \eta_{sp} = kc_v \qquad (3)$$

where η_{sp} is the so-called specific viscosity of the solution.

[46] *W. Philippoff*, Die Viskosität der Kolloide, Dresden & Leipzig 1942.

Thus, according to this rule, η_{sp} is proportional to the concentration of the solution. If η_r or η_{sp} is plotted against the concentrations of the solutions, a straight curve results only with extreme dilutions, but it soon departs from the straight line as concentration increases and the course it takes is, moreover, liable to be dependent upon the velocity gradient during determination (see diagram Fig. 124).

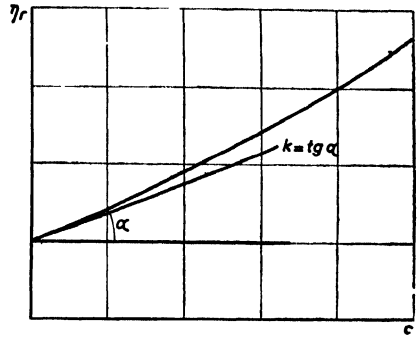


Fig. 124. Diagram showing how the viscosity depends upon the concentration; $tg\alpha = (d\eta_r/dc)_{c=o} = [\eta]$

It now appears that the constant k found for the most extreme dilutions represents a constant of the material characteristic of the dissolved substance. It is the slope of the tangents to the $\eta_r - c$ or $\eta_{sp} - c$ curve at the point $c = 0$ and is found by differentiation of formulas (1) and (2) and extrapolation to $c = 0$.

$$k = \left(\frac{d\eta_r}{dc}\right)_{c=o} \quad \text{and} \quad k = \left(\frac{d\eta_{sp}}{dc}\right)_{c=o} \qquad (4)$$

On page 104 it was shown how to find it from metrical evidence. If there is structural viscosity as well to be taken into account, there must further extrapolation to the gradient of flow 0:

$$k = \left(\frac{\eta_r}{c}\right)_{c=o;\, D=o} \qquad (5)$$

Following *E. O. Kraemer* [47], it is generally customary nowadays to apply the symbol [η] to the characteristic constant of the material, k. Kraemer was also responsible for the introduction of the term "intrinsic viscosity", which has since been generally adopted in the Anglo-Saxon countries. (No uniform term has as yet been universally accepted for the German language; the suggestions are: Viskositätskonstante, Eigenviskosität, Grundviskosität, Viskositätszahl, Grenzviskosität [48].

It must now be pointed out that the numerical value of the constant [η] depends upon the measure by which the concentration is expressed. Accord ng to *E. O. Kraemer*, the concentration is indicated as **g substance in 100 ml of the solution. A different constant is** found if this is expressed as a percentage by weight; g in 100 g of the solution, when it is [η]g. If the concentration is expressed by volume of dissolved substance per ml of the solution, yet another constant is found, viz., [η]φ. This is tabulated below.

TABLE XL.

	Measure of Concentration.	Characteristic constant	Dimension
c	(g in 100 ml)	[η]	cm-³g
cg	(g in 100 g)	[η]g	without dimensions
cv	(ml per ml)	[η]φ	„ „

[47] *E. O. Kraemer*, Ind. Eng. Chem., 30, (1938) 1200.
[48] See *W. Philippoff*, Kolloid-Z., 98, (1942) 91.

If the density of the dissolved substance in the dry state is d and that of the solvent D, we get the following:

$$[\eta] = \frac{1}{D}[\eta]g = \frac{1}{d}[\eta]\varphi \cdot 10^{-3} \qquad (6)$$

The measure of concentration recommended for practical purposes is c or cg, because an exact value for d is often not known, or is difficult to ascertain.
In the theoretical *Einstein* fundamental equation:

$$\eta_{sp} = 2.5\ c_v$$

c_v represents that fraction of the total volume of the solution which is occupied by the particles conceived to be rigid and spherical.
Now if η_{sp} is generally found to be far in excess of $2.5\ c_v$ in solutions of high-molecular substances, this may, quite formally, be considered as signifying that the volume occupied by the particles in the solution (apparent solvation volume) is larger than the volume of the undissolved dry substance, and that by a factor V:

$$\eta_{sp} = 2.5\ Vc_v \qquad (7)$$

H. L. Bredée and his collaborators defined the factor V, which is another function of the concentration, as the "voluminosity" of the particles. Extrapolating to infinite dilution, one then gets:

$$(\eta_{sp})_{c=0} = 2.5\ V_o c_v \qquad (8)$$

and therefore:

$$\left(\frac{\eta_{sp}}{c_v}\right)_{c=0} = [\eta]\varphi = 2.5\ V_o \qquad (9)$$

Here V_o is the "voluminosity at infinite dilution", or, according to *Bredée*, merely the "voluminosity", which, therefore, is also a constant of the material,
The *Staudinger* equation discussed on page 104, viz.,

$$\left(\frac{\eta_{sp}}{c}\right)_{c=0} = P \cdot K_m \qquad (10)$$

links up this viscometric constant of the material with the molecular weight. It must not be forgotten, however, that *Staudinger* expresses the concentration in grams per litre, so that, according to (6), we have the equations:

$$[\eta] = 10\ PK_m \qquad [\eta]g = 10\ D \cdot PK_m \qquad [\eta]\varphi = 1000d \cdot PK_m \qquad (11)$$

It is evident from (9) and (11) that the equations

$$K_m = 2.5 \times 10^{-4}\ V_o/Pd \qquad (13)$$

and

$$[\eta] = 0.025\ V_o/d \qquad (12)$$

exist between *Bredée's* V_o and *Staudinger's* K_m constant.
Hence, $[\eta]$, V_o and P are quantities proportional to each other.
We have dealt with this matter in some detail because, for the reasons explained, the relationship between $[\eta]$, V_o and P is one of practical interest.

2.3. *Concentrated Solutions*

Concentrated solutions are always used in actual practice. The viscosity of these solutions increases in a far greater degree than the concentration, especially in the case of substances containing chain molecules, like cellulose and its derivatives. For many of these solutions empirical formulas can be drawn up which accurately represent the relationship between $[\eta]$, or V_o the concentration of the solution and its viscosity. The advantage of using such formulas is that, with their help, it is possible to ascertain the characteristic constants, and sometimes also the degree of polymerization according to *Staudinger*, from viscosity determinations applied to concentrated solutions.

When the solutions exhibit structural viscosity, their viscosity should first be determined at the lowest possible velocity of flow; it is better still to extra-

polate the readings to 0 velocity gradient. The coefficient of direction of the tangent at zero point given by $(d\tau/dD)_{D=0}$ represents $(\eta_r)_{D=0}$. The formula suggested by *H. L. Bredée* and *J. de Booys* [49], viz.,

$$\eta_r = \left(1 + \frac{2.5\, V_0}{6}\, c_v\right)^6 \qquad (14)$$

is especially useful to show how these quantities depend upon the concentration. It gives a very close approximation for most solutions of cellulose and its derivatives. (See the original treatise for certain refinements introduced later into this formula).

Taking formulas (6) and (9) into account, formula (14) may alternatively be written thus [50]:

$$\eta_r = \left(1 + \frac{1}{6}\,[\eta]c\right)^6 \qquad (15)$$

or

$$[\eta] = \frac{1}{c} \cdot 6 \left(-1 + \sqrt[6]{\eta_r}\right) \qquad (15a)$$

This is the best form for practical uses, as again the concentration is expressed in grams per 100 ml.

The sixth power in equation (15) is indicative of the enormous increase in relative viscosity with the concentration, with $[\eta]$ and, therefore, also with the degree of polymerization P (11). This is clearly apparent in Fig. 125.

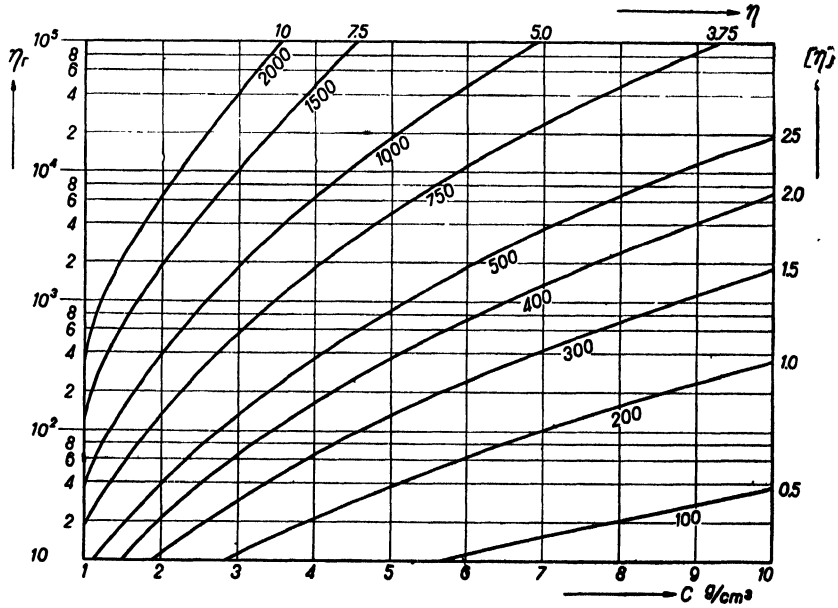


Fig. 125. The relative viscosity (to logarithmic scale) as a function of the concentration of the solution in g/100 cm³ on the basis of the formula stated by *Bredée—de Booys*. Parameters: $[\eta]$ and P, where *Staudinger's* K_m constant is 5.10^{-4}.

[49] See the list of papers consulted at the end of this Chapter for the relevant excerpts. Further articles and books on the relationship between viscosity and concentration are also fully quoted in *Bredée's* publications.

[50] Cf. *A. Matthes*, Die Chemie, 54, (1941) 517.

As η_r covers several orders of magnitude, this quantity has here been plotted to a logarithmic scale. The curves refer to the values of $[\eta]$ and P indicated in the figure, viz., for the case in which $K_m = 5.10^{-4}$ (cf. Table IV, page 105). By means of formula (15a) it is now possible to find $[\eta]$ from viscosity measurements applied to solutions outside the category of extreme dilution. Nevertheless, relative viscosities above roughly 50 often involve complications, which should be a warning against the indiscriminate use of (15) for this purpose where concentrated solutions are concerned. We have seen that the viscosity of many solutions within the range of concentration met with in technical spinning liquors (4—10% cellulose) may depend not only on $[\eta]$, but on other factors as well, such as the composition of the solvent (see page 53). And this also applies to the viscose. Yet these anomalies disappear after the viscose has been amply diluted with a four percent. solution of caustic soda, so this provides a means of obtaining reliable $[\eta]$ values in this case, too [51].

Unfortunately, however, there are other obstacles to the use of formulas (11) and (15) for viscose. Firstly, it is not always easy to show how the viscosity η_0 of the "pure" solvent is to be established, for it consists of an aqueous solution of sodium hydroxide and salts, the concentration of which can only be computed after carrying out troublesome analyses. Secondly, the evidence as to the K_m constant of viscose is too inconclusive. *H. Staudinger* and *F. Zapf* [52] have it that it varies with the γ-number (xanthate ratio) of the viscose, but the recorded numerical values of these investigators require revision, unpublished experiments having made it plain that they are not altogether reliable. This matter calls for further study. *G. Jayme* and *J. Wellm* [53] have taken an important step in the right direction by their very careful investigations recently published. They worked out a standard method by which wood pulps of the most various kinds can be reproducibly converted to a four per cent. solution of viscose without any noticeable degradation [54], and the DP determined by measuring the viscosity of this solution. These investigators used the formula proposed by Hess and Philippoff to convert the measured relative viscosity; this equation has the same form as (14), except that the sixth power is replaced by the eighth. Their results were verified by comparison with the determination of the *DP* by *Staudinger's* method in dilute cuprammonium solution. The resultant formula was:

$$246 \cdot [\eta] = P .$$

As the concentration was expressed in g/100 ml, the K_m constant appearing in this procedure is calculated according to (11) to be 4.07×10^{-4}.

Formula (15) does good service in practice when changes in viscosity, caused

[51] The influence of the velocity gradient of flow should, however, still be taken into account. (Cf. Part I, Chapter III § 4.4).
[52] *H. Staudinger* and *F. Zapf*, J. prakt. Chem., 156, (1940) 261.
[53] *G. Jayme* and *J. Wellm*, Kolloid-Z., 107, (1944) 163.
[54] A solution of 2 per cent. strength is used for P between 1000 and 2000, and of 1½ per cent. for $P > 2000$.

by variation in the average degree of polymerization or in the concentration of cellulose, have to be estimated. For instance, say that two equally viscous viscoses are required with 6% and 8% by weight of cellulose, formula (15) at once shows by rule of thumb that the *DP* of the celluloses must be taken in inverse ratio (so 4 : 3), and so forth.

The absolute viscosity of the usual commercial viscoses is within the order of magnitude of 50 to 100 poises. Hence these solutions are roughly 5000 to 10 000 times more viscous than water.

2.4. *Structural Viscosity*

Viscose is a system of pronounced structural viscosity. In formula (1) η is not a constant for it, but is still a function of the velocity gradient D; indeed, η declines considerably with increasing values for D. This is represented in diagram in Fig. 126. It is, however, clear from measurements made by *W. Philippoff* and *H. E. Krüger*[55] that the viscosity of viscoses of 4 to 10 per cent. may be regarded as constant at all shearing stresses below about $\tau = 250$ dynes/cm². Viscosity measurement taken with the instruments commonly used in practice are usually well below this figure, so the complication arising from the structural viscosity does not yet make itself felt[56].

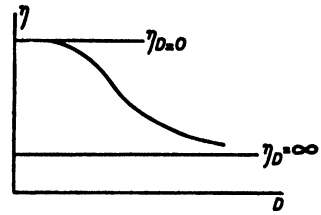


Fig. 126. Diagram showing the course of the absolute viscosity η of a technical viscose with the velocity gradient D in the viscometer.

As *H. L. Bredée* and *J. de Booys*[57] have demonstrated, however, τ-values of the order of 5.10^5 dynes per cm² do occur when the viscose is pressed through the narrow capillaries of the spinning nozzles at the customary pressure gradients in large-scale spinning of approximately 2 atmospheres excess pressure. The viscosity of the viscose then drops to one-tenth to one-twentyfifth of its value in the falling ball test. But for this striking phenomenon, the viscose would have to be fed to the nozzles under extremely high pressures of the order of 50 atmospheres, and spinning would therefore become impossible with the usual equipment.

For further particulars respecting the rheological properties of viscose reference may be made to *W. Philippoff's* book[58]. The intrinsic mechanism of these phenomena still awaits elucidation and the task must needs be a heavy one on account of the complications undoubtedly inherent in concentrated solutions[59]. Nevertheless, further systematic investigations into the structural viscosity of viscose as a function of its composition and preliminary treatment cannot fail to be rewarding in connection with the

[55] *W. Philippoff* and *H. E. Krüger*, Kolloid-Z., 88, (1939) 215.
[56] For the computation of τ from the dimensions of a capillary viscometer see, e.g., *W. Philippoff*, Cellulosechemie, 17, (1936) 57.
[57] *H. L. Bredée* and *J. de Booys*, Kolloid-Z., 96, (1941) 24.
[58] *W. Philippoff*, Die Viskosität der Kolloide, Dresden and Leipzig 1942.
[59] Cf. e.g., *H. L. Bredée* and *J. de Booys*, Kolloid-Z., 99, (1941) 171.

important questions touched on (see pages 47ff, 54 and 77), relating to the structure of the spinning solutions and its influence upon the properties of the resulting gels.

§ 3. SOME PRACTICAL DATA ON VISCOSE COMPOSITION

The composition of the viscose depends upon the following:

1. The composition of the alkali cellulose.
2. The quantity of carbon bisulphide used for sulphidation.
3. The quantity and composition of the solvent liquor.
4. Any other additions.

The sulphite pulp commonly concerned contains 87 to 90% of α-cellulose and 10 to 13% of hemicellulose (β- plus γ-cellulose). The so-called "purified" celluloses often have a higher α content.

A portion of the hemicellulose is eliminated in the steeping process (usually 60—70%, consisting predominantly of γ-cellulose). The steeping liquor always contains a certain amount of hemicellulose, varying in different factories and according to the steeping process applied between 0.8% and 3%.

The alkali cellulose is calendered to 2.8—3.2 the weight of the dry starting material (the aim, latterly, being to keep the pressing factors as low as possible). As the percentage of sodium hydroxide in the alkali cellulose differs little from that in the liquor squeezed out, the press factor has but little influence upon the sodium hydroxide content of the material to be pressed and only its cellulose content changes. As stated on page 332, the pressed alkali cellulose contains about 15—16% of NaOH and 30—34% by weight of cellulose.

The amount of CS_2 used for sulphidation is 32—36% of the weight of the quantity of cellulose present in the alkali cellulose, i.e. approx. 0.7 to 0.75 mole per mole $C_6H_{10}O_5$. After sulphidation, only about 0.5 mole of this and merely about 0.35—0.40 mole in the viscose is bound as xanthate.

The xanthate is dissolved in dilute caustic soda solution, possibly containing hemicellulose. The common practice is to express the composition of the viscose as a percentage by weight. The cellulose content varies in different factories from 6 to 10%, but is usually 7—8%. Besides this, the "alkali content" is recorded, a figure which comprehends all the sodium compounds coming under the head of NaOH. On the basis of the composition of the alkali cellulose, the alkali content amounts to at least half the cellulose content, but is frequently consideraby higher, up to roughly 90% of the cellulose content. The lowest possible alkali content is, however, generally chosen for reasons of economy. Limits — as a rule very narrow ones — are set to the composition of the viscose for each individual operation.

For scientific purposes the content of all viscose constituents is more conveniently expressed in moles per litre (see page 341).

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CHAPTER III

THE TECHNICAL SPINNING PROCESS

§ 1. INTRODUCTION

It being the purpose of this book to present those theories which, from the scientific point of view, are fundamental, a detailed discussion of the many technically interesting particulars of the spinning process would be outside its province. As every specialist knows, the subject is almost inexhaustible and could easily form the theme of an elaborate monograph, though most of the research work devoted to it has not been published.

In the following sections we shall discuss only a few general points of view and some of the results of published investigations. We shall endeavour to select those processes which, from the standpoint of fundamental research, are of prime importance, thereby laying down a basis for, and a vindication of, the classification of the material and the framework of its treatment in this book. Some such guiding lines seemed indispensable to the systematization of the author's train of thought when he planned the book, but, as we are committed to an excursion into a territory in part barely explored, we incur the risk of maybe confining the plan within too narrow limits. Although the author is fully aware of this, his ultimate decision was to adhere nevertheless to the original scheme. It is to be hoped that skilful research will supply the remedy for the undoubted deficiencies and inadequacies in the selected mode of presentation.

§ 2. DIVISION OF THE SPINNING PROCESS INTO COAGULATION AND ORIENTATION

Industrial spinning processes are exceedingly complicated stationary processes in which numerous chemical and physical processes take place in a very short space of time (generally no more than fractions of a second), either simultaneously, or in quick succession. They do not, therefore, offer a suitable or easy means of investigating, or tracing quantitatively those fundamental partial processes which are the subject of our enquiry.

It may be said that two primary processes are involved in the transmutation of the isotropic spinning liquid into a solid, anisotropic filament, viz., *coagulation* (the reassembling and cohesion of the dispersed particles) and *orientation* (the alignment of the particles).

The fluid jet of spinning liquor extruded at constant velocity from a nozzle is exposed to conditions which cause it to *coagulate*. At the same time the filament, formed ultimately by the congelation of the spun material, is drawn off at a constant rate, so that a stationary condition is maintained. As the take-off velocity always by far surpasses the velocity of delivery of the liquid from the nozzle, a stationary gradient of velocity is established which in some way is distributed over the spinning filament between the nozzle and the take-up device. The existence of a velocity gradient in the spinning filament signifies, of course, that the filament is subject to an axial deformation, a stationary stretching.

The total s t r e t c h — i.e., the ratio between the velocities of take off and delivery at the nozzle — is easy to ascertain, for the average rate of delivery [1] of the spinning liquid from the orifice is given by the volume fed to the nozzle per unit of time and by the diameter of the hole. If these are known and also the rate of take-off, the total "stretch" can be calculated [2].

It is known that in any case the o r i e n t a t i o n which results from spinning is induced by the stretching, but it is more difficult to find out how the total stretch is distributed between the various individual phases along the spinning filament and its particular effect upon the orientation. It will be readily understood that the distribution of the stretch will be determined on the one hand by the external resistances which the filament meets on its way and, on the other, by the internal resistance which the filament itself exerts against its deformation. If for a moment we set aside the former, we shall see that the greatest stretch will be where this internal resistance is at its least, that is to say in the still fluid section close to the nozzle. This is actually the case, as we shall see directly.

There are "wet" and "dry" spinning processes. In the former, coagulation is brought about by a liquid spinning bath through which the spinning filament is drawn. In this, chemical reactions, "salting-out effects", withdrawal of solvent, or a combination of all these, are liable to play a part.

Two principal types are differentiated in the "wet" spinning process, known as the "ordinary" and the *Thiele* funnel processes. The latter is often also, not very felicitously, referred to as the "stretch spinning process" [3].

In the "dry" spinning process the spinning filament is in a gas chamber, if need be heated, and coagulation is brought about by gradual evaporation of the solvent. As far as stretch is concerned, this process most nearly resembles the funnel process.

We shall now begin by considering the outward differences between the various spinning processes, after which we shall see that intrinsically they

[1] Owing to lamellar flow in the jet capillary, parabolic distribution of velocity prevails over the diameter, so one can only speak of an *average* rate of delivery.

[2] If the concentration of the spinning liquid is also given, the dry denier of the spun filament at the take-up device can likewise be computed.

[3] Cf.e.g., the presentation of this subject by *O. Faust* in his book "Kunstseide", Dresden & Leipzig 1931, p. 43.

are very much alike. The primary difference between the funnel and dry processes, on the one hand, and the ordinary wet process, on the other, is the difference in order of magnitude of the total stretch. For the former relatively wide nozzle orifices of 0.5 — 1.0 mm diameter are used to spin filaments of the customary fineness, viz., 1 — 4 denier, whereas the orifices used to produce filaments of the same yarn number by the ordinary wet process are of 0.05 — 0.1 mm diameter; which means to say that they are of smaller area by the factor 10^{-2}. Thus, given the same yarn number and concentration of the spinning liquor, the stretches in the two cases are as 100 to 1. Under normal practical conditions the absolute values are of the order of 500 and 5 respectively [4].

Then, it has become the practice to have slow and gradual coagulating baths for the funnel process and rapid action baths for the ordinary process. Obviously, therefore, in the former case the filament retains its liquid consistency for a relatively long distance after leaving the nozzle and then coagulates slowly. The still liquid section is marked with an arrow in the diagram of Fig. 127a[5]. In the funnel process the spinning bath is allowed to flow with increasing velocity towards the take-up. The friction of the bath, which moves with a higher velocity than the filament, has a bearing on the distribution of the total stretch. It tends to increase the amount of stretch in the region nearer to the nozzle[6].

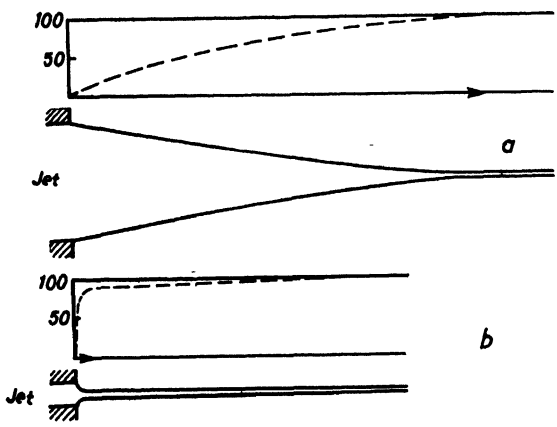


Fig. 127. Diagram showing the constriction and velocity of the filament as a percentage of the rate of take-up, a) in the Funnel and Dry Spinning processes, b) in the ordinary Wet processes. (The lateral dimensions are shown in hundredfolds as compared to the longitudinal dimensions). The arrow marks that section of the spinning filament which is still entirely fluid (or almost so).

In the other type of process most commonly used for viscose, the filament enters a far more potent coagulation bath (see Fig. 127 b). Here the still fluid section of the spinning filament is very short indeed, being of the order of only 0.2 mm (run through, therefore, in something like 0.002 sec). As soon as the jet of fluid emerges from the orifice, a congealed skin is formed on

[4] The common rates of take-up in the funnel and dry processes are roughly 200—300 m/min. and, in the ordinary process, from 60 to 90 m/min. Given the same yarn number, this difference does not, of course, affect the stretch, because the quantity of spinning liquid fed per second to the jet hole and, therefore, its rate of delivery must then increase in proportion to the take-up.

[5] In the tunnel and dry processes the liquor is actually spun straight downwards, so that the effect of gravity upon the liquid jet has also to be taken into account.

[6] Cf. *T. Tomonari*, J. Cellulose Inst. Japan, 13, (1937) 33.

its surface, gradually spreading inwards (Fig. 128). The result is that at a very short distance from the nozzle, the velocity of the filament skin has practically reached the rate of take-up and then, compared to the total stretch (which here, after all, still amounts to 150 to 400 per cent.), undergoes only a minor amount of stretching, i.e., about 10—20%.

Once again, therefore, by far the greatest part of the stretch is effected at the quite short, still fluid section near the nozzle. What takes place, therefore, is an abrupt constriction of the cross-section in a short, cone-shaped section (Fig. 127b)[7]. Any further diminution of the cross-section that may take place subsequently is due almost solely to shrinkage and in only a minor degree to stretch.

In this case the spinning bath is not intentionally made to flow in the direction of the filament. In contrast to the funnel process the friction of the bath tends to decrease the amount of stretch in the region nearest to the nozzle. However, for the reasons just mentioned, the greatest part of the total stretch is still effective in that region and only a small part in the coagulated portion of the filament.

The slight stretch referred to just now, to which the coagulated part of the filament is still subject, is due almost entirely to this friction of the bath liquor. It even drops to nearly nil at slow absolute rates of take-up (below roughly 30 m/min) and only gradually increases at higher velocities as the result of increasing friction of the liquor.

The degree of orientation of the spun filament depends upon how the spinning process is conducted. In the wet process, the greater the external friction to which the spinning filament is exposed, the better will be the orientation. This friction increases with the distance the filament has to travel in the bath and with the rate of take-up. The range of variation within practical control, however, is seldom such as to ensure, by this means alone, the degree of orientation which is required. In actual practice, therefore, external friction is enhanced by making the emergent filament pass at an angle along a thread guide, or over godets rotating at different speeds[8]. In both cases subsequent "stretching" takes place.

Any increase of the total stretch merely — which can be obtained by, for example, reducing the rate of delivery by enlarging the orifice of the nozzle — has little or no effect upon the orientation reached[9]. Accordingly, there is no very appreciable difference as regards the degree of orientation attainable between the funnel and the ordinary spinning processes, although in these

[7] "Spinning capacity", i.e., the property of a liquid thread which enables it to be drawn out (a phenomenon investigated by *H. Erbring*, Kolloid-Z. 98, (1942) 164), is probably an important factor in the shaping of this narrowing jet of liquid.

[8] See for this matter *K. Götze*, "Kunstseide und Zellwolle nach dem Viskoseverfahren", Berlin 1940, p. 410 ff.

[9] *H. Rauch* and *J. Harms* have, it is true, referred to some influence exercised by variation of the size of the jet upon the mechanical properties (Zellwolle, Kunstseide, Seide 47, (1942) 282, but it was relatively slight and, moreover, may be associated with other effects inherent in the nature of the technical spinning process applied.

two cases the stretch differs by two powers of ten [10]. In both processes most of the total stretch is accomplished in the liquid portion and therefore scarcely affects the orientation at all.

All these facts tend to show that, if it be asked in which phases of the spinning filament the stretch has most effect upon the orientation attained, the answer must be that stretch in the fluid state does not contribute at all, or at best in a very minor degree to the orientation.

Admittedly, it follows from the birefringence of flow in the case of many solutions of high polymers that a certain orientation of the dissolved particles may take place in a liquid jet drawn by a velocity gradient, even as it does with flow through the narrow jet capillary; obviously, however, this effect plays at most a subordinate part in spinning [11]. In the spinning process, therefore, the total stretch cannot by any means be regarded as a measure of the orientation [12]. We know, on the other hand, that the stretching of a viscose gel already completely coagulated is a very effective factor indeed as regards the orientation. The small portion of the total stretch referred to above, which becomes effective upon the coagulated section of the filament, is, as we shall see later, amply sufficient, as far as order of magnitude is concerned, to account for the moderate orientation attained in the filament emerging from the bath.

Very little is known as to the result of deformation in the intermediate conditions, if any, between the liquid and the coagulated states; if there are such intermediate states, they might be expected to play some part, especially in funnel spinning. For obvious reasons, the matter would be very difficult to investigate experimentally, inasmuch as transitional states of the kind are by no means well defined and are subject to rapid change with time.

That, however, the deformation in these transitional phases really cannot be of much account may now be inferred from interesting investigations carried out by *H. Hoffman* [13], who studied the dry spinning of viscose in a dry cell heated by hot air. Although he applied a 1 to 5 stretch, he obtained barely isotropic filaments, which could only be orientated by subsequent further stretching. Thus, whereas, with the high cellulose content (15%) of the viscose, its unusually high viscosity and the rapid spinning rate applied (more than 200 m/min), any orientating effect of stretching upon the liquid or semi-liquid state should in this case have been particularly pronounced,

[10] Under optimum conditions and without the help of subsequent stretch, it appears to be easier to obtain good orientation with the funnel than in the ordinary process. The reason of this maybe that in the former case the orientation is more homogeneously distributed in the cross-section of the filament (no difference between skin and core, as in the second case; see further below).

[11] *O. Faust*, Kunstseide, Dresden and Leipzig 1931, p. 46 ff. reports that he was unable, to detect any birefringence of flow in viscose. This statement, however, is not conclusive. cf *E. Signer* and *W. Meyer*, Helv. chim. acta, 28, (1945) 325.

[12] Also cf. *W. Matthaes*, Die Kunstseide 18, (1936) 334.

[13] *H. Hoffman*, Zellwolle, Kunstseide, Seide 46, (1941) 87.

such was n o t found to be the case. *A. Sippel* [14] states that with dry spinning of acetate rayon, too, increased stretch leads merely to a finer fibre and not to any improved orientation.

To probe more deeply into the processes of orientation, it would be necessary to carry out quantitative investigations under well-defined conditions into the relationship between deformation and orientation, on the one hand, and the other properties of the material associated with the orientation, on the other. Such investigations are hard enough to actualise with liquid material and harder still with it in its semi-fluid transitional states, but they are quite feasible with thoroughly coagulated objects. It is therefore a happy circumstance that, in the actual spinning process, those deformations which are "effective" as regards the decisive processes, do not take place until the material has become thoroughly coagulated. We shall see later that these processes can be "isolated" in model experiments and then examined individually at leisure.

The quantitative analysis of the complicated stationary spinning process is, on the contrary, a most exacting task. All the transitions occur between liquid and gel, the degree of deformation and also the rate of deformation are spread over the consecutive sections in obedience to no easily detectable quantitative rule and, moreover, the degrees of swelling and of decomposition are constantly changing from the moment of the emergence of the thread from the jet until fully spun. It will be evident, therefore, that the conditions are exceedingly complicated. Although there are expedients by which the stationary velocity gradient can be determined, there seems to be little prospect of accurately defining, or experimentally establishing, the state of coagulation and swelling along the filament.

Though, in itself, it should be possible to measure the birefringence along the spinning filament, this could not serve as a measure of the orientation, because the composition and swelling of the filament, changing constantly, as they do, create conditions so hopelessly involved as to render its quantitative evaluation a sheer impossibility.

All this is even further complicated in the ordinary viscose spinning process by the formation of the primary skin already referred to (Fig. 128), the growth in thickness of which it is also difficult to follow experimentally. The orientation and also the swelling degree of the outer layer of artificial fibres spun in this way is known to be different from that of their core, a fact made patent by, for instance, differences in the birefringence, in the absorption of dyestuffs, etc. (Part II, Chapt 1, § 2).

An argument frequently advanced to explain this is that the primary skin is stretched immediately after it is formed and thereby already becomes orientated, whereas the initially liquid and gradually solidifying core of the filament does not become orientated till later. It does not seem likely, however,

[14] *A. Sippel*, 4. Forschungstagung Weimar, p. 17, (1943).

that so simple a theory suffices to explain skin formation and there are certainly other contributory factors which are not yet known[15].

According to *F. F. Morehead* and *W. A. Sisson*[16] the skin effect is correlated with the transient formation of cellulose zinc xanthate at the outer part of the filament, owing to the reaction between the zinc ions present in the spinning bath and the cellulose sodium xanthate. (For further details see next section.)

The analysis of the spinning process is further complicated by the ordinarily very irregularly shaped cross-section of the finished spun filament. We shall revert in § 3 to these irregular shapes of the cross section, for which the composition of the bath and many other factors are largely responsible.

These exceedingly complicated matters, which we have only cursorily touched on here, are a serious impediment to the quantitative investigation of the processes in the spinning filament. It is for this reason that, notwithstanding a highly developed and perfected technique, until recently the important quantitative relations between stretching, or deformation, and the orientation attained have not been understood at all. The industrial spinning process provides no reliable evidence by which the state of coagulation and swelling — which is determinative so far as the effect of the deformation is concerned — or the degree of deformation taking place can be exactly established. If, nevertheless, we are to penetrate any further into the quantitative relations, it will be necessary, instead of enquiring into the stationary total process "dynamically", to isolate temporarily the rapidly successive individual processes and study each of them "statically".

Taking the viscose process first, we have primarily the following main processes:

1. The coagulation of the cellulose xanthate solution to a cellulose xanthate gel not yet orientated and, therefore, isotropic.
2. The chemical decomposition of the xanthate gel into a cellulose gel.
3. The orientation of the gel by deformation, either as xanthate gel, or as cellulose gel.
4. The shrinking of the cellulose gel.

Investigations along these lines were started a few years ago for the first time by the author and his collaborators and it transpired that in this way many fundamental questions respecting the spinning process actually did become accessible to experimental enquiry. The results so far obtained will be dealt with in the following chapters; they would certainly seem to warrant the pursuit of the matter on this basis. The procedure is, then, to let the

[15] Interesting views as to the course of the technical spinning process are to be found in: *O. Faust*, Kunstseide, Dresden and Leipzig 1931, p. 43 ff; Kolloid-Z., 61, (1932) 257. *H. L. Bredée*, Chem. Weebl., 30, (1933) 51. *L. A. van Bergen*, Chem. Weekbl., 30, (1933) 55. *W. Schramek* and *E. Zehmisch*, Kolloid. Beih. 48, (1938) 93, where skin formation is also dealt with. Recently *A. Sippel* has offered a mathematical theory of the wet spinning of acetate rayon (Z. Elektrochem. 50, (1944) 152, 256). These papers contain some very interesting elements, though the theory as such seems to be highly speculative.

[16] *F. F. Morehead* and *W. A. Sisson*, Textile Res. J., 15, (1945) 443.

isotropic spinning liquid coagulate first in the form of a homogeneous cylindrical gel filament, without any stretching at all, and then to examine the resulting isotropic model filament, by subjecting it to deformation, either immediately, or else after certain preliminary treatment (e.g., decomposition of the xanthate, contraction) and to keep a record both of the process of orientation and of the alteration to the properties of the thread. The processes of coagulation and deformation can be investigated individually by means of model filaments of the kind, subject to external conditions.

In industrial viscose spinning, as well, there is primarily coagulation in the form of the cellulose xanthate. It has become evident from many investigations [17] that, when it leaves the bath, the major part of the freshly spun filament consists of undecomposed xanthate, which is only later gradually converted to cellulose. Thus, in actual practice also, the orientation takes place mainly in the xanthate state through the inducement of stretching. The diagram of Fig. 128 illustrates how, in the spinning filament, the transformation to layers of xanthate and cellulose may be imagined to take place. The dimensions lengthwise have been considerably shortened and it must be remembered that the transition from xanthate to cellulose is, of course, a gradual one

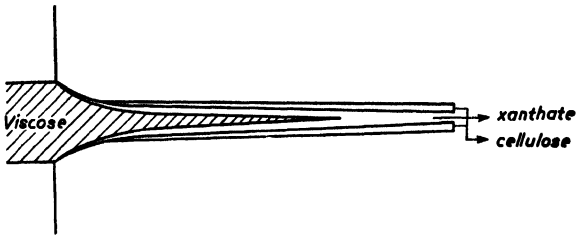


Fig. 128. Diagram of the spinning filament. Formation of a skin of cellulose xanthate, which gradually decomposes to cellulose. (Scale in the fibre direction very considerably shortened).

It is true that, in the "static" examination of model filaments just mentioned, the case under observation is always merely the deformation acting upon the already fully coagulated gel. It remains to be seen whether in actual spinning other special processes take place which ought not to be ignored, or effects produced which do not come into play in model experiments of the kind. We have already proved that in all probability special effects such as these are not induced by the stretch in the fluid or semi-fluid state.

There is another objection, presumably a more important one, which involves a limitation of the representative character of the model experiments. Using simple experimental technique, only the deformatory behaviour of the undecomposed xanthate gel — or degraded in the suggested degree — or of the pure cellulose gel can be examined at leisure. Even the stretch of a filament with irregular distribution of the degree of decomposition inwards, and the stationary state of diffusion of acid, salt and alkali are difficult to realize in model experiments. Yet these may bring about striking effects in technical spinning processes, as demonstrated by the marked differentiation between skin and core.

[17] See, for example, *R. Inoue*, J. Soc. Chem. Ind. Japan, 41, (1938) 334.

In model experiments, moreover, the examination of deformation during decomposition of the xanthate is complicated by considerable technical difficulty, for this is again a stationary process dependent to a great extent upon time. There is, however, reason to believe that, under these conditions, effects take place, interesting from the technical point of view, but not yet fully understood[18].

Another difficulty which should not be underestimated is this: The great speed with which the various processes take place in actual spinning cannot be reproduced in the model experiment. (The spinning filament passes through the entire bath length, or spinning funnel, in 0.2 to 0.3 second.)

Model experiments, nevertheless, concerned only with the deformation of the isotropic gel in its completely coagulated condition, may reproduce with very close approximation many features of the fundamental processes of orientation resulting from spinning, and their effects. Their usefulness in paving the way to deeper insight into the intrinsic processes of spinning and the associated mental separation of those processes into those of the isotropic coagulation and those of the orientating deformation, justifies our classifying our material according to them. Our standpoint will therefore be that, essentially, the usual spinning process depends upon the successive occurrence of these two processes[19]. This may apply in the same degree to the funnel and to the ordinary process; as will be evident from the foregoing there is no fundamental difference between the two. The filament produced by the former method differs mainly from that resulting from the ordinary process in that there is no, or far less, difference of condition between skin and core, while as a rule the cross sections of the spun filaments are also more regular.

§ 3. SOME FURTHER DATA ON THE SPINNING PROCESS

3.1. Orientation during spinning

Up to the present there have not been many publications on what takes place in the complicated technical spinning process. In addition to the works mentioned in the footnote on page 362, we would cite the older publications by *Kämpf*[20], *W. Matthaes*[21] and *T. Tomonari*[22], and also the, theoretically, almost incomprehensible paper by *L. Lilienfeld*[23], which we shall not discuss here. Not long ago *G. Krebs*[24] published some interesting research respecting the X-ray spectroscopy of the orientation in the spinning process, from which it appears that the filaments emerge from the spinning bath slightly orientated and then undergo further stretching and orientation through certain special subsequent stretching devices.

[18] We are here thinking of, for instance, the very special effects, discovered empirically, which are produced when spinning viscose in baths of high sulphuric acid concentration (*Lilienfeld* process) with subsequent stretching, of the primary xanthate filaments in hot water. Thus a sudden big increase in thread strength is obtained, for the inner cause of which no explanation has yet been found.

[19] This view is limited to the spinning of cellulose and its derivatives. Matters may be different in entirely different modes of spinning, such as that of polyamide fibres and other thermoplastic polymers, and also in the spinning of protein fibres. An exception may also have to be made for the *Lilienfeld* process, which has not yet received enough attention in this respect.

[20] *Kämpf*, Die Kunstseide 9, (1927) 361.

[21] *W. Matthaes*, Die Kunstseide 18, (1936) 334.

[22] *T. Tomonari*, J. Cellulose Inst. Japan, 13, (1937) 33.

[23] *L. Lilienfeld*, Die Kunstseide 12, (1930) 128.

[24] *G. Krebs*, Kolloid-Z., 98, (1941) 200.

Parallelism was shown to exist between the breaking strength of the filaments and their orientation. *Krebs's* investigations were the first in which an attempt was made to follow orientation in the spinning process quantitatively and *Krebs* also tried to record in curves the thread speed along the filament. The stretch is indicated by the slope of the tangents to these curves. The results thus obtained, however, are not correct, as they derive from cross-sectional measurements of samples taken at various places of the spinning filament and the samples were dried before they were measured. *Krebs*, having failed to allow for the anisotropy of the swelling (which is very considerable, especially in barely orientated filaments), finds velocities which are far too low for the sections of the thread near the jet. His work, however, admirably exemplifies how modern expedients may be utilized to discover what goes on during the process of spinning.

J. Löbering[25] and *F. H. Müller*[26] have studied the spinning process from the point of view of molecular physics, but, as their standpoint will be considered elsewhere in this book, we shall now devote only a few words to the matter.

Both authors are of the opinion that the molecules in the spinning liquid should be considered primarily as flexible single filaments which, owing to the stretching which takes place, are laid out somewhat in parallel juxta-position and stretched. *F. H. Müller* regards the spinning liquor as a felted structure with mechanical relaxation; in his view, any assumption of relatively rigid, rodlet-shaped molecules must be rejected. Only where micellae or crystallites are formed can there be any question of more rigid particles (compare pages 28 and 74).

J. Löbering points out that it should not be assumed that the chain molecules in the spinning liquor have complete freedom of movement. He maintains that every possible kind of reciprocal influences, such as swarm formation and association, occurs in the sol of 7—8% concentration, where already a certain amount of structure is formed (cf. pages 28ff, 56). The influencing of the structure in the sol itself should be allowed for liberally as a contributory factor when considering filament formation (p. 42).

Both authors also stress the inevitable differences between skin and core which occur in industrial spinning.

3.2. The Irregular Shape of the Cross-sections and the Differentiation of the Skin and Core

Filaments spun in accordance with the common viscose process mostly exhibit serrated cross-sections of very irregular shape (Part II, Chapter I § 2). This fact is usually thought to be due to the differentiation between skin and core. The formation of the "primary skin" is said to originate just behind the jet orifice, where the diameter of the filament is still relatively large. This skin retains its girth and must therefore necessarily fold inwards upon the subsequent considerable contraction of the filament in diameter.

Both phenomena, i.e., irregularity of shape and skin forming, however, need to be further studied and are still far from being clarified[27].

The view has often been expressed[28] that osmotic forces are responsible for the marked influence of the composition of the spinning bath, especially the concentration and nature of the salts in it[29]. A certain amount of water is said to be withdrawn from the spinning filament, varying with the concentration of the electrolyte within and outside it. But, it may be asked, does osmosis bring us any nearer to a clarification of the matter? For osmosis presupposes a semi-permeable membrane which lets through the solvent, but not the dissolved substances. The swollen gel, however, is by no means impervious to the dissolved electolytes. Some transportation of water will certainly take place, but it is very difficult to analyse.

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[25] *J. Löbering*, Papierfabrikant T. w. T., 37, (1939) 9.

[26] *F. H. Müller*, Physik. Z., 42, (1941) 123.

[27] Theories on the skin effect are to be found in: *J. M. Preston*, J. Soc. Chem. Ind., 1931, T. 199; *R. Klaus*, Die Kunstseide, 15, (1933) 9, 357; *K. Ohara*, Sci. Papers Inst. Physic. Chem. Res. Tokyo, 25, (1934) 152; *S. Poznanski*, (Abstract), Z. angew. Chem., 51, (1938) 768; *O. Succolowsky*, Mitt. deutsche Forschungs Inst. f. Textilind. Dresden, 1, 1935) 6; *W. Schramek* and *J. Helm*, Kolloid. Z., 85, (1938) 291; *W. Weltzien* and *K. Windeck Schulze*, Zellwolle Kunstseide, Seide 44, (1939) 399; *P. A. Koch*, ibid, 46, (1941) 51; *F. F. Morehead* and *W. A. Sisson*, Textile Res. J., 15, (1945) 443.

[28] *A. Lottermoser* and *C. Schiel*, Z. angew. Chem., 43, (1930) 80.

[29] See e.g. *R. O. Herzog*, Text. Forsch., 8, (1926) 87.

It may be quite right to say that the formation of a primary skin plays an essential part in this case; but, if the core of the filament is still fluid, mere mechanical action might account for the folding up of the skin. It may quite conceivably be emptied to some extent at the back by the stretching which begins to take place in the bath (that is to say, therefore, that the liquid contents move more slowly than the skin, which is more directly exposed to the take-up).

A fact which seems to corroborate that the inside of the filament is still fluid at first is that sometimes, when there may be greater evolution of gas (e.g., with viscose containing carbonate), hollow filaments are obtained. The gas is then evolved in the still liquid core of the filament and inflates, the fibre to some extent. This could not take place so easily in a completely coagulated gel. On drying, the skins thus produced collapse and become like flat bands, but *W. Schramek* and *E. Zehmisch*[30] succeeded, by a special method of preparation, in retaining the rounded shape of the skin and in illustrating it. If an oil emulsion is added to the viscose prior to spinning (as a delustrant), the oil droplets are sometimes found to be concentrated near the boundary between skin and core after spinning. This is only comprehensible if it is assumed that, after formation of the skin, the filament core has remained liquid long enough to allow migration of the oil droplets. All this, however, does not explain the nature of the differentiation between skin and core encountered in ordinary viscose rayon, nor the pronounced difference in their properties.

Morehead and *Sisson* [16] state that the degree of swelling of the core is anything up to 40% greater than that of the skin, a statement confirmed by *Preston* by comparative measurements taken from cross-sections in the dry and wet states [31]. If it be considered furthermore that there is in any case a difference in orientation (of whatever nature it may be; see below), it will be evident that, together with changes in degree of swelling, stresses will occur between the skin and the core, which may also have something to do with the folding of the skin. It is not clear, however, whether this difference in orientation is primary, or whether it is the result of stresses caused by differences in degree of swelling.

There are several phenomena which make it plain that peculiar states of stress arise in the so-called "jacket fibres", precisely in the contact area of skin and core. For example, minute cracks, or gas bubbles, approaching the limit of microscopic visibility, are formed, most often at the borderline between skin and core (the phenomenon of milkiness; cf. Fig. 137, p. 372).

Round cross-sections are formed in the slower and more uniformly operating precipitating baths, such as neutral ammonium salt solutions, and also in the funnel process. This would bear out the theory of anisotropic contraction.

It is, moreover, a fact that, given otherwise unchanged conditions, if additional frictional resistance, or a stretching device, be introduced between jet and take-up device, either the fibre cross-section becomes more serrated, or its "circularity coefficient" diminishes. The introduction of appliances such as these naturally reduces the velocity of the thread near the jet and herefore increases both the diameter and the surface of the filament. The skin is therefore laid on more amply. (For this see also *Schramek* and *Zehmisch*[30].) As the ultimate yarn number is not changed, the result must be either more pronounced crumpling, or a lower "circularity coefficient" of the cross-section[32]. This phenomenon is quite compatible with both the hypotheses expounded above, i.e., the emptying, or discharging, theory and the theory of contraction.

[30] *W. Schramek* and *E. Zehmisch*, Kolloid Chem. Beih., 48, (1938) 93.

[31] Private Communication; (Cf. also ref. 33 where it is shown that also the optical density of the skin is greater than that of the core).

[32] The "circularity coefficient" of a fibre cross-section is proportional $\frac{t}{b}_2$, where t is the yarn number and b the maximum diameter of the cross-section. Its magnitude diminishes in proportion as the cross-section deviates from circularity. (Cf. *J. M. Preston*, Modern Textile Microscopy, London 1933).

In a recent paper *F. F. Morehead* and *W. A. Sisson*[16] made some valuable suggestions respecting the skin effect problem. They have shown that the thickness of the skin is affected very little, if at all, by the amount of stretch and other mechanical conditions of spinning. It is, however, distinctly dependent on the composition of the viscose and that of the spinning bath. Under otherwise comparable conditions, a thicker skin is obtained if the viscose is richer in free alkali, or if the degree of xanthation is increased. This conforms with the present author's observation that the thickness of the skin diminishes if the acid concentration in the bath is raised. The alkali-acid ratio seems to be the determining factor. Thicker skins are also formed if the concentration of bivalent ions, like zinc and cadmium, in the spinning bath is increased.

From this work it would seem that those conditions which favour long life of the xanthate and the formation of a layer of the xanthate of a bivalent metal ion (usually zinc xanthate) tend to increase the thickness of the skin. The authors claim that a difference in orientation is not the main feature of the skin effect, but that it is rather another intrinsic difference in the structure of the gel which, they suggest, is a difference in degree of lateral order. They believe that the skin contains more and smaller crystallites than the core, owing to the fact that the bivalent zinc ions form cross links between the xanthate, which would hinder the formation of a lateral order. A typical skin may already be formed at very low concentration of zinc ions in the bath.

The author of this book has found that, if isotropic model filaments consisting of undecomposed xanthate and lying in an ammonium sulphate solution, are transferred to another ammonium sulphated solution containing 1% zinc sulphate, a sharp boundary line is seen to penetrate slowly into the filament (Fig. 129). This boundary line marks the skin which is converted to zinc xanthate[32a].

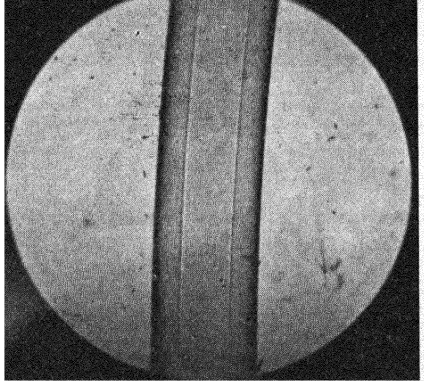


Fig. 129. Boundary lines due to zinc ions penetrating into a xanthate filament

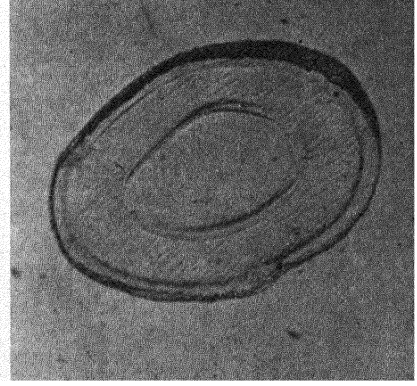


Fig. 130. Cross-section of the filament shown in Fig. 129 after treatment with water.

[32a] For the general conditions governing the formation of sharp boundary lines in diffusion, see *J. J. Hermans*, J. Colloid Sci 2, (1947) 387.

If a cross-section of the filament is made before the boundary lines have reached the centre of the filament and is laid in water, the core, still free from zinc, dissolves, whereas the skin, consisting of insoluble zinc xanthate, remains unchanged (Fig. 130). If the filament shown in Fig. 129 is stretched a little and then examined in polarized light, using a *Becke* compensator, it is clearly seen that the birefringence of the skin is larger than that of the core (Fig. 131). This is demonstrated by the retrograde course of the

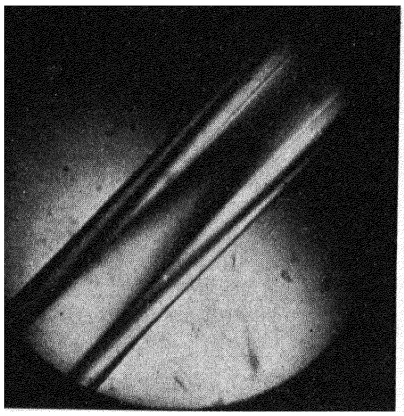


Fig. 131. Filament in Fig. 129 after being stretched, viewed between crossed nicols and using an *Ehringhaus* compensator.

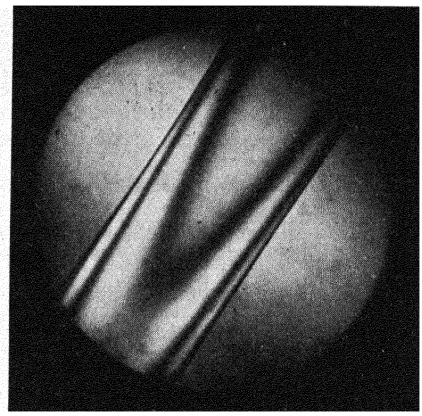


Fig. 132. Ordinary stretched xanthate filament for comparison with that shown in Fig. 131.

black lines in the centre of the filament (which mark the lines where the phase difference is equal to a whole number of wavelengths). For comparison the corresponding picture of a stretched homogeneous xanthate filament (not exposed to zinc salt) is shown in Fig. 132. If, therefore, a filament having a zinc xanthate skin is produced in actual spinning, stretching of this filament must give rise to a different birefringence between its skin and core. This fact alone, however, cannot serve to explain the differential staining effects observed in viscose rayon, since model filaments treated as shown in Fig. 131 do not exhibit this effect. It would only explain the occurrence of a different orientation and it would seem that other factors, as yet unkown, come into play. The explanation offered by *Morehead* and *Sisson*, which relies entirely on the transient formation of a zinc xanthate skin, does not account altogether for the observed skin effects.

This is evidenced particularly by the fact that rayon spun in a bath not containing zinc is also liable to exhibit a typical skin, even though that skin be usually thinner than that coming from baths in which zinc is present.

The author has examined several samples of rayon spun in a zinc-free sodium sulphate-magnesium sulphate bath, which displayed a typical skin when dyed with Victoria blue by the method advocated by *Morehead* and *Sisson* recently simplified by the present author[32b] and by other methods of staining (cf. below).

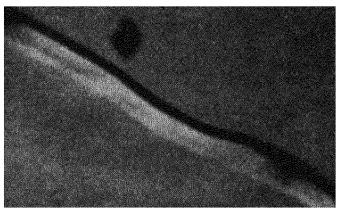


Fig. 132 A

Skin formation may also be observed if a thin layer of viscose spread on a slide is exposed to an ordinary spinning bath. Fig. 132A shows a cross-section of a film so obtained, dyed according to the Victoria blue technique. This seems to demonstrate that some as yet unknown peculiarity in the process of diffusion of the bath components into the viscose is mainly responsible for the phenomenon of skin formation.

[32b] *P. H. Hermans*, Textile Res. J., 18, (1948) 9.

The writer has shown that the examination of rayon cross-sections in the polarization microscope reveals some interesting facts which may help to divulge the nature of the skin-core effect [33].

At first sight, the appearance of cross-sections between crossed nicols is rather confusing. A pattern is seen of dark and light patches separated by dark lines. The pattern changes, of course, when the stage is revolved. The analysis of the optical character of the sections can, however, be facilitated by two means, viz.,

a) Selecting sections having only coarse serrations (which were found in a viscose rayon spun in a zinc-free bath containing 8.5% H_2SO_4, 18% Na_2SO_4 and 4% $MgSO_4$).

b) Using a compensator, by which the magnitude of the birefringence can be determined; also the orientation of the direction of the largest refractive index in any part of the sections.

In this work the compensator used was of the *Ehringhaus* type. To measure the birefringence of a particle, the stage of the microscope is rotated until the particle shows maximum brightness between crossed Nicols. Its main refractive indices then lie at an angle of 45° to the polarization planes of the polarizing and analyzing prisms. Now operating the micrometer screw of the compensator (by which a crystal plate is slowly rotated around an axis also lying at 45° to the crossed nicols), the light transmitted through the particle can be either extinguished, if its main refractive index lies perpendicular to the axis of rotation of the crystal plate, or not, if the two directions are parallel. (Positions of subtraction and addition of the double refraction of the particle as compared to that superimposed by the compensating crystal).

The compensator enables the operator to find the direction of the largest refractive index n_α in a birefringent particle by rotating the particle until its transmitted light can be extinguished by operating the compensator screw. The largest refractive index then lies parallel to a fixed direction in the field of vision at 45° to the polarization planes of the polarizing and analyzing prisms. In the following illustrations this direction, which we shall call the direction of compensation, will be indicated by an arrow.

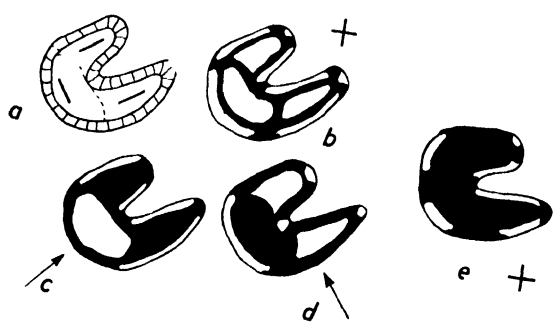


Fig. 133. Diagram showing optical behaviour of viscose rayon cross-sections (see text).

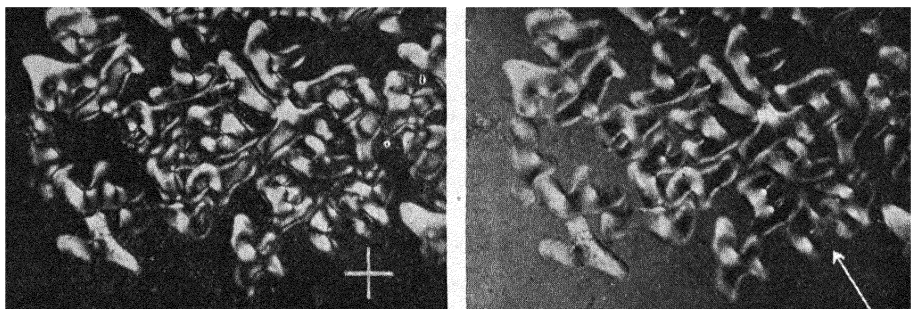
Fig. 133 serves to illustrate the general features of the optical character of many viscose rayon sections. In Figure *a* the straight lines indicate the orientation of the largest refractive index n_α. In the skin the latter always lies perpendicular to the surface; in the core it lies parallel to the prevailing direction of the circumference.

Figure *b* shows the appearance of the section between crossed nicols. Wherever n_α is parallel to the polarization planes (indicated by the cross),

[33] *P. H. Hermans*, Communication at the XIth Int., Congress of Pure and Applied Chemistry, London, 1947 (in preparation).

no light is transmitted. It will also be seen that a black line shows up where adjacent patches of a section, having n_a at mutually perpendicular directions, meet. Figs. *c* and *d* show the appearance of the section after adjustment of the compensator, the directions of compensation being indicated by arrows. Finally, Figure *e* shows what is seen if the section b is rotated 45° between crossed nicols (without compensation).

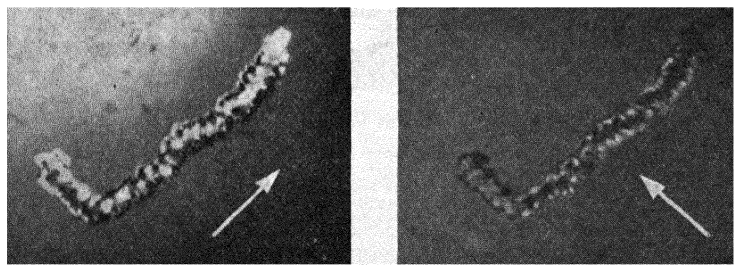
Fig. 134 shows two micrographs of the same set of sections of a viscose rayon spun in a zinc-free bath a) in polarized light between crossed nicols); b) after compensation in the direction as indicated by the arrow. On examining these illustrations it will be seen that the sections behave in the manner schematically represented in Fig. 133. The areas transmitting light in Fig. 134a appear extinguished in Fig. 134b if the direction of their greatest refractive index lies perpendicular to the arrow.



A B

Fig. 134. Cross-sections of rayon (5-denier filaments) spun in zinc-free bath, A. in polarized light between crossed nicols, B. the same with compensating birefringence superimposed in the direction of the arrow.

Fig. 135 reproduces section micrographs of ribbon-shaped rayon filaments spun from a slit in a bath containing zinc and taken between crossed nicols with compensation. They demonstrate even more strikingly the general rules incorporated in Fig. 133. As shown by the relative orientation of the ribbons

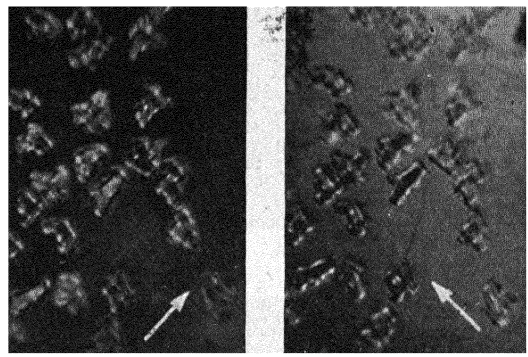


A B

Fig. 135. Cross-sections of ribbon type of viscose filaments (spun from slit-orifice) photographed between crossed nicols with compensation; A and B, same object with superimposed compensating birefringence in mutually perpendicular directions indicated by arrows.

towards the direction of compensation (arrows), n_a of the skin lies perpendicular to its surface and, in the core, parallel to the prevailing direction of its circumference. (Note the interchange between black and white where one of the sections is accidentally bent 90°.)

Finally, Fig. 136, shows section micrographs of a tyre cord viscose yarn having a relatively thick skin and which was photographed under similar conditions of illumination and compensation. It will be seen that the skin has the same optical character as in the previous cases.



A B

Fig. 136. A and B, same set of cross-sections of tyre cord yarn type of viscose rayon (spun in bath containing zinc), photographed between crossed nicols with compensation in the directions indicated by the arrows.

Not in all viscose rayons the optical behaviour of the cross-sections is as simple as in the previous cases. Many ordinary textile rayons which have a relatively thin and finely serrated skin show a somewhat more complicated optical structure.

It should be noted that the birefringence effects observed on cross-sections are to be considered as secondary effects of orientation, such as will occur if lateral stresses are applied to uniaxially orientated filaments (see Part II Chapter IV, § 8, where this case was explained). The conclusion drawn from quantitative measurements of the birefringence of cross-sections, as compared to that of the filaments in the longitudinal direction, is that there is as yet no evidence which would warrant the assumption of "higher orientation" (cf. p. 248) of biaxial elementary particles. All the values found can be accounted for in terms of uniaxial particles. It was found that, in conformity with the foregoing, the birefringence observed in cross-sections decreases as the longitudinal orientation increases[33].

The optical behaviour of the skin would seem to indicate that it has been subjected to tangential compression. As explained in the paper referred to above, this becomes comprehensible if it be assumed that, at some time after the birth of the filament, the core shrinks more than the skin. Under such conditions the skin substance will tend to become birefringent with its n_a perpendicular to that of the core.

Though the full story of the skin-core effect is as yet by no means clear, all facts tend to bear out the assumption of the greater shrinkage of the core. Its higher degree of swelling — as demonstrated by *J. M. Preston* —, its greater accessibility to substantive dyes (Part II, Chapt. I § 2) and to chemical attack [34] seem to support this hypothesis.

[34] Micrographs published in a paper by *K. Schönleber*, Zellwolle Kunstseide, Seide 46, (1941) 51, demonstrate how the core may also be preferentially dissolved following attack by micro-organisms.

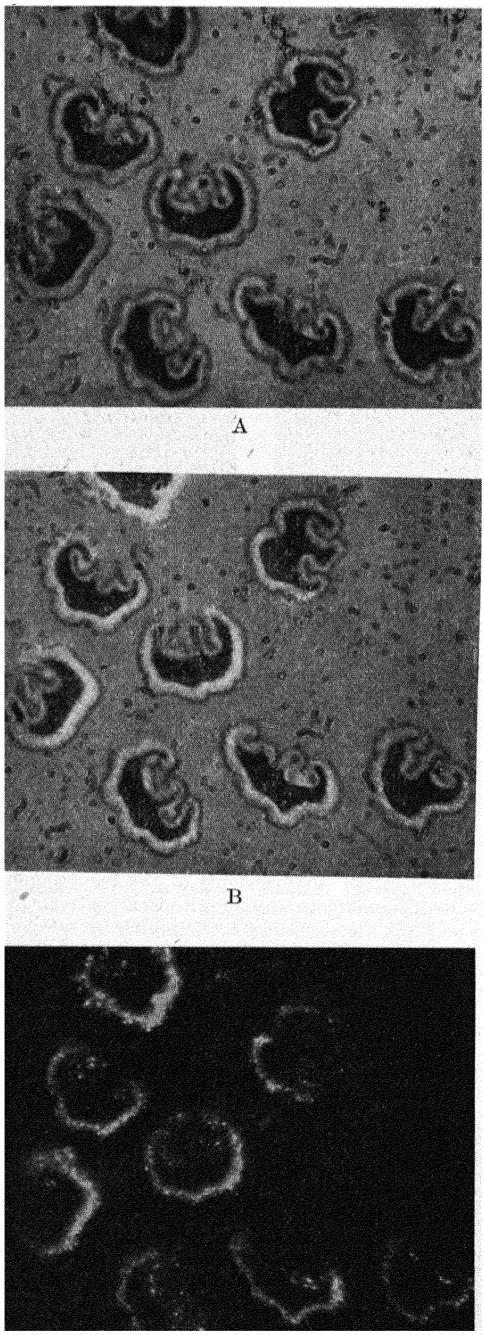


Fig. 137. Same set of rayon cross-sections (core selectively stained), photographed with Leitz combined bright and dark field condenser. A, bright field illumination only; B, combined bright and dark field illumination; C, dark field illumination only (cf. text).

It is evident that, with swelling and shrinking, internal tensions will preferably occur at the boundary between skin and core. Here too, under certain conditions, tiny cracks may appear in the gel, which are responsible for the "milkiness" in rayon (cf. p. 366). This can be observed microscopically in sufficiently powerful dark-field illumination, when rows of tiny bright spots concentrated at the boundary between skin and core become visible.

Fig. 137 *a* reproduces sections of a cord tyre yarn dyed with solophenyl-blue-green BL (Geigy) and imbedded in a liquid of equal refractive index; these were photographed with ordinary bright-field illumination. The core is dyed; the skin, whose outer circumference is just visible, is not. In photograph 137 *b*, dark-field illumination superimposes the bright-field illumination. Bright spots appear and it will be seen that they are mainly located at the boundary between skin and core. Finally, in photograph *c* the bright-field illumination has been shut off and only the bright spots are seen. It will be noted that they are particularly concentrated where the skin is thickest (next to those parts of the skin where the serrations are least pronounced and where the greatest tensions would actually be expected to occur).

The phenomena described in the foregoing may serve to show yet again how exceedingly complicated and elusive is the nature of the technical spinning process. It is patent that further study of these phenomena is of the utmost importance. They constitute an aspect of the problem which cannot be studied with the help of model filaments spun in salt solutions, whose structure is homogeneous.

CHAPTER IV

FUNDAMENTAL PROCESSES UNDERLYING SPINNING AND AFTERTREATMENT IN RELATION TO THE STRUCTURE OF ARTIFICIAL FIBRES[1]

§ 1. INTRODUCTORY REMARKS

We saw in the preceding chapter (p. 356) that the transformation of viscose to an artificial fibre may conveniently be divided up into four distinct principal processes, which we shall now consider more closely. We shall then try to define the determinative factors governing the structure of the finished fibre.

§ 2. GELATINATION THE FIRST PHASE OF THE SPINNING PROCESS

The fundamental primary process called into being by the manufacture of filaments and films from a solution is the gelatination of the solution to a coherent gel. All reactions leading to the formation of a coherent gel are, in principle, potential producers of films and filaments. In actual practice, artificial fibres are manufactured, almost without exception, either by evaporating the solvent (dry spinning process), or by gelatination by the action of relatively concentrated electrolyte solutions upon aqueous solutions of the substance under treatment.

If we are to penetrate more profoundly into these processes and the structure of the resulting system, we must have a clear picture both of the structure of the solution and of the intrinsic nature of gelatination.

The structure of cellulose solutions may be briefly recapitulated as follows:

1. The former view that the intrinsic nature of these solutions is closely associated with a state of polymolecular dispersion has been superseded, as has also that which held that pre-formed, well-defined rod-like particles ("Micels") occur in the solid substance.
2. In the case of certain solvents at any rate, some authors assume that there are pre-formed polymolecular aggregates originating from the raw material. If such actually exist, they must have the character of "fringe-micels" (p. 30).

[1] The train of thought set down in this section is a direct corollary of the matters dealt with in Part I, Chap. II § 4, 6 and 8 and Chap. III § 6, with which, therefore, the reader is assumed to be conversant.

3. In by far the majority of solutions, however, dispersion in extreme dilution has been proved to proceed right down to single molecules. The rare exceptions are due to particles whose osmotic activity points to associations of a few (2 to 3) single molecules, such cases being particularly liable to occur in non-polar solvents if the molecule still carries free hydroxyl groups (p. 53).

4. Concentrated cellulose solutions have a structure. The molecules enter into association, or at any rate have a distinct reciprocal effect upon each other, and this in a higher degree the greater the concentration. (Page 56).

5. These interactions probably lead to a low-distance order of the molecules (approximate parallelization), becoming more marked as the concentration of the solution increases, and thus also, in the statistical sense, to a transition from a more or less kinked to a more straightened shape of the chain (p. 127).

6. The association leads to local, statistically distributed secondary bonds between the chains, which are constantly dissociating again and re-forming elsewhere and are, therefore, short-lived (brief relaxation). Fluidity is thus maintained.

7. When a cellulose solution is nearing those conditions which are conducive to gelatination, ever more and longer-lived bonds are formed between the chains (junction points of longer time of relaxation), which might be termed the local first stages of the gel. In like manner, the newly produced solutions from a swollen cellulose compound may for some time contain similar aggregates, only slowly dissociating, which should be considered as the last stages of the swollen gel state (p. 55, 79). Obviously the structure of these aggregates is very similar to the picture we have of the "fringe-micels".

8. Once definite gelatination has set in, so many local stable bonds (junction points) have been formed between the molecules that a coherent frame may be said to have been built up permeating the entire liquid.

If point 2 were to apply to certain cellulose solutions, the principle of low-distance order would undoubtedly be found to hold good for concentrated solutions in this case too [2]. The make-up of a solution of the kind would then not be very different from that of a solution with monomolecular dispersion approaching coagulation. The structure of the gels formed from these solutions under comparable conditions should also be similar and would therefore only be distinguishable in minute points. Even if it be insisted that the matter is still inconclusive, there is no reason why a general idea of the structure of spinning solutions and that of the gels obtained from

[2] *O. Kratky*, Kolloid-Z., 68 (1934) 347.

them should not be formed with some show of probability. We shall now try to build up a picture of the kind, linking to it a working hypothesis for later views as well, for, if we are to make any progress in our difficult subject, we shall certainly need as wellfounded a working hypothesis as we can formulate. We present in Fig. 138 a diagram of the structure of a relatively concentrated cellulose solution conforming to the principle of lowdistance order. The molecular chains are represented as approximately straightened, with neighbouring chains generally in more or less parallel orientation. Corroboration of this picture is afforded by the evidence of agitation tests applied by *H. A. Stuart*[3] to chain models. (The figure does not reproduce the probable occurrence here and there of more kinked sections of the chains).

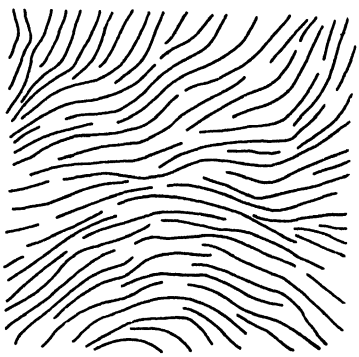


Fig. 138. Diagram of the structure of a relatively concentrated cellulose solution with "low-distance order".

A viscose with 8 per cent. cellulose of 300 DP will contain flexible rodlets approximately 300 μμ long, 1 μμ thick, with voids in the middle of about 3 μμ filled with the solvent. Although the macroscopic viscosity of the solution is exceedingly high and any Brownian movement of microscopically visible particles would seem out of the question, the thermal movement of the solvent molecules in the smallest voids between the chains is certainly far less restricted (little "microviscosity"). By transmission of this impulse to the single members of the chain, these too will be in constant vibration, with the result that the distances between them will be continually changing.

The question now arises as to whether the chain molecules in this picture are also to be considered as "free" and whether this is, strictly speaking, a "state of monomolecular dispersion". This is where we need the associations in the concentrated solutions, assumed under point 5, to complete the picture. These must be thought of as local aggregations of parallel chain section of adjacent molecules, distributed at random within the whole in the diagram of Fig. 138. The reason why there is as yet no mechanical cohesion of all the chains throughout the liquid is that there are equilibria and each assembly point is of limited duration (see point 7). If the conditions are altered in a way to reduce the "solubility", the constantly changing bonds become permanent and the state of gelatination is approaching[4].

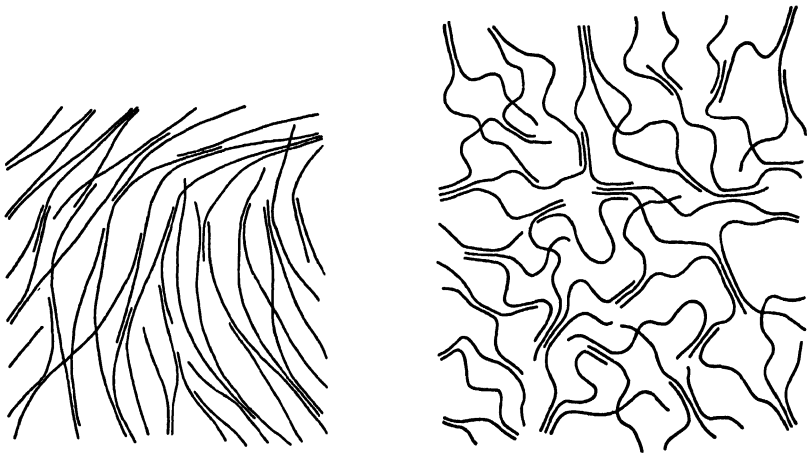
The essential principle of the process of gelatination was fully discussed in Part I, Chap. II, § 8. In the manufacture of artificial fibres from viscose, gelatination results from the action of salt solutions, or from extraction of

[3] *H. A. Stuart*, Naturwiss., 31, (1943) 123.
[4] Cf. *P. H. Hermans, J. J. Hermans* and *D. Vermaas*, Kolloid-Z., 105, (1944) 199; *J. J. Hermans*, Kolloid-Z., 106, (1944) 95.

the solvent (sodium hydroxide) (p. 341). In the end, either comes to a lowering of the solubility of the cellulose xanthate. As just described, the chain molecules then join and the cohesive gel frame is thus built up. Where the chains are compulsorily parallelized, the junction points are in the nature of centres or nuclei of crystallization.

Since coagulation takes place in the fraction of a second (at all events in actual spinning practice) and the large molecules diffuse very slowly in the viscose (p. 43), the structure of the gel cannot be very different from the original structure of the solution. This inference finds support in the noteworthy fact that even the gels formed by the action of highly concentrated, strongly de-hydrating coagulation solutions on viscose retain, with but little loss, their volume in the sol state (cf. Chap. VIII § 1).

Figs. 139 A and B show in diagram the structure of the primary gel formed during coagulation, along the lines of Fig. 138. In Fig. 139 A the molecules are assumed to be straighter; and a higher degree of low-distance order is assumed to exist, than in Fig. 139 B. The difference will be about the same



A B

Fig. 139. Diagrams of the structure of the primary xanthate and cellulose gels, after coagulation. Molecules assumed to be more straightened and in more advanced low-distance order in A than in B.

as that to be expected in the coagulation of a concentrated and a dilute solution (see point 6).

O. Kratky[5] thinks the chain molecules have a random kinking and a crystallizing tendency. During the process of gelatination the latter predominates over the former tendency and the molecules assemble section-wise in the depicted pattern. Association complexes, to some extent pre-formed in the solution, may be built into the frame.

If, from the very beginning, there existed some "fringe micels" in the solution, or minute fragments of gel formed before complete coagulation, even then

[5] *O. Kratky*, Kolloid-Z., 96, (1941) 301.

the final structure of the gel could hardly be essentially different from that presented here. The hotly disputed points at issue, therefore, are relatively unimportant to further enquiry into the intrinsic structure of gels.

More detailed features of the structures cannot be known until comprehensive evidence respecting the behaviour of the gels is available (for which see Chap. XI).

The picture here presented of the primary isotropic gel comprehends a number of possible variants which, from now on, can be related to the distinctive behaviour of gels produced under different conditions (also cf. p. 49 ff). Such variants are the number and distribution of the junction points, also their lengthwise and lateral size ("degree of crystallinity"), kinkiness in the unordered chain fringes and the degree of orientation in the small regions.

It need hardly be said that the following make their imprint upon the developing structure:

1. Concentration and temperature of the solution.
2. Composition of the solvent.
3. The means by which coagulation is brought about (coagulant, rate of coagulation, temperature).

The isotropic model filaments mentioned on page 385 embody the result of gelatination. A clearer insight into their structure may, it is hoped, be obtained by examining their properties and behaviour during their conversion to cellulose, under deformation and contraction, tried out by as many experimental methods as possible and with systematic variation of the above operational conditions. This has only been partly done; some of the results will be considered in the following chapters.

§ 3. THE CHEMICAL DECOMPOSITION OF THE PRIMARY XANTHATE GEL

This calls for comparatively little comment. There is nothing intrinsically mysterious about the fundamental process, viz., the cleavage of all the xanthogenic acid residues bound to the chains. The actual problem is: whether and how the structure of the gel is thereby altered. As will be made plain later, what we see externally is merely a partial shrinking of the gel brought about, not by a change of medium, but by the process of decomposition, itself.

As, presumably, the chains are uniformly occupied by xanthate groups prior to gelatination, these are likely to be present both in the junction points and in the intermediate regions, an assumption strengthened by the fact that xanthate gels are still soluble in water and are only stable as gels in sufficiently concentrated salt solutions [6].

[6] The ready solubility of primary xanthate gels in water does not support the view upheld by *K. H. Meyer* (Hochpolymere Chemie, Vol. II, p. 541, Leipzig 1940) that junction points are formed selectively between those sections of the chains which no longer carry xanthate groups.

The highly hydrophilic xanthate groups probably bind fairly large quantities of water which, accordingly, are also present "intramicellarly" in the junction points. This is corroborated by the X-ray pictures of xanthate dried at low temperature in the ice-box after replacing the salt solution by alcohol. They show a blurred and shifted 101 interference[6a]. If the xanthate groups are split off water will at the same time issue from the junction points. This explains to some extent at least why the degree of swelling tends to decrease. After the degradation, the newly formed, very swollen cellulose gel is insoluble in water. Thus a radical change has taken place in the nature of the junction points, a fact manifested also by the deformatory properties of the material, as we shall see later.

The transformation of the xanthate gel into cellulose is comparable to the saponification of a cellulose ester in its fibrous form. In both cases mechanical cohesion is maintained during the chemical reaction. The isotropic xanthate gel is exceedingly extensible, and so is the isotropic cellulose gel, but, quantitatively, their reaction to deformation is different.

§ 4. THE DEFORMATION OF THE PRIMARY GEL AS THE SECOND PHASE IN THE SPINNING PROCESS

The processes called into play by deformation — especially by elongating the primary gel in a favoured direction (say in the direction of the axis in the case of filaments) — are very important indeed. It has long been known that the structure thereby becomes orientated, in the sense of a selective alignment of the molecular chains in the direction of elongation.

Of particular interest to us is the mechanism of this deformation, though no conclusive explanation of it has as yet been forthcoming. Yet it opens up many valuable vistas, on which we shall expatiate later, confining ourselves at present to the following observations.

Looking at Fig. 139 on p. 376, it will be seen that the newly formed, swollen gel represents a three-dimensional network structure (also cf. Fig. 16 on p. 30). The junction points are as the "nodal points" of this network and the chains connecting them are as the edges of the meshes. Investigations made by *O. Kratky*[7] and also by *P. H. Hermans* and co-workers[8] respecting the orientation as a function of the degree of elongation have now shown that the orientation actually does take place more or less as expected in the deformation of a network structure. Figure 140 represents the deformation of a two-dimensional network in diagram; the network, losing

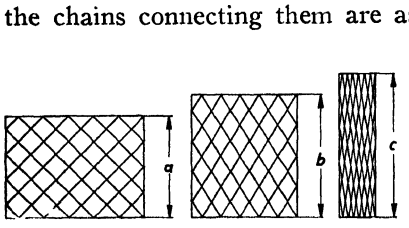


Fig. 140. Diagram representing the "closing up" of a two-dimensional network. a, isotropic initial state; b, stretched slightly; c, stretched further. (Volume decreases).

[6a] Unpublished results.
[7] *O. Kratky*, Kolloid-Z., 84, (1938) 152.
[8] *P. H. Hermans*, Kolloid-Z., 81, (1937) 143; 83, (1938) 71.
[8] *P. H. Hermans* and *A. de Leeuw*, Kolloid-Z., 81, (1937) 300.

heavily in volume, is drawn together. The optimum orientation coincides with the limit of extensibility. This presentation of the facts, with the junction points acting as hinges, as it were, is, of course, a very rough one, though essentially true. It may be applied to the actual threedimensional micellar frame as shown in Fig. 16 (p. 30) and Fig. 139.

In actual fact, a very considerable reduction in volume (down to less than half the initial volume) is observed when highly swollen, primary, isotropic gels are elongated; see Chapter VIII, § 2. Moreover, their maximum extensibility (which is approximately 100 per cent.) is of the same order as that expected for three-dimensional networks[9]. It will be readily understood, however, that, compared to this over-simplified model, actual micellar frames will display many complications and modifications, some of which we shall now enumerate.

1. If the junction points of the network structure are formed by the crystalline regions, they occur, not as dots, but as relatively elongated regions behaving like rigid oblong particles.
2. The meshes are not all of the same size and are far less regularly interlinked. This may mean (as will at once be evident from Fig. 16) that not all the meshes will contract in an equal degree and extensibility will be obstructed before all the meshes are closed and all the chains are straightened out in alignment. There might even have to be involuted chains with retrograde loops and freak entanglements.
3. It is far more difficult to probe the function of the "hinges". Nor is there any obvious proof that it is precisely the junction points that act in this capacity; if necessary, any parts of the free sections of the chains might do so.
4. We do not know what shape the chains have outside the junction points; whether they are stretched out straight approximately, or whether they are more or less coiled or sinuous. It is, however, just this "more or less" which will govern the maximum extensibility as also the orientation (cf. Fig. 139A with Fig. 139B).
5. It is quite conceivable that the junction points do not behave like unchangeable elements of the structure during the process of deformation, but rather increase or diminish in size under the strain. A junction point here and there might even be torn out of place, while others again might be built up.

Here again, then, we have a number of possible variations which, together with the variants dealt with on page 377, greatly complicate the problem of the structure of the primary gel.

The hypothesis by which the processes taking place during deformation of the primary gel are said to be in essence comparable to the "straightening out" of a network structure provides us with only a very sketchy guiding

[9] *P. H. Hermans*, Kolloid-Z., 83, (1938) 71.

line, for it must be remembered that this network has very special properties differentiating it from the fundamental schema.

If the primary isotropic gel is allowed to shrink before the deformation, there will be further complications (§ 5).

It is the task of artificial fibre research to study these various manifestations and to devise methods and means of subjecting the problems presented to experimental analysis. These may be found by studying extensibility, the changes in volume through elongation and the orientation resulting from elongation — all this under the most varied conditions. We already have to hand the foundations for optical and X-ray methods, laid down in Part II, Chapters IV and V, with which to study orientation. The former furnish information on the average orientation of all components of the gel frame; the latter on that of the crystalline regions.

§ 5. THE AFTER-TREATMENT (SHRINKAGE)

Since the customary after-treatment of the freshly spun artificial fibres with water and various chemicals in dilute solutions for the purpose of washing, desulphuration and bleaching does not involve any further intrinsic structural changes, we need only consider the drying process, that is to say the shrinking of the gel, in which determinative structural changes will take place. Let it be said at once that the degree of swelling[10] of freshly spun isotropic xanthate filaments is of the order of 10, becoming about half that after the degradation of the xanthate in fresh cellulose filaments. Thus, when objects of this kind are dried, their volume is reduced to a tenth or a fifth of the original volume. Looking at the diagrams of Figs. 16 and 139, we shall realize that this must entail very radical structural changes. Far from being a simple process, it is astonishing that this drying should proceed in so simple a manner and with such apparent ease. We shall come across phenomena which imply that in actual fact quite radical structural changes are involved and that these take place by no means as smoothly as would at first sight appear. It has, moreover, long been practical knowledge that the properties of artificial fibres are in no wise unresponsive to the drying procedure, which is a rather exacting operation. We should like to mention the following views:

1. The contraction of network structures (particularly if they are presumed to be isotropic) is indisputably unimaginable if they consist of rigid structural elements, unless the original junction points be assumed as constantly dissolving and reforming elsewhere. In this case it was said that in the drying process the cellulose chains are able to glide past each other continually in the junction points, an assumption which must, of course, be immediately rejected.

[10] In this part "degree of swelling" denotes the ratio between the volume of the swollen to that of the air-dry gel (conditioned at 65% r.h.). It will be designated by the letter q. The degree of swelling referred to the bone-dry condition is 1.17 times greater.

2. The ineluctable inference from the fact that greatly swollen celluloses (and other gels) are liable to shrink to compact "Xerogels" by the mere withdrawal of solvent is that, if they really are network gel frames, they must contain flexible structural elements capable of involution during shrinkage [11]. It is flexible elements such as these that we have in the "free" molecular chains lying outside the crystalline regions and linking these. There is no avoiding the assumption that shrinkage must go hand in hand with some change in the shape of this chain, be it involution or coiling [12]. Later on we shall come across phenomena which bear out this view.

   W. F. Busse [13] was one of the few investigators who early on quite clearly related the mechanism of shrinkage and the re-swelling of the gels of polymeric substances to the folding up and unfolding of the molecular "strings" of the gel frame. (The same author also developed useful hypotheses respecting the deformatory mechanism of these systems). At a later date, *F. H. Müller* [14] and the present author [15] also invoked the theory of the involution of molecular chains to explain shrinking.

3. On shrinking, the frame becomes ever more compact and new points of contact and new junction points, consisting of cellulose-cellulose bonds, will also be formed. To distinguish them from the *primary junction points* already present in the primary gel, they might be called *"secondary junction points"*. The nature of the latter will depend upon the local orientation of the specific chain sections.

   In the immediate vicinity of the primary junction points with parallel chain orientation (Fig. 141 at *x*), the chains there striving to part company will have an enhanced chance of meeting each other, while shrinking is going on, in a manner favourable to the formation of a lattice order. There would then possibly be a growth of the regions of lattice order (increase in size of the crystallites), besides which new lattice regions might be formed in other favourable places.

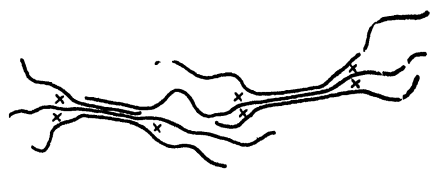


Fig. 141. Plan showing growth of crystalline regions during the shrinkage of a gel (x marks the places where particulary favourable conditions prevail).

4. A glance at Figs. 16 and 139, however, will show that there can only be limited growth of the well-ordered regions, or new formations of them, and that a considerable proportion of the structure can only contract into a less

[11] For this cf. *H. R. Kruyt*, Chimie et Ind., 42, No 4 (1938).
[12] A view somewhat different from the assumption of a simple "folding up" of single chains, though essentially tantamount to the same, is discussed by *P. H. Hermans*, Kolloid-Z., 97, (1941) 231.
[13] *W. F. Busse*, J. Phys. Chem., 36, (1932) 2862.
[14] *F. H. Müller*, Kolloid-Z., 95, (1941) 153.
[15] *P. H. Hermans*, Kolloid-Z., 97, (1941) 231.

well-ordered amorphous substance, during which process numerous junction points will be formed in rather haphazard order, in which the chains will meet in unpropitious positions.

5. It is to be expected that, a complete *spectrum of secondary junction points,* varying in extent, order and binding power, will be formed on the way from the swollen primary gel to the Xerogel, at one end of which spectrum the primary junction points will join on continuously.

6. An important question is whether an *increase in the portion of crystalline substance during shrinking* can be ascertained at all. *O. Kratky,* with *A. Sekora* and *R. Treer*[16] believed, on the evidence of X-ray data, that the crystalline portion really does increase when isotropic primary gels shrink. These investigations, however, need to be verified and amplified[17]. All the same, it is a fact that the lattice of the crystalline regions in primary cellulose gels immediately after decomposition of the xanthate in the cold, is still imperfect. The X-ray interferences are still somewhat blurred and the A_3 and A_4 interferences of the $(10\bar{1})$ and (002) planes (see Part II, Chap. V) have merged into one. The interference A_0 of the (101) plane is particularly indistinct and has shifted inward. The crystalline regions still consist of Cellulose Hydrate II and therefore still contain water. When the gel is dried, and also when the swollen gel is boiled in water, A_0 becomes more distinct and shifts to the correct place and A_3 and A_4 are now seen to separate[18].

   X-rays will not reveal the formation of small new regions of parallel orientation, consisting of only a few, or of short chain sections, as an increased amount of crystalline substance, because regions of such small size do not diffract selectively.

   The positions of the isotherms of sorption before and after the first drying (Fig. 55) are additional witnesses to the probable formation of more junction points (non swelling substance) during drying.

7. It is not difficult to see that the course of the shrinking process and the ultimate structure of the Xerogel will depend upon the particular conditions of drying, such as rate of drying and temperature. Both the time factor and the mobility of the members of the chains will tell upon the internal formation of the structure. It is to be expected that the last steps of this process, in particular, when the gel is nearly dry, will put up the greatest resistance to this shrinkage and will be influenced by the factors mentioned (see Chapter VIII).

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[16] *O. Kraky, A. Sekora* and *R. Treer*, Holz als Roh- und Werkstoff, 4, (1941) 273.

[17] After completion of this Ms. a treatise by *O. Kratky* and *A. Sekora*, (Kolloid Z., 108, (1944) 169 appeared in which this matter is subjected to close enquiry. It thereby transpired that the quantity of crystallized substance — within a margin of accuracy of about 10% — *changes neither upon elongation nor upon shrinkage of swollen fresh cellulose filaments.* This is a very important discovery. Apparently, therefore, the formation of crystalline regions ceases when gelatination is completed.

[18] *P. H. Hermans,* Contribution to the Physics of Cellulose Fibres, Amsterdam-New York 1946, p. 102.

8. In view of what has just been said, it is obvious that the process of shrinking will vary to some extent all according to whether the substance is an isotropic gel, or one orientated from the first by deformation.

§ 6. THE DEFORMATION OF THE SHRUNK PRIMARY GEL

We must briefly consider the case in which deformation does not take place until the primary gel has shrunk. We have an example of it when elongation is applied at a time when the primary xanthate gel, subjected to contraction, has already been entirely or partly decomposed to a cellulose gel. We are confronted with a similar case even when we elongate a dry or re-swollen filament, such as is the practice when testing the mechanical properties of finished products.

According to the foregoing, we then elongate a modified gel frame, differing from the primary one in that it possesses more involuted or coiled network strings and, all according to the degree of swelling considered, more or fewer secondary junction points. The "junction point spectrum" extends further towards the side of the junctions possessing less binding power but, besides these, the primary junction points have persisted and may even have been strengthened. We need not be surprised, therefore, if we find later that the specific character of the primary gel is retained after its shrinkage and is imprinted even more distinctly upon the general behaviour of the shrunken gels. In what way the properties change upon shrinkage is a question with which we shall concern ourselves later on.

The decisive part played by the structure of the primary gel frame in relation to the behaviour of the gel systems resulting from it by shrinking, is bound up with the views expounded and will run, like a red thread, through all our further discussion (in particular, see Chap. XI and XII).

There exist records of early observations of gels which agree in the main with these views. *R. A. Gorter* and *W. F. Hofman* [19] found that the rate of swelling and also the swelling capacity of dry gelatins depended in a high degree upon the primary conditions of gelatination. They allowed gelatin solutions of varying concentration to gelatinize and dried the gels thoroughly. The more dilute the solution from which it was originally obtained, the more did the gelatin expand when re-swollen in water. The authors concluded from this fact that certain permanent structures are formed during gelatination.

§ 7. ADDITIONAL REMARKS ON THE STRUCTURE OF ARTIFICIAL FIBRES

The finished artificial fibre is the product of the manifold components of the processes set in motion by its manufacture. It must therefore be obvious — and, indeed, it has been impressively manifested in the practical experience of the industry — that the finer points of the structure of the fibre will vary exceedingly with the conditions of manufacture in the widest sense.

If the artificial fibre is regarded as an aggregate of cellulose molecules, it

[19] *R. A. Gorter* and *W. F. Hoffman*, J. Amer. Chem. Soc., 43, (1921) 2199; Proc. Soc. Exp. Biol. and Med., 11, (1922) 257; J. Phys. Chem., 31, (1927) 464.

may be said that its structure is determined by the position of all the monomeric glucose residues and by the nature and size of the forces holding these together. It is impossible to obtain an exact picture of this structure in all its details; it can only be understood and described by statistical standards.

As a guide, we shall here enumerate the most important moments and points of view.

1. *Chemical Points of View.*
   a. The distribution of the chain length.
   b. The nature of the end groups and the nature and distribution of any alien groups.
   c. The nature and quantity of any alien molecules (contaminations).

The essentials of the methods for the exploration of these points were dealt with in the preceding chapters.

2. *Physical Points of View.*

The primary points of enquiry are the configuration and relative positions of the molecules in the fibre; also the forces acting between the molecules. Generally speaking, these points are not open to direct experimental approach.

Invocation of the concepts average state of order, average orientation and density of packing will help to clarify the first two points. The following points would then not seem to be impervious to enquiry:

a. Quantitative proportion, distribution of size and orientation of the crystalline regions, or those considered to be approximately in a lattice order.
b. Quantitative proportion of the less orderly regions and general indications of shape, mobility and average orientation of the chains in these regions.
c. Size and distribution of the voids between the molecules, or their mean density of packing.

Most of the methods and points of view bearing upon these points have likewise been discussed in the preceding part of this book. This is where X-ray, electron-optical and ordinary optical methods are of material assistance. There are, besides, other methods, such as the measuring of swelling, sorption, density and diffusion, by which physics is able to supplement the results of chemical investigations respecting solubility and swelling, the course of chemical reactions in the fibrous form and chemical interlinking reactions, etc. Then, deformation experiments and examination of the so-called mechanical properties serve a very useful purpose [20]. The latter play a very important part in the practical assessment of an artificial fibre; so scientific researchers would do well always to pay due attention to the bearing of structural facts upon the mechanical properties of the product.

We shall enter more fully into these matters in the following chapters.

[20] The term "mechanical properties" is used here in its broadest sense; a more felicitous term might possibly be "deformatory properties", that is to say, all those properties which come into play under the stress of pulling, bending or pressure, and in wear-and-tear tests.

CHAPTER V

ISOTROPIC FILAMENTS FOR MODEL EXPERIMENTS RELATING TO THE VISCOSE PROCESS

§ 1. PRODUCTION OF ISOTROPIC FILAMENTS AS MODELS OF THE PRIMARY GEL

As was emphasized in Chapter III, § 2, the only hope of getting to grips with the fundamental processes succeeding each other in the complicated and rapid industrial spinning process, is to break up the latter into individual phases and study each apart. One way of doing this is to work on model filaments.

H. G. Bungenberg de Jong[1] was the first to make and describe objects of this kind. As from 1937 the author of the present book took up the former's investigations from the point of view just mentioned.

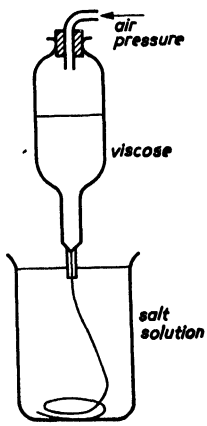


Fig. 142. Apparatus used for the spinning of model filaments from viscose.

Model filaments are relatively thick threads obtained by slowly injecting viscose under pressure from a glass capillary of 0.5 to 1.0 mm inner width into a concentrated salt solution. Suitable apparatus is shown in Fig. 142, with interchangeable capillaries. The necessary constant excess pressure (roughly 5—15 cm Hg) is maintained in the upper vessel. The slowly issuing viscose coagulates on coming into contact with the spinning bath, which should preferably consist of an ammonium sulphate solution of 1.08 to 1.10 specific gravity, and sinks under gravity in uniform slings to the bottom of the lower vessel[2]. It is therefore necessary that the specific gravity of the bath should remain lower than that of the viscose; otherwise the filament will not sink to the bottom[3].

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1 *H. G. Bungenberg de Jong*, Z. physik. Chem. Cohen Festb., (1927) 205.
2 *P. H. Hermans* and *A. J. de Leeuw*, Kolloid-Z., 81, (1937) 300.
3 The length of filament spun per unit of time varies with the spinning pressure and is of the order of 15 cm per min. The length of filament spun per min. can be increased by heightening the drop, but the filament then, of course, becomes thinner. With the same height of fall, the length of the filament increases with progressive difference between the specific gravity of the bath and that of the viscose. The diameter of the filament then also usually decreases, but also depends, of course, upon the degree of swelling which the filament acquires as the concentration of the spinning bath is varied.

Being subjected to practically no strain at all, the filaments thus produced are quite isotropic, being merely gelatinized viscose formed into a thread. As the salt solution only coagulates, leaving the cellulose xanthate otherwise unchanged, the still very swollen filaments are xanthate filaments of almost the same xanthate ratio *(XR)* (see Chap. II, § 3) as that possessed by the viscose at the moment of spinning.

The process of the production of these filaments, therefore, is no other than gelatination of the viscose, and the filaments consequently are models of the primary gel.

It is easy to make long stretches of the filaments with a uniform circular diameter up to 1 to 2%. As they retain their cylindrical shape after other manipulations (swelling, shrinking, stretching), they are in many respects very useful objects for examination. Their volume can be easily ascertained by measuring their length and thickness. Their properties naturally vary with the composition of the viscose and of the spinning bath and, by testing these properties while systematically varying these factors, valuable data can be collected as to their effect upon gelatination as the first phases in the spinning process.

One may then proceed to study the second phase, viz., the fundamental processes of deformation, by stretching the filaments and noting the changes in their properties, such as their volume, orientation and mechanical reactions, as the result of stretching. It is, of course, a great advantage to be able to start from the isotropic fundamental state as zero point. Thus, instead of the dynamic-stationary process of stretching in technical spinning, which it is so difficult to probe, we have static investigation under well-defined conditions.

In the next section we shall discuss some general properties of the model filaments which have served as standards in their assessment.

§ 2. GENERAL PROPERTIES OF ISOTROPIC MODEL FILAMENTS

2.1. Degree of Swelling. The Four Principal States of Swelling

The degree of swelling, q, of newly spun isotropic xanthate filaments is very high. With a normal viscose containing 8% by weight of cellulose and an ammonium sulphate solution of 1.08 specific gravity for the coagulating bath, it amounts to 10—11 [4]. Thus 10—11 cm^3 of gel contain 1 cm^3 of air-dry cellulose. It is a fact worth mentioning that the volume alters little during gelatination, for 14—15 cm^3 of viscose contains 1 cm^3 of air-dry cellulose [5].

If the ripeness figure of the viscose is not unduly low, the fresh xanthate filaments dissolve readily in water.

When the xanthate filaments are degraded to cellulose filaments, the degree

[4] The figures for the degree of swelling are referred to the air-dry state procured by desorption (65% r.h.).

[5] Calculated from the following data, Sp.gr. of the viscose 1.12, dry cellulose content 8% wt.; regain of the cellulose at 65% r.h. (desorption) 15.6% as referred to dry substance; specific gr. of moist cellulose 1.474.

of swelling drops to roughly 5.5, irrespective of whether degradation is brought about by immersion in cold dilute acid, by heating in the ammonium sulphate solution or by leaving the xanthate for days on end in the coagulating bath, when it gradually decomposes. Even if the still highly swollen cellulose filaments are set aside for months at a time, the degree of swelling remains practically unchanged[6]. It is not, therefore, affected by accidental factors, but is closely associated with internal structural conditions. (See Chapter VIII). We shall henceforth describe filaments of this kind as "fresh cellulose filaments". Their condition is comparable to freshly spun rayon, i.e., ready spun, washed artificial fibres which have never been dried. These, too, are known to have a high degree of swelling[7].

In a certain sense, however, the degree of swelling of such objects is metastable. Dried slowly at room temperature in standard atmosphere, the more water they have lost, the less will they swell on re-immersion in water. After having been in equilibrium with the standard atmosphere, they swell only to $q = 2.2$ to 2.3[8]. Again, even after repeated drying, this degree of swelling remains virtually reproducible[9] corresponding to the degree of swelling acquired by industrial artificial fibres on swelling in water.

Thus, for model filaments, there are four distinct *main states of swelling* which lend themselves most conveniently to investigation and which we shall from now on distinguish by the letters listed in Table XLI.

TABLE XLI

Survey of the four main states of swelling of model filaments and their swelling degree

	Object.	Approximate degree of swelling.
X	Xanthate filaments	10—11
F	Fresh cellulose filaments	5—6
D	Air-dry filaments	1
R	Re-swollen filaments	2.2—2.3,

Whereas isotropic *F* filaments are easily obtained from isotropic *X* filaments, completely isotropic *D* filaments are less easy to produce, owing to unavoidable stresses set up during drying (especially after the water content has dropped below about 25%). As a result, the *D* filaments become slightly negatively birefringent outside and slightly positively so inside. *R* filaments also retain this anisotropy, but it is only very slight[10].

[6] Kept in water, fresh cellulose filaments are very susceptible to attack by bacteria, owing to which they soon lose their extensibility. This tendency (formerly wrongly ascribed to a form of ageing) can be wholly counteracted by the addition of suitable disinfectants (e.g. "Raschit").

[7] The fact that this degree of swelling is less than 5.5 is due to the stretch which takes place in this case (see Chap. VIII).

[8] For comparison with the "swelling number" common in practice see page 209.

[9] The degree of swelling only decreases a little more after complete drying at 100° (Chap. VIII).

[10] The best results were obtained when filaments of moderate length were dried slowly without tension and then again swollen and dried (cf. *P. H. Hermans*, Kolloid-Z., 97, (1941) 326.

2.2. Extensibility and Altered Properties Resulting from Deformation.

In each of the main states of swelling previously mentioned the isotropic model filaments are as a rule very extensible (mostly to 100 per cent. and more) and they are therefore suitable subjects for stretching experiments [11]. When stretched, the filaments become anisotropic; they become positively birefringent with reference to the fibre axis and their swelling also becomes anisotropic [12]. When an isotropic filament of q degree of swelling is dried, both in length and thickness it becomes $q\frac{1}{2}$ times smaller. Longitudinal and lateral swelling are equal. But if there has been previous extension, the lateral swelling increases and the longitudinal swelling diminishes. Like orientated natural and artificial fibres, highly orientated filaments swell in thickness only, or almost only.

Extension is also responsible for interesting changes in degree of swelling, of which we shall speak in Chapter VIII.

§ 3. ON THE KIND OF EXPERIMENTS PERFORMED WITH MODEL FILAMENTS

3.1. General Survey

Where isotropic filaments are concerned, the degree of swelling in the four main states of swelling is of principal interest. There is little else that can be measured in the isotropic object. Nevertheless, the phenomena brought into play by the deformation of these filaments offer an exceedingly fertile field of research.

The investigations hitherto have been concerned with the absolute extensibility in the four main states of swelling, the change in degree of swelling following extension and the phenomena associated with shrinkage generally. The spontaneous shortening of the filaments while swelling (swelling retraction), after having been extended, is also interesting. These matters are dealt with in Chapter VIII.

We also have various investigations into orientation during extension in several states of swelling (see next section and Chapters XI and XII). The methods employed are swelling anisotropy, optical anisotropy and X-ray analysis (Chapter VI).

Finally, there are experiments respecting the mechanical properties (elasticity, SS diagrams, breaking data) in conjunction with the trend of orientation (Chapters XIII—XV).

These experiments are not limited to isotropic filaments in the four main states of swelling as starting material. Filaments which have been previously stretched to various lengths in a given state of swelling (viz., the X state) can thereafter be converted to air-dry orientated cellulose filaments and used again in this state as initial material for fresh elongation tests. Experiments

[11] We shall come across exceptions presently.
[12] *H. G. Bungenberg de Jong*, Z-physik. Chem. Cohen-Festband, 205 (1927).

of this kind are models for the manufacture and properties of industrial artificial fibres, for there too the primary gel is first elongated in the X state (some times, too, partially in the F state) during spinning and is then converted to air-dry cellulose (cf. Chapter III).

The field of research is greatly expanded by the fact that, in an endeavour to discover what part manufacturing conditions play in these matters, all the experiments touched on here were carried out with fibrous material produced with varying composition of viscose and precipitation bath. This in itself involves numerous variables.

We shall now proceed to describe the principal evidence of these experiments and see how it fits in with current theories.

When we discuss general data appertaining to swelling and extensibility in Chapter VIII, we shall also consider the influence of manufacturing conditions, but it will be more convenient to consider their effect upon orientation (Chap. X) in a separate Chapter (XI).

It has been found necessary to pay special attention to what is understood by "degree of extension" during the examination of deformation phenomena in various states of swelling, for it is of the utmost importance to establish a rational standard for this. This matter being of supreme importance, it is dealt with apart in Chapter IX.

3.2 Extension Series

The extension series is a form of experiment with model filaments which we shall come across again and again in investigations to be discussed later. To obviate the necessity of digressing into irksome explanations further on, we shall briefly describe it here.

Isotropic model filaments produced from a given viscose in a specific coagulating bath are examined in the four main states of swelling. Filaments are made elongated progressively in series, for which purpose they are clamped into a suitable yarn testing dynamometer and stretched a given amount, after determination of their degree of swelling from measurements of length and thickness (degree of extension v_2) The dynamometer is then brought to a standstill and the filament remains clamped for a certain time (usually 2 minutes), after which it is released and measured anew several hours later (when after-effects have subsided). This gives the degree of extension after recovery (v_3), the elastic retraction and the degree of swelling q_3 after extension [13].

The filaments thus obtained in series of progressive degrees of extension are shrunk by drying in the air X filaments being converted to F filaments before they are dried [14] and are then re-swollen in water and dried once, or maybe

[13] The indices refer to the successive states of the filament. 1 denotes the isotropic initial state.

[14] For reasons to be explained later, it is often advisable to boil the filament for a short while before the first drying.

several times, again. The length and thickness of the filaments are measured again in every state of swelling [15], from which data are obtained the anisotropy and degree of swelling.

Finally, from every main state of swelling is obtained a series of air-dry filaments which have been conditioned by desorption at 65% r.h., and the birefringence of these is determined[16], X-ray photos being taken and evaluated.

All the values of the birefringence mentioned in the ensuing pages refer to the conditioned state. With the help of known data they can easily be converted to the birefringence in the bone-dry state (see Part II, Chap. IV, § 4).

The programme of an extension series also comprises the stress-strain diagram and breaking data of the isotropic filaments in the four main swelling states and procuring the same data for dry *(D)* and re-swollen *(R)* filaments previously stretched in the xanthate state to various lengths; for in their history and properties the latter objects are closely related to their industrial counterparts. (An example of the SS curves of one of these series has already been given in Fig. 105). For further details of experimental technique the reader is referred to *P. H. Hermans* and *A. J. de Leeuw* [17] and also *P. H. Hermans* and *P. Platzek* [18].

§ 4. THE LIMITS OF COMPARABILITY BETWEEN THE PROPERTIES OF MODEL FILAMENTS AND THOSE OF INDUSTRIAL ARTIFICIAL FIBRES

In the course of our work on model filaments we have often had to ask ourselves to what extent comparison with artificial fibres produced on an industrial scale was justified and whether the evidence was really germane to practical problems. This question cannot yet be answered definitely, but we may, perhaps, be allowed to anticipate the following.

It has been stressed in the foregoing chapters that the aim of the experiments hitherto made with model filaments was to study the processes taking place in ordinary viscose rayon production; this in itself imposes a limitation upon comparability.

There are, in point of fact, many results which affirm comparability with this limitation. The behaviour of model filaments, differently orientated, in relation to sorption, swelling, density, optical, and X-ray data, is on the whole comparable, both qualitatively and quantitatively, with that of commercial viscose rayon of varying orientation. The two objects of comparison also have similar mechanical properties. Though the maximum tensile strengths obtained are of the same order, the results are a little better with commercial fibres. Here the question arises as to whether this is in any way due to the very great difference in the absolute thickness of the two kinds of filaments; for examples are not wanting to show that the strength of a fibre is in inverse ratio to its thickness. (A very marked case in point is furnished by quartz filaments). Cellulose filaments have not yet been seriously studied from this angle.

It will be seen at once that properties such as bending and knotting strength depend very greatly upon the absolute thickness of the fibre. Differences amounting to several orders of magnitude are therefore to be expected in this case, and have, indeed, been found[19].

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[15] As lengths are measured between marks made on the filaments, the ends clamped into the dynamometer do not affect the reading.

[16] The whole wavelengths of the phase difference are measured as indicated by *P. H. Hermans* and *P. Platzek*, Z.physik. Chem. A. 185, (1939) 260 — (where see illustration) by cutting a wedge and counting the interference bands. Fractions of a wavelength are measured with a compensator.

[17] *P. H. Hermans* and *A. J. de Leeuw*, Kolloid-Z., 81, (1937) 300; 82, (1938). 58.

[18] *P. H. Hermans* and *P. Platzek*, Kolloid-Z., 98, (1941) 62.

[19] *P. H. Hermans*, Kolloid-Z., 208, (1944) 180.

Another difference is that model fibres have a far more homogeneous structure than viscose rayon fibres, which are known to be "mantle fibres" (Part II, Chap. I, § 2). We do not yet know, however, what this actually entails and so far investigations have thrown no conclusive light on the matter.

Little can as yet be said as to the comparability with cellulose fibres spun by the funnel process from viscose or cuprammonium solutions, as investigations are still in progress. But the fibres spun by the *Lilienfeld* process undoubtedly belong to a different category. The breaking strength of these fibres is known to be roughly twice to three times that of ordinary commercial viscose fibres and they differ from the latter in many other ways as well, as has been pointed out several times before (Part II, Chap. I, § 2, Chap. V, § 3, Chapter VI, § 3.4). Despite the strenuous efforts to clarify it, we are still almost entirely in the dark as to the nature of the intrinsic reactions fundamental to the *Lilienfeld* process.

Model filements are, of course, far more suitable subjects for research into orientation processes than industrial fibres; indeed, it may be said that their introduction put research into this matter on a rational basis. All investigatory experiments of any importance on this subject have been performed with model filaments.

The question of comparability will be discussed again in Chapter XVI.

CHAPTER VI

CURRENT METHODS FOR THE QUANTITATIVE EVALUATION OF THE ORIENTATION OF CELLULOSE GELS AND THE THEORIES ON WHICH THOSE METHODS ARE BASED

§ 1. ORIENTATION EXPRESSED QUANTITATIVELY

The only case we shall deal with here is that of the uniaxial (longitudinal) orientation of rod-shaped uniaxial particles, the orientation of which is given by the angle of their rodlet axis to the fibre axis. It is immaterial whether we consider cellulose crystallites, chain links or monomeric glucose residues as our elementary particles.

The state of orientation is described by means of the unit sphere used by *Polanyi*. Think of a sphere with radius 1 and for every particle present in one cm³ of the body in question insert a radius vector, the spatial orientation of which is the same as the axis of the particle. The direction of the fibre axis Y is supposed to be vertical, i.e., as the solar axis of the sphere (Fig. 143).

Let us first consider an isotropic body with N particles per cm³. Then the N cutting points of the radius vectors with the surface of the sphere are everywhere equally distributed. Let the surface density (number per unit

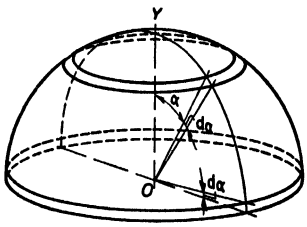


Fig. 143. Unit Sphere.

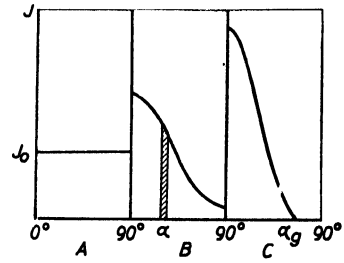


Fig. 144. Distribution curves of surface density with isotropic (A) and orientated objects (B and C).

surface) of the intersecting points on the sphere's surface be I_0. If we plot the surface density on the sphere in dependence upon the spatial angle α made by the vectors with the fibre axis to be from 0° to 90°, we get with the isotropic body a horizontal straight line (Fig. 144), as there is no preferential orientation.

The number of particles dN orientated within an angular interval $d\alpha$ is, of course, larger on the Equator ($\alpha = 90°$) than at an angle α (see the two rings on the unit sphere in Fig. 143) and, depending on α, is given by

$$dN = 2\pi I_0 \sin \alpha \, d\alpha \qquad (6.1)$$

Integration over half the sphere gives

$$N = \int_0^{\frac{1}{2}\pi} 2\pi I_0 \sin \alpha \, d\alpha = 2\pi I_0 \qquad (6.2)$$

If orientation has taken place, the surface density I on the surface of the sphere will no longer be uniform, becoming greater towards the pole. If we again represent it as a function of α, we get a curve somewhat like that in Fig. 144 B, or, with better orientation still, like that in Fig. 144 C. In the last instance the surface density on the Equator is nil and there are no more points of intersection above the angle α_g which we denote as the "peak" angle.

We can now fully describe the orientation by means of these distribution curves of the surface density, which can be represented as a function $I(\alpha)$ of α.

The surface of a narrow strip having $d\alpha$ width (Fig. 144 B), multiplied by $2\pi \sin \alpha$ represents the fraction of the particles dN/N, the orientation of which lies in the angular interval between α and $\alpha + d\alpha$:

$$dN/N = 2\pi I(\alpha) \sin \alpha \, d\alpha \qquad (6.3)$$

Naturally, since the number of the particles is the same before and after orientation,

$$\int_0^{\frac{1}{2}\pi} 2\pi I(\alpha) \sin \alpha \, d\alpha = \int_0^{\frac{1}{2}\pi} 2\pi I_0 \sin \alpha \, d\alpha = 2\pi I_0 \qquad (6.4)$$

and thus

$$\int_0^{\frac{1}{2}\pi} [I(\alpha) : I_0] \sin \alpha \, d\alpha = 1 \qquad (6.5)$$

This equation serves for normalization when curves of this kind have to be evaluated by graphic integration.

Where there are crystalline particles, the distribution curve can be found experimentally by evaluating the intensities of the X-ray diagram (Part II, Chap. V, § 2).

§ 2. THE METHOD BASED UPON ANISOTROPY OF SWELLING

It has already been stated that, when isotropic filaments are elongated, the anisotropy of swelling increases with the degree of extension and, therefore, with the orientation. In many past investigations made by the author and his co-workers since 1937 he attempted to use the anisotropy of swelling as a measure of the orientation[1].

[1] *P. H. Hermans* and *A. J. de Leeuw*, Kolloid-Z., 81, (1937) 143; 81, (1937) 300; 82, (1938) 58; *P. H. Hermans* and *P. Platzek*, Kolloid-Z., 87, (1939) 296; Kolloid-Z., 88, (1939) 68. In botanical literature the anisotropy of swelling had very much earlier often been the subject of extensive research; e.g., see *Steinbrinck's* publications as from 1886 (compiled in 1906) and *Schwenderer's* (1891).

The anisotropy of swelling, it was argued, is the result of the orientated position of oblong particles, similar to rodlets, in the fibre (Fig. 145). If the swelling solvent penetrates uniformly between the particles, there will obviously be more lateral than longitudinal swelling (cf. Part II, Chap. § 6).

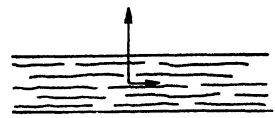


Fig. 145. Diagram to show the anisotropy of swelling according to *A. Frey* (1927). Vectors of swelling indicated by arrows.

On this simple basis we now tried to calculate the quantitative relation between the distribution of orientation $I(\alpha)$ and the anisotropy of swelling Q, and derived the following general expression[2].

$$Q = \frac{1}{\int_0^{\frac{1}{2}\pi} |I(\alpha) : I_0| \sin^3 \alpha d\alpha} - \frac{1}{2} \qquad (6.6)$$

Q should then stand in the following relation to the average angle of orientation αm and the orientated factor f, as defined in Part II, Chap. IV, § 6.4.

$$Q = \frac{1}{\sin^2 \alpha_m} - \frac{1}{2} \qquad (6.7)$$

$$Q = \frac{1}{2} \cdot \frac{2 + f}{1 - f} \qquad (6.8)$$

Q stands for the following. If the length and thickness of the filament in the swollen state are l_q and b_q and in the dry state l_t and b_t, respectively, then

$$Q = \frac{B}{L} = \frac{b_q/b_t - 1}{l_q/l_t - 1} \qquad (6.9)$$

where B and L represent the specific lateral and longitudinal swelling.

The calculation relies on oblong particles which contribute to the swelling only in directions perpendicular to their longitudinal axis.

The advantage of the method based upon the anisotropy of swelling is its great simplicity, requiring, as it does, merely length and thickness measurements and, therefore, very little equipment. Judging from the evidence so far collected, it would certainly seem that the anisotropy of swelling of objects similarly produced does provide a certain measure for the orientation, though it is not clear exactly what quantitative measure it is. Measurements evaluated in accordance with equation (6.8) do not reflect the orientation determined optically or by X-rays and, on the whole, indicate far too high an orientation.

It is clear, then, that the theory hitherto adopted does not correctly interpret the conditions of swelling.. We also know now that the mechanism of swelling does not fit in with the simple representation of anisotropically swelling, independent elementary particles. Firstly, the particles are everywhere interconnected and, secondly, the water absorption in the molecular felt structure of the amorphous regions does not fit into the picture on which the computation is founded.

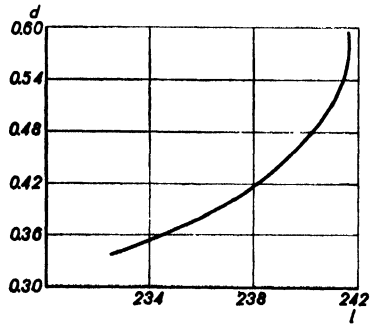


Fig. 146. Change in length and diameter of a highly swollen model filament on shrinking (scale in mm).

The lack of quantitative conformity with other standards of orientation, however, does not mean to say that the results thus far obtained by measurements of the anisotropy of swelling are without value. They have been useful in disclosing certain interrelationships and have pointed the way for other investigations. It is only their quantitative significance which cannot at present be assessed. (cf. however, p. 461 and 477 ff)

A further drawback to the anisotropy of swelling method is that, as later investigations have made plain (e.g. in the shrinkage of anisotropic *F* filaments), length and thickness do not decrease in the same proportions, but as shown in Fig. 146. It is only with the low degrees of swelling (left in the Figure) that the curve is approximately,

[2] *P. H. Hermans* and *P. Platzek*, Kolloid-Z., 87, (1939) 296. Cf. *J. J. Hermans*, Rec. trav. chim., 65, (1946) 121.

linear[3]. Hence with highly swollen filaments we cannot speak of a constant anisotropy of swelling during the whole process of shrinking. Rather should it be said that with every degree of swelling q goes a given differential anisotropy of swelling, which can be defined as

$$Q_{diff.} = \frac{\Delta b/bt}{\Delta l/lt}$$

All future references to anisotropy of swelling determinations will relate to measurements applied to low degrees of swelling between air-dry and $q = 2$ or 2.5, where the simplest conditions prevail and the value of Q approximates that of Q *diff.* Later on we shall see (Chap. X, § 4) that is has been found empirically that the anisotropy of swelling thus ascertained is quantitatively related to the optical anisotropy, though as yet no theoretical interpretation of the fact has been suggested.

If we assume cellulose fibres to be mixtures of amorphous and crystalline components, then we must expect *the anisotropy of swelling to be primarily an expression of the orientation of the amorphous constituents*, for it is to them that the motive principle of swellling must be attributed; the participation of the crystalline portions is nil or, at best, negligible.

§ 3. THE OPTICAL METHOD

The principles underlying the determination of orientation with the aid of polarized light having been dealt with fully in Part II (Chap. IV, § 6), we may be brief on this subject here. As we have seen, swollen fibres are subject to rather complicated conditions and there is little purpose, therefore, in measuring the birefringence of the swollen objects in order to determine their orientation. The practice is, then, to carry out the optical measurements associated with extension series after the subject filaments have been dried.

If, from these, inferences are to be made respecting orientation in the swollen state, it must be assumed that the orientation of an anisotropic filament does not change during shrinkage. This assumption is by no means self-evident as a matter of course, but there is experimental evidence[4] to show that it is approximately, if not exactly, consonant with the facts.

The relationship between the orientation factor and the distribution of orientation is given by

$$f = 1 - \frac{3}{2}\int_0^{\frac{1}{2}\pi} [\, I\,(\alpha) : I_0 \,] \sin^3 \alpha \, d\alpha \qquad (6.10)$$

It may be well to remind the reader here that the orientation factor derived from *optical* measurements symbolises the orientation of all monomeric residues in the fibre and, therefore, *represents a mean value for both the amorphous and the crystalline portions* (with this reservation that the quantity of the crystalline portion be constant).

§ 4. THE X-RAY METHOD

We may again refer to Part II (Chapter V) for the fundamental principles of this method.

Intrinsically the X-ray method is just as applicable to swollen as to dry

[3] The fact that this effect is not to be found in earlier publications is due to a coincidence, on which we shall not expatiate here.

[4] E.g., X-ray measurements made by the author and his co-workers, J. Polymer Sci., 2, (1947) 632.

objects and is therefore, in this respect, more serviceable than the optical method. There is again, however, a certain reservation, in that, with highly swollen filaments, the diffuse diffraction ring of the swelling agent and the more pronounced, incoherent scattering (background) are liable to be disturbing factors, especially as the objects have to be sealed in *Keesom* (or *Mark)* tubes. Sometimes, too, the interferences of swollen filaments are somewhat broadened and indistinct (cf. page 382). With *F*-filaments the latter difficulty can be overcome by boiling them for a short time in water. The limit up to which the diagrams can be reasonably evaluated is approximately between *X* and *F* filaments.

The orientation derived from *X-ray measurements relates only, of course, to the crystalline portion* of the fibres. Apart from the orientation factor as an expression for the *mean value* of orientation, conclusions may also be drawn from the X-ray diagrams respecting the *distribution of orientation,* so as to the function $I(\alpha)$; and this not only for the orientation of the rodlet axes, but also for the other important crystallographic axes or planes of the crystallites. Hence in this respect the information to be obtained from X-ray diagrams is far more comprehensive than that furnished by optical data. Moreover, the theoretical principles are fully guaranteed. For this reason X-ray evidence carries most weight; but, as we shall see, the complementary facts deducible from the other methods are of the utmost value.

CHAPTER VII

SHORT SUMMARY OF THEORIES FORMERLY HELD AS TO THE MECHANISM OF THE DEFORMATION OF CELLULOSE AND OTHER HIGH POLYMERIC SUBSTANCES

§ 1. INTRODUCTORY REMARKS

In this chapter we shall describe the basic principles of the attempts made to picture the processes of deformation occurring in high polymeric substances, deeming that description to be an appropriate forerunner to the treatment of more recent experimental evidence and the interpretation put upon it.

The mechanism of the deformation of solid substances is one of the major problems of technical physics; nor is that of high polymeric substances much simpler. In the latter case, however, the immense variability of this class of substances, in conjunction with the knowledge we have of their molecular constitution, comes to our aid, since striking differences in the behaviour of certain extreme types offer us a welcome clue as to how the problem should be broached. A further alleviation is the possibility of examining these substances in their swollen — or, so to speak, in a "dilute" — state, especially where cellulose is concerned.

Swelling diminishes the cohesion, and, therefore, the interaction of forces between the elementary particles, and it is precisely molecular interaction which always raises the most difficult theoretical problems. The outstanding successes attending the theory of the elasticity of rubber are likewise primarily due to the fact that the cohesive forces between the molecules of rubber-like substances are weak and that the behaviour of those substances is subject mainly to other factors.

We shall only consider substances made up of chain molecules. Passing the various theories in review, they would seem to emanate from diametrically opposed points of view and models and often, at a first glance, would seem to be devoid of any common ground. On the one hand the theories applied to rubber-like substances are founded on flexible kinked molecular chains. On the other hand cellulose was believed to comprise particularly rigid rodlet-like elementary particles and utterly divergent views have been invoked in attempts to describe their movements.

These theories, nevertheless, illuminate various aspects of the problems to some extent and, as we shall see later, these various aspects converge in the

most recent work on cellulose and tend towards a synthesis. Once again we shall find the duality in the structure of cellulose, with its crystalline and amorphous components already emphasized in previous chapters. This duality in a sense, will serve as an intermediary. The similarity in molecular structure of all linear polymeric substances must ultimately be reflected in common traits of physical behaviour.

When discussing the theories pertaining to cellulose, which are relatively recent, we shall follow their historical development. We shall only briefly recapitulate the theory of rubberlike substances, referring the reader who wishes to have fuller details to the many excellent treatises on the subject. After that we shall pass on to generalities on the deformation of linear polymers.

As to the more specific problems with which we shall be concerned in our study of cellulose, let it be said in advance that these theories aim especially at discovering *quantitative relationships between deformation and orientation* capable of being tested experimentally. Then corroboration or otherwise by the experimental results is taken to be a measure of the extent to which the basic assumption is borne out by reality. We shall, that is to say, be considering the geometry of the matter.

Attempts to handle also the *mechanical* properties quantitatively, where forces between the elementary particles are concerned, are still in their infancy. We have, it is true, fairly advanced qualitative interpretations, but the discussion of these will be reserved for Chapter XIV.

§ 2. THEORIES RELATING TO THE DEFORMATION OF CELLULOSE AND THEIR VERIFICATION

2.1. Earliest Views

The first attempts to explain the mechanism of the deformation of cellulose are entirely within the province of the former "Micellar theory". *R. O. Herzog* and his collaborators fathered them and they regard cellulose primarily as a polycrystalline aggregate. Falling into line with the metallurgists, they represent the elementary particles of cellulose as rodlets sliding past each other [1].

This idea will still be found guiding in *H. Mark's* well-known book on the physics and chemistry of cellulose. It persisted for a long time and until a few years ago was still the foundation upon which most hypotheses rested. Owing to undue emphasis laid upon the crystalline character of the substance, these propositions are so one-sided that we need not expatiate upon them at the present time.

It is important to note that *K. H. Meyer, H. Mark, M. Polanyi* and *J. J. Trillat* also endorsed the view that orientation comes to pass, not by gliding crystallographic planes as it often does in the case of metals, *but through rotation of the oblong crystallites in the direction of the extension.*

To *Herzog's* pupil *O. Kratky* falls the honour for having very considerably stimulated further research into the mechanism of deformation and for

[1] E.g., see *R. O. Herzog*, Naturwiss., 12, (1924) 955.
[2] *H. Mark*, Physik und Chemie der Cellulose, Berlin 1932.

having contributed very essentially to its further development. It was thanks to his investigations that the way was opened to a quantitative treatment of the process of orientation on a rational basis [3].

2.2. *Mechanism of Deformation according to O. Kratky's "First Borderline Case"* [4]

O. Kratky was the pioneer of the mathematical approach to the process by which the crystallites turn inwards in the direction of extension. He took as his object of study the borderline state of very high degrees of swelling, where interaction between, or mutual disturbance of, the particles in their movements may be disregarded as virtually non-existent.

The ideal model represents a biphasic mixed body consisting of rigid rodlets embedded, freely suspended, in a completely plastic medium, no other assumptions being made respecting the latter. The system is so dilute that the rodlets — thought of as being infinitely thin — do not hinder each other in their movements. At first the alignment of the rodlets is isotropic and it is calculated what the distribution will be after uniaxial extension of the system, when, of course, the uniaxial symmetry (symmetry of the fibre) is maintained, but the rodlets orientate selectively in the direction of extension.

The calculation relies on the presentation of a process which *O. Kratky*[5] described many years later as "affine deformation". We only give the principle of the calculation here, referring any reader who wishes to see how it is carried through to the original.

Consider around a given rodlet *S* (Fig. 147 A) an element of unit volume of the body, e.g., the rectangular prism described, the axis 1 of which runs parallel to the direction of extension (fibre axis) and whose space diagonal coincides with the rodlet.

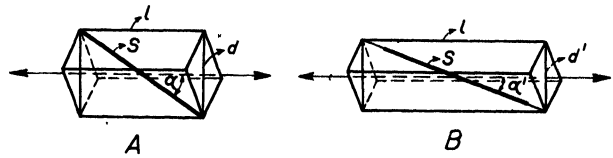


Fig. 147. Principle of orientation according to *Kratky's* first borderline case (affine deformation). A single rodlet S with surrounding prismatic element of volume. A, before, B, after elongation.

That part of the continuum which is situated in this prism will, upon extension v, pass into the prism of Fig. 147 B the length of which has increased and whose cross section has become smaller. Presuming the density to have remained the same, then:

$$v = \frac{l'}{l} \quad \text{and} \quad v = \left(\frac{d}{d'}\right)^2$$

Rodlet *S* meanwhile remains in the space diagonal of the prism and rotates over a certain angle towards the axis of extension. In so doing its orientation changes from α to α' and it will be plain that

$$\frac{tg\alpha'}{tg\alpha} = v^{-\frac{1}{2}} \qquad (7.1)$$

[3] *O. Kratky* and co-workers. Naturwiss., 18, (1930) 461; Kolloid-Z., 64, (1933) 213; 68, (1934) 347; 70, (1935) 14; 80, (1937) 139; 84, (1938) 149, 268; 86, (1939) 245; 88 (1939) 78; Z. physik. Chem., B. 50, (1941) 255; B. 52, (1942) 142.

[4] *O. Kratky*, Naturwiss., 18 (1930) 461; Kolloid-Z., 64 (1933) 213.

[5] *O. Kratky*, Z. physik. Chem., B. 50, (1941) 255.

Thus the rotation which the rodlet undergoes is a function of its initial position α and of the degree of extension v. Starting from the original distribution I_0 of the rodlets in the isotropic body (see Chap. VI, § 1), it is now possible to calculate by pure geometry their distribution $I(\alpha)$ on the unit sphere after extension v. The result is as follows:

$$\frac{I(\alpha)}{I_0} = \frac{v^3}{[1 + (v^3 - 1)\sin^2\alpha]^{\frac{3}{2}}} \qquad (7.2)$$

The expression gives the relative surface density $I(\alpha)$ on the unit sphere compared to that in the case of isotropic distribution (I_0).

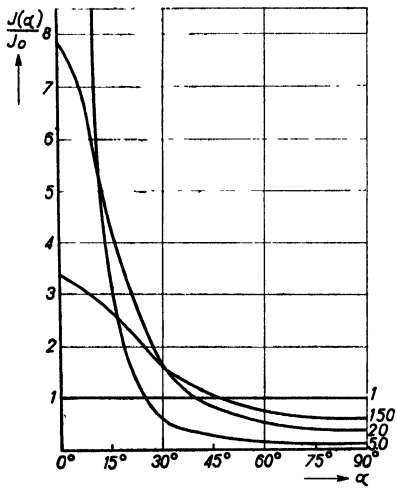


Fig. 148. Distribution curves of orientation (relative surface density I_α/I_0 on the unit sphere) at different degrees of elongation v, for the "first borderline case" according to *Kratky*.

In Figure 148 we illustrate the result of the numerical evaluation for a degree of extension v.

Prior to extension, $v = 1$ and we find a horizontal straight line. As the distribution curves show, the relative number of particles with better orientation increases steadily in proportion to increasing degree of extension, though a certain number of particles retain large orientations, up to 90°. (There is no critical angle here. Also cf. Fig. 150). *This mechanism imposes no limit upon the extensibility of the object.*

By carrying out the necessary integrations, it is possible to foretell how the degrees of orientation which can be approached by experiment, such as optical orientation factor f_o and anisotropy of swelling, would proceed with deformation taking place according to this mechanism in dependence upon the degree of extension; this could be done by substitution of (7.1) in (6.6) or (6.10)[6]. The result is given in Figs. 151 and 152 (curves I)[7]. *Kratky*[8] has also shown how the intensity distribution along the diatropic and paratropic interferences can be calculated from the distribution function (7.2). (Cf. Part II, Chap. V). He tested his theory by comparing X-ray photographs of swollen films of cellulose amyloxalate[9] and found that it was corroborated at a first approximation. (With this object it was possible to reach degrees of extension up to $v = 5$).

At a later date *Kratky* and *Platzek*[10] reported on the behaviour — similar to that of the first borderline case — of swollen films of cellulose acetate, but, for various reasons upon which we shall not now dwell (obscure optical conditions), these experiments were far less valuable.

The importance of *Kratky's* work lies less in the discovery of a few cases

[6] The first calculation was worked out by *Kratky*, Kolloid-Z., 64, (1933) 213; the second by *P. H. Hermans* and *P. Platzek*, Kolloid-Z., 87, (1939) 296. Also see *O. Kratky* and *P. Platzek*, Kolloid-Z., 86, (1939) 245. A more explicit calculation of the optical factor of orientation depending upon the degree of extension was later published by *W. Kuhn* and *F. Grün*, Kolloid-Z., 101, (1942) 248, the result being as follows:

$$f = \frac{2v^3 + 1}{2(v^3 - 1)} - \frac{3v^3}{2(v^3 - 1)^{\frac{3}{2}}} \text{ arc tg } \sqrt{v^3 - 1}$$

The initial slope at zero extension is 0.6.

[7] Although, as already stated, the basic equation (6.6.) for the calculation of the anisotropy of swelling still has defects, the results have been recorded, because they have played their part in the evolution of this subject.

[8] *O. Kratky*, Kolloid-Z., 64, (1933) 213.

[9] *O. Kratky*, Kolloid-Z., 70, (1935) 14.

[10] *O. Kratky* and *P. Platzek:* Kolloid-Z., 86, (1939) 245; 88, (1939) 78.

(of minor practical significance, for that matter) bearing out the theory, than in the impetus it gave to further research, both by method and later development; of the latter we shall speak in section 2.4.

2.3. *Mechanism of Deformation according to O. Kratky's "Second Borderline Case"* [11]

Kratky ascribed the agreement between theory and experiment in the instances just recorded not only to the high degree of swelling of the objects, but — — and that chiefly — to the weak secondary valence forces in the cellulose esters, whose chains should be fairly well screened off, especially in the higher esters like amyl oxalate.

Kratky [12] suspected that films of regenerated cellulose, which he also examined and found to be far less extensible, were subject to a totally different mechanism of deformation. The behaviour of these objects seemed to imply a *network structure.*

Taking a second extreme borderline case, *Kratky* then studied a model in which the rodlets could no longer move independently, but were somehow or other interdependent. He considered this interconnection in the light of newer theories which had meanwhile come to the fore respecting the structure of cellulose fibres, according to which the crystallites are linked by continuous molecular chains [13]. He was therefore obviously led to consider "cross linking" at the extremities of the rodlets in his model.

The schema chosen by *Kratky*[14] for the purpose and which be worked out to its logical conclusions later[15] is shown in Fig. 149. A chain of rigid rodlets hinged together stretches between points A and B. When the chain is extended, the angles α formed by the individual rodlets and the axis of extension become smaller until finally, when the chain is fully stretched, they disappear altogether. This gives a well-defined limit of extensibility which is attained in ideal orientation.

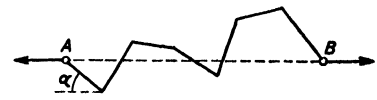


Fig. 149. Model of rigid rodlets hinged together, forming a chain, according to *Kratky's* second borderline case. There is a well-defined limit of extensibility.

If into one of these chains stretched in three-dimensional space the orientations of a large number of rodlets are divided in conformity with the statistical distribution function prescribed for the isotropic state, calculation shows the maximum degree of extension to be exactly $vmax = 2^{16}$. *Kratky*[17] then ascertained mathematically how the distribution of orientation would take place in relation to the degree of extension, the mathematical assumption being that the velocity with which the individual rodlets rotate is proportional to $sin\alpha$[18]. The reader is referred to the originals for the rather complicated calculations.

[11] *O. Kratky,* Kolloid-Z., 70, (1935) 14; 84, (1938) 149, 268.
[12] *O. Kratky,* Kolloid-Z., 70, (1935) 14.
[13] *O. Kratky* and *H. Mark,* Z. physik. Chem., B. 36, (1937) 129.
[14] *O. Kratky,* Kolloid-Z., 70, (1935) 14.
[15] *O. Kratky,* Kolloid-Z., 84, (1938) 149, 268.
[16] *P. H. Hermans,* Kolloid-Z., 83, (1938) 71; 88, (1939) 172.
[17] *O. Kratky,* Kolloid-Z., 84, (1938) 149, 268.
[18] *P. H. Hermans* and *J. de Booys* (Kolloid-Z., 88 (1939) 73) proved later that the *mean* orientation as a function of the degree of extension is practically independent of this assumption and, if taken proportionally to α, $tg\,\alpha$ or $tg\,\frac{1}{2}\alpha$, produces the same result.

(There are hyperbolic functions, as in the majority of chain models). The relationship between $I(\alpha) : I_0$ and v, which now takes place of equation (7.1), is here given by the expressions:

$$\frac{I(\alpha)}{I_0} = \frac{e^{2\tau}\,(1 + tg^2\tfrac{1}{2}\alpha)}{(1 + e^{2}\,tg^2\tfrac{1}{2}\alpha)^2}; \qquad v = \frac{\sinh 2\tau + 2\ln\cosh\tau - 2\tau}{\sinh^2\tau} \tag{7.3}$$

where τ is an auxiliary quantity for the calculation.

Fig. 150 shows the distribution of the orientation for degree of extension $v = 1.9$, notably in conformity with the $\sin\alpha$ and α mathematical assumption. It is seen that, in this model, there is a critical angle αg and the intensity at that place suddenly drops to nil.

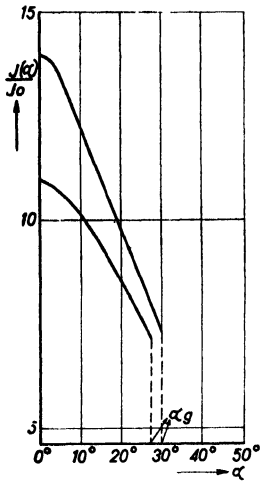


Fig. 150. Distribution curves of orientation (relative surface density on the unit sphere) for $v = 1.9$ in *Kratky's* "second borderline case" ($\sin\alpha$ — and α_m assumption).

Similarly to the first borderline case, deductions can be made from this model as to how the anisotropy of swelling (*Hermans* and *Platzek* loc.cit.), the optical orientation factor and the intensity along the *Debye-Scherrer* orbits in the X-ray diagram[19] will proceed, these deductions being quantitative in dependence upon the degree of extension.

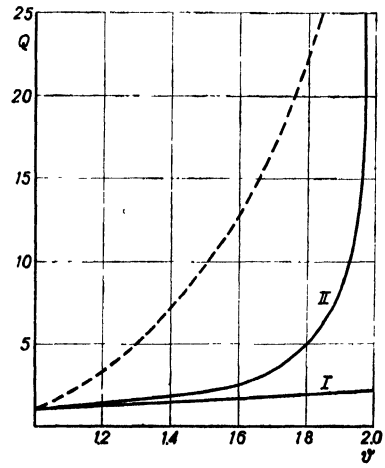


Fig. 152. The anisotropy of swelling Q as a function of the degree of elongation v. Full curves are the theoretical ones for *Kratky's* first and second borderline cases.

Fig. 152 (curve II) shows the course of the anisotropy of swelling and Fig. 151 that of the optical orientation factor.

The second borderline case was, of course, expected to apply primarily to unswollen, or slightly swollen objects.

It would be as well to mention here that a far simpler presentation of the case, viz., the closing up of a three-dimensional cubic network (of which the two-dimensional kind shown in Fig. 140 offers an example) likewise brings us to a progressive orientation very similar to that of the second borderline case, except that the maximum degree of extension is $v \approx 1.7$.

2.4. *The Theory Applied to Regenerated Cellulose. Results and Difficulties Encountered*

The isotropic model filaments of regenerated cellulose meanwhile introduced into deformation experiments are excellent objects on which to test the theory. Fig. 151 records the results of determinations made by *P. H. Hermans*

[19] *O. Kratky*, Kolloid-Z., 84, (1938) 149, 268.

and *A. J. de Leeuw* [20] of the anisotropy of swelling applied to highly swollen isotropic xanthate filaments. Curves I and II show the theoretical course of Q depending on the degree of extension according to the first and second boundary case respectively, and the broken line represents the values found experimentally.

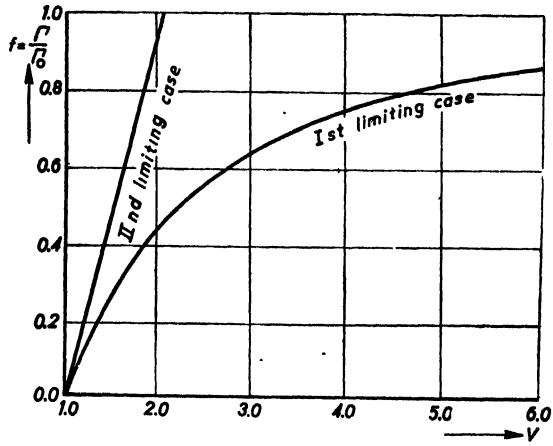


Fig. 151. Theoretical course of the optical orientation factor f_0 as a function of the degree of elongation v; I. *Kratky's* first, II, *Kratky's* second borderline case.

It will be seen that, with degree of extension below v = 2, the ascent in orientation according to the first critical case is quite insignificant, whereas, according to the second critical case and also according to the experiment, there is a far more marked increase.

This fact, together with the observed considerable decrease in volume of the highly swollen objects when elongated, persuaded these investigators, as well, that they possessed a network structure, an assumption which derived support from the fact that the attainable maximum extension was generally in the neighbourhood of v = 2 (though often appreciably more).

Optical tests then further convinced *O. Kratky* and *P. Platzek* [21] that isotropic model filaments stretched in the *F* state (cf. Chap. V § 2.1) fall within the terms of the second borderline case.

P. H. Hermans, O. Kratky and *P. Platzek* [22] collaborated in testing the theory by X-rays. Whereas the distribution of intensity along the paratropic interference A_0 in the X-ray diagram of model filaments extended progressively (in the *F* and *D* states) tallied pretty well with that calculated for the second borderline case, there was appreciable discrepancy as compared with that calculated for the first case. However, despite the apparent success, difficulties soon arose. For it was evident from the first records published by *P. H. Hermans* and *A. J. de Leeuw* [23] that the rough corroboration of the theory upon the extension of X filaments as demonstrated in Fig. 151 must be a pure coincidence. When model filaments were stretched at other degrees of swelling (*F, R, D* states), it was found that the progress of orientation judged by the

[20] *P. H. Hermans* and *A. J. de Leeuw*, Naturwiss., 25, (1937) 524, 794; Kolloid-Z., 81, (1937) 143, 300.
[21] *O. Kratky* and *P. Platzek*, Kolloid-Z., 86, (1939) 245; 88, (1939) 78.
[22] *P. H. Hermans, P. Platzek* and *O. Kratky*, Kolloid-Z., 86, (1939) 245.
[23] *P. H. Hermans* and *A. J. de Leeuw*, Naturwiss., 25, (1937) 524, 794; Kolloid-Z., 81, (1937) 143, 300; 82, (1938) 58.

standard of anisotropy of swelling *depended very much upon the degree of swelling in the initial state* (Fig. 153).

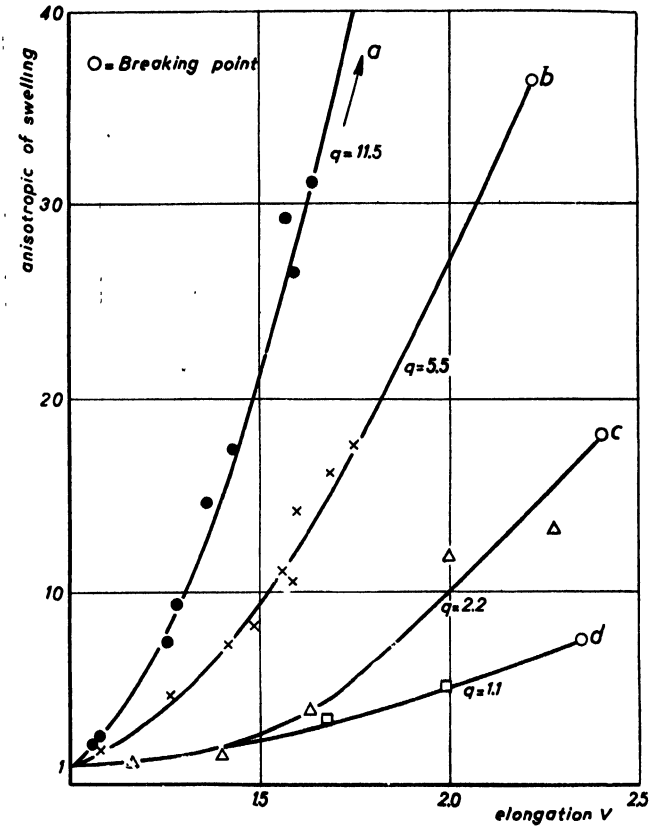


Fig. 153. The anisotropy of swelling as a function of the degree of elongation for model filaments in the four main states of swelling. (q = degree of swelling; o = breaking point).

There is obviously no longer any trace of agreement with the theory of the second critical case. There is, moreover, the striking fact that, the lower the degree of swelling in the isotropic initial state, the more slowly does orientation progress. Only very imperfect orientation takes place with the air-dry *D* filaments. Contrary to all expectation, it was precisely with the least swollen objects that some approximation to the first critical case was found (cf. the theoretical curves in Fig. 151).

As will be seen from Fig. 154 (later determinations by the author), optical measurements likewise show that the curves for the rise in birefringence, as a concomitant of the degree of extension with *X*, *F* and *R* filaments, exhibit the same sequence[24]. It is clear from comparison with the broken

[24] The birefringence was measured after the stretched filaments had passed into the air-dry state. The curve (not shown) for *D* filaments lies a little below the curve for q = 2.3.

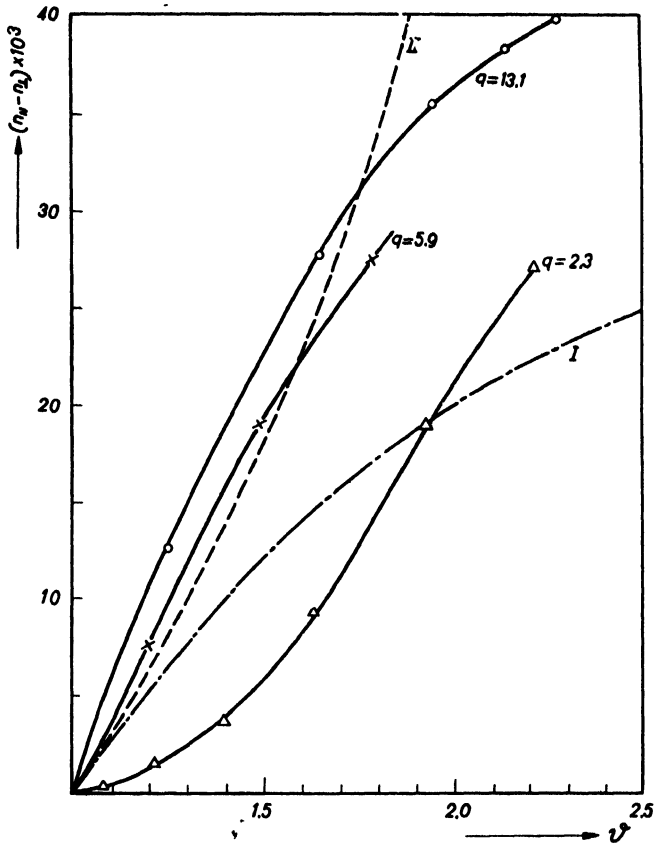


Fig. 154. Birefringence as a function of the degree of elongation for model filaments in three main states of swelling. The broken lines are the curves of the theoretical position according to *Kratky's* first and second borderline cases.

lines, which stand for the theoretical progress in accordance with the first and second critical cases, that, where there is any similarity at all to the second critical case, it applies only to the curves of the highly swollen filaments [25].

In a joint publication, *P. H. Hermans, O. Kratky* and *R. Treer* [26] next reported exact repetition of the X-ray data, thus confirming the influence of the degree of swelling upon the course of the orientation which is apparent from Figs. 153 and 154, and so establishing it beyond doubt. Immediately after, *P. H. Hermans* [27] pointed out that approximate quantitative agreement could now be demonstrated with the determinations of the anisotropy of

[25] The now known value 0.047 (see Part II, Chapter IV) for the birefringence coinciding with ideal orientation (in standard atmosphere) has been inserted in the theoretical curves. As things now stand, the optical measurements made by *Kratky* and *Platzek* just mentioned (Kolloid-Z., 86, (1939) 245; 88, (1939) 78) are no longer to be regarded as authoritative for several reasons, such as incompatibility with the *Wiener* theory, incorrect value given to the birefringence in the ideal orientated state.

[26] *P. H. Hermans, O. Kratky* and *R. Treer*, Kolloid-Z., 96, (1941) 30.

[27] *P. H. Hermans*, Kolloid-Z., 96, (1941) 38.

swelling. Yet, as we shall see presently, neither the conclusions drawn from the X-ray evidence then available, nor the others were unassailable in a quantitative sense.

Two principal tasks ensued; one was to discover what the influence is of the degree of swelling and to seek a corresponding theoretical model representation on a quantitative basis; the other to provide further experimental foundations. Before following this trail, we would do well to consider the parallel qualitative speculations developed on the premise of the network structure.

2.5. Development of the Network Theory

Although the idea of the second borderline case seemed to be discredited, the arguments in favour of a network structure were so telling that they invited elaboration [28].

In their first publications the Dutch research workers discussed the build-up of network structures consisting of crystalline and amorphous portions, stressed the decisive significance of the latter and sought to make them account for the pronounced elasticity of highly swollen cellulose filaments. They adopted the view, already dealt with in Chapter IV, that more junction points are formed between the molecules during shrinkage or deformation. The irreversible portion of the deformation was associated with the creation of new junction points as the result of decreasing volume during elongation [28a].

A system of rigid rodlets only, such as that of *Kratky's* second mathematical model, has no place for the intrinsic extensibility of the amorphous regions due to the more or less kinked shape of the chains, and would, therefore, lead to a different kind of behaviour. Furthermore, the impossibility of explaining how networks of rigid rodlets could swell and contract was stressed and it was suggested instead that the strings of the nets "fold up" during shrinkage.

This paved the way to the conception of the structure of gels and the mechanism of deformation which was able, qualitatively, to account for the behaviour noted in experiments.

The growing recognition of the dualistic nature of the structure of cellulose gels, as being composed of amorphous and crystalline portions, was evident in this development of the qualitative and quantitative theory by the prominence at one time of the crystalline and at another of the amorphous component, all according to the properties and phenomena under consideration at the moment.

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[28] The idea of network systems as being the structural principle of gels will be found as far back as *C. von Nägeli*, Theorie der Gärung, 1879, pp. 102, 127, and *H. G. Bungenberg de Jong*, Z. physik. Chem. Cohen-Festband (1927) 205.
It first appears in its present form for polymeric substances in *O. Gerngross* and co-workers (*O. Gerngross, K. Herrmann* and *Abitz*, Biochem. Z., 228, (1930) 409; *O. Gerngross, K. Herrmann* and *R. Lindemann*, Kolloid-Z., 60, (1932) 276.

[28a] *P. H. Hermans* and *A. J. de Leeuw*, Kolloid-Z., 81, (1937) 300.

Figures 155 and 156 (see their subscripts) show examples of attempts to define the structure of the network frame more specifically. Both presentations try to do justice to *Kratky's* principle of "low distance order"[29]. The crystallites are imagined to be connected

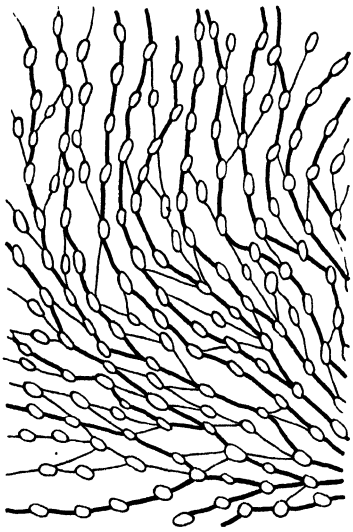


Fig. 155. Diagram of the network structure according to *O. Kratky* (1938). The crystalline regions are represented by thick lines; the amorphous connecting parts by ellipses. Continuous chains of crystallites represented by thick lines; lateral linking crystallites by thin lines.

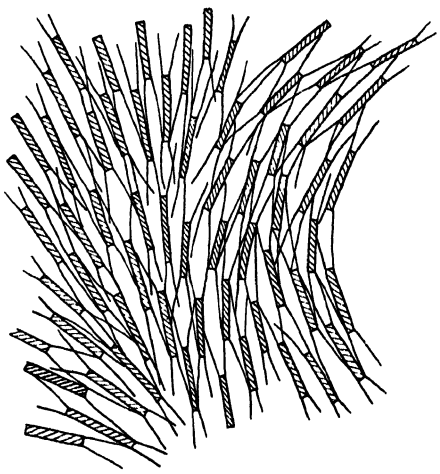


Fig. 156. Diagram of the network structure according to *P. H. Hermans* (1938). The shaded rectangles are the crystalline regions. They are surrounded and interconnected by amorphous regions consisting of chains projecting, like a fringe, from the crystallites. (For the sake of clarity, only a few of these chains have been sketched in, their course being merely indicated).

by amorphous intermediate regions, flexibility, or deformability, being attributed to the latter. In Fig. 156 the cohesion through the agency of lateral forces comes to the foreground; in Fig. 155 greater prominence is given to the chains passing through several crystallites. Both points of view undoubtedly have their merits. Systems answering to the fundamental form of the *"Kratky* chain" shown in Fig. 149 are readily recognized in Fig. 155 certainly, but, as *Hermans*[30] has pointed out, are also to be found in the hypothetical picture represented by Fig. 156 (Fig. 157, broken line).

The views of lasting value emerging from these investigations are the following:

1. *Hermans*[30] considered the possible processes when a structure like that represented in Fig. 156 is stretched. It appears again, in a simplified form, in Fig. 157, the amorphous component being omitted. It is supposed that the stresses would primarily fall upon the regions by chance orientated in the direction of extension, while the regions differently orientated would be partially rotated, partially drawn apart and would then orientate anew. For, in the last case the cohesive forces should be more easily overcome in accordance with the principle of "progressive uncoupling".

[29] *O. Kratky*, Kolloid-Z., 60, (1934) 347; *P. H. Hermans*, Kolloid-Z., 83, (1938) 71; 88, (1939) 172.
[30] *P. H. Hermans*, Kolloid-Z., 83, (1938) 71; 88, (1939) 172.

As an analogy the author recalled the example of a sheet of paper stuck with a little adhesive to a glass plate (Fig. 158). The paper is far more

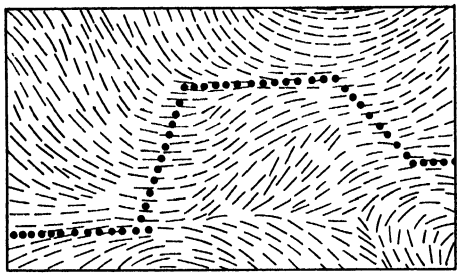


Fig. 157. Submicroscopic element of volume from an isotropic gel. Crystalline regions represented by dashes; amorphous component not shown. The dotted line passes only through regions orientated as $\alpha = 0$. The configuration of this curve is that of a *Kratky* chain.

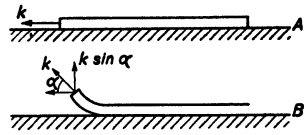


Fig. 158. Graphic representation of the principle of the progressive neutralization of cohesive forces. Sheet of paper stuck with glycerine to a glass plate. (A. Difficult to detach by pulling it parallel to the plane of the paper; B. Easier by pulling at the angle α or at right angles to the glass plate).

difficult to detach from its base by pulling it parallel to the plane of the glass plate (Fig. 158 A) than in a direction perpendicular to it (Fig. 158 B). The ease with which the paper is detached is a function of the direction α of force K. Progressive loosening is effected by the component $K \sin \alpha$. We have here an argument in favour of the view, recurring later in a different context, that in the process of extension some of the junction points — or, maybe, even of the crystalline regions — become detached and re-form in some other orientation. This idea gave birth to an explanation of the course of the stres-strain curves[31].

2. Shortly after, *Kratky* speculated on the general theory of micellar networks of the kind reproduced in Figs. 155 and 156. The argument went to show that it is not primarily the degree of swelling which makes a system behave similarly to the first or second critical case, but rather the strength of the cohesive forces. The fresh highly swollen model filaments of regenerated cellulose represent *intermediate non-equilibrium states of swelling.* Their high degree of swelling does not imply weak cohesion. If, on the other hand, *swelling up* produces high degrees of swelling as *a state of equilibrium*, then a relationship does exist between swelling capacity, cohesion and deformatory behaviour.

If one and the same substance — say, cellulose acetate — is treated with composite swelling agents of different dissolving power — e.g., mixtures of dioxane and water — it will be found that the degree of swelling and the deformatory behaviour run parallel. For instance, cellulose acetate behaves more like a substance of network structure in dioxane of low concentration than in high-percentage dioxane, in which it swells more.

Kratky next discussed some of the properties of network frames composed of crystallites — behaving like rigid rodlets — and flexible amorphous intermediate zones

[31] *P. H. Hermans*, Kolloid-Z., 88, (1939) 172.

interlinking them. In a net like that represented in Fig. 155 one may choose at random continuous chains of crystallites (in fat print) and "lateral bonds" (drawn faintly); true, the nature of the choice is ambiguous and branching may have to be assumed with the one as with the other. If preferred, the chains may be laid in the direction of extension and the lateral bonds built in afterwards. In selecting continuous chains, retrograde chain links ($\alpha > 90°$) as occurring in Fig. 159 B should be obviated. Advancing from one end to the other, the individual links, then, should form angles at most up to 90° (Fig. 159 A) with the connecting direction of these extremities.

If, conversely, a network of these single chains is built up synthetically, it will soon be necessary to ask how many cross links are to be assumed (Fig. 160). One may construct "loose" nets with few links or, alternatively, "close" nets with many cross links. Let us first consider two extreme cases, viz., ideal loose and ideal close nets. Upon extension, the former would behave as though there were only chains, while the latter would, as a rule, exhibit far more limited extensibility. For instance, in Fig.

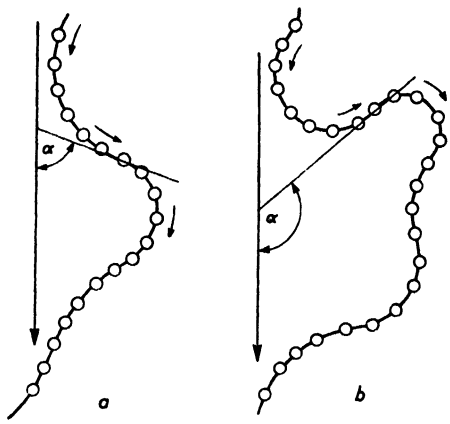


Fig. 159. Chain of crystallites. A. Continuous type. B. Retrograde type.

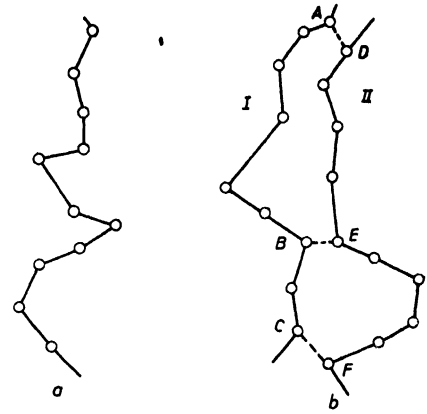


Fig. 160. A. Chain of crystallites. B. sector of a network of such chains. The broken lines stand for the cross links.

160 B extensibility will cease when the stretch reaches *DEBC*, when the longer stretches *AB* and *EF* can no longer be spanned.

The presence of many cross links will progressively "block" the nets, which will contain an increasing quantity of single parts incapable of full extension. This might explain why mere stretching never produces ideally orientated fibres. This would only be possible in so far as ideally loose nets are involved.

This hypothesis of networks of crystallite-chains has much in common with that dealing with *networks made up of kinked molecular chains,* as worked out later by *F. H. Müller*[32] and others and to which we shall revert in Section 3.3β. The current view is that there are molecular chains thus more or less kinked. In the process of extension, therefore, allowance must be made for the straightening out of these chains, as *Hermans* and *de Leeuw* suggested in their initial investigations. Pursued to its logical conclusions, this view offers an acceptable explanation of the ever-present tendency towards recovery.

3. *Hermans*[33] tried to evolve a model which would take into account the fact that, with a given gel, the lower the degree of swelling selected for deformation, the less steeply does the orientation increase with the degree

[32] *F. H. Müller,* Kolloid-Z., 95, (1941) 181, 307.
[33] *P. H. Hermans,* Kolloid-Z., 96, (1941) 311; 97, (1941) 231.

of extension. It implied an interpretation which is related to the "folding up of the strings of the net" during shrinkage which had already proved to be a necessary assumption. A diagrammatic representation of the fundamental idea is given in Fig. 161.

Let a_1 be the mesh of an isotropic net, the degree of swelling of which is 8. By some standard let its dimension in the x direction be expressed as 200. When bone dry, all the dimensions become smaller by $\sqrt[3]{8} = 2$ times. Hence in the x direction the crumpled mesh b_1 measures 100.

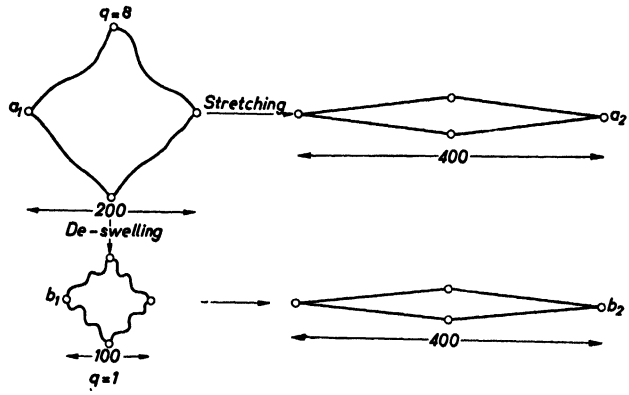


Fig. 161. Diagram of the shrinking and elongation of a network at two different degrees of swelling. The same orientation was attained in the swollen state at a lower degree of elongation than in the shrunken state.

When the swollen net is extended, the meshes close up and the strings of the mesh between the nodal points become orientated (a_2). Let extensibility be to maximum orientation $v_{max} = 2$ (as computed for 3-dimensional nets), then, after extension, the length of the system will be 400. If the material is being stretched in the dry state, it will be necessary to stretch from 100 to 400, i.e., till $v = 4$, in order to obtain the same orientation. It is obvious that, with a given degree of extension, orientation becomes less and less as the degree of swelling diminishes.

In the foregoing imaginary and over-simplified picture the shrinking of the net has been associated with a "folding or curling up" of the net's strings. The picture becomes credible the moment the strings of the net are thought of as chain molecules and its nodal points as molecular junction points. *P. H. Hermans* [34] has suggested a variant to the interpretation of the curling up of a net a little different from that represented in Fig. 156 and allowing for "low-distance order".

The idea depicted in Fig. 161 also shows that *equal degrees of extension are not equivalent at different degrees of swelling* and must in some way be related. We shall revert to this in Chapter IX.

2.6. *The Theory of "affine deformation".*

We saw in Section 2.4 that the quantitative representation of the process of deformation with regenerated cellulose by *Kratky's* first two mathematical models was not satisfactory. A few years ago *B. Baule, O. Kratky* and

[34] *P. H. Hermans*, Kolloid-Z., 96, (1941) 311; 97, (1941) 231.

R. Treer[35] helped very materially to solve this problem and gave powerful momentum to the development of the subject. While we shall deal with their work in greater detail in Chapter X, its main points need to be touched on here.

1. Again, the fundamental principle of the deformation model is that *affine deformation* ("affine Verzerrung des Raumes") of which use was made for the "First Critical Case" (Section 2.2).
2. The crystallites considered were thin lamellae (which are much longer than they are broad) instead of thin rodlets. (Respecting lamellae in cellulose cf. Part II, Chap. V, § 2)[36].
3. The *change in volume* of the objects extended is taken into account. (Model filaments in the X and F states exhibit very considerably reduced degree of swelling when extended, while exuding appreciable amounts of swelling liquid; *vide* Chap. VIII).

Affine deformation denotes a spatial transformation in which every element of unit volume, however small, changes its shape in the same proportion as any larger one. When subdivided into ever smaller elements of unit volume, a real body, of course, must eventually depart from affine deformation in its strict definition, since it must ultimately be resolved to the smallest systems (molecules), which are no longer deformed, but simply change their positions. Moreover, in the micellar system it will be the crystalline zones that are reminiscent of rigid bodies in their behaviour, but, if they are embedded in a medium undergoing affine deformation, they will alter their orientation as shown in diagram in Fig. 147.

In the affine deformation of a geometrical figure, not only do straight lines remain straight lines, but planes continue to be planes. *Kratky* and co-workers calculated how the lamellar plane A_0 and the "side plane" of the platelets standing at right angles to it (which we have denoted as A_3A_4; vide Fig. 77), change their orientation in space during affine deformation. It is then possible to predict for every degree of extension orbits of the relevant (paratropic) interferences in the X-ray diagram (Part II, Chap. V, § 2). *It is then found that the lamellar plane A_0 is more quickly orientated than the A_3A_4 plane.* We have noted before (Part II, Chap. V, § 3) that this actually does happen regularly with viscose rayon and model filaments. (E.g., see Figures 82 and 84). This gives us a very interesting explanation and it is at the same time apparent that, when merely taking account of the A_0 interference, the first assessment of the X-ray diagrams did not constitute reliable evidence (cf. p. 403).

If there is any decrease in volume during extension this means, as the theory clearly implies, that orientation is taking place more quickly (and vice versa). In a case of that kind, a relative degree of extension, v, employed is equivalent to a degree of extension v_a in which extension proceeds without change of volume, whilst:

$$v'_a = v \left(\frac{q_i}{q_f}\right)^{\frac{1}{3}} \qquad (7.4)$$

[35] *B. Baule, O. Kratky* and *R. Treer*, Z. physik. Chem., B. 50, (1941) 255.

[36] That the crystallites in regenerated cellulose are lamelliform was proved conclusively by the results of diffraction tests with small angles. *(O. Kratky, A. Sekora* and *R. Treer;* Z. Elektrochem., 48, (1942) 587).

where q_i represents the degree of swelling of the body at the beginning of extension and q_f that at the end. If there is a reduction in volume during extension, then $q_i > q_f$ and, therefore, $v_a > v$. This means that the effect of an extension v upon orientation is the same as that of a greater extension v_a where there is no change in volume.

Testing the theory by the X-ray experiments reported in the relevant publication, *P. H. Hermans, O. Kratky* and *R. Treer* [37] found satisfactory corroboration, notably with model filaments stretched in the four main states of swelling. It therefore looked as though the dependence of the slope of the initial state mentioned in Section 2.4, does not stand in relation to this itself, *but to the relative reduction in degree of swelling which has taken place during deformation.* The latter actually does diminish in the sequence *X*, *F* and *R* filaments. (Chap. VIII, § 2).

As their results are somewhat distorted, we shall not illustrate the intensity curves found and calculated by *Kratky* and his collaborators. The v_α values according to equation (7.3) upon which their calculation for filaments extended in the swollen state is based are incorrect and the superimposition of the interference (021) (for which cf. p. 256) was not taken into account. A repetition of these experiments will be dealt with in Chapter X. Though agreement fell short with filaments extended in the swollen state, the theory even here approximates actual observations [38].

This theory opened up yet another approach to the experimental material collected in the interim. We shall consider the further development of this subject in Chapter IX and have only to say now that the new quantitative theory itself, as also its experimental verification by X-ray, relates to the crystalline portions.

Kratky and co-workers next tried to account for the part played by the amorphous component and to show how it is related to the network theory [39].

The first thing to do is to find out how the distances between the crystallites change during affine deformation. This is shown diagrammatically in Fig. 162 (where the direction of extension is vertical). In Fig. 162 A a rectangular volume element of the body is drawn around two successive crystallites. As extension proceeds, the rectangles then assume the shapes shown in Fig. 162 B and C. The crystallites lying in the middle of the diagonals at the beginning of the deformation retain the direction of the former and the central points of crystallite and diagonal remain in congruence. The distance between the crystallites is then found to diminish, until they form an angle of 45° with the direction of extension, when it again increases. Thus those crystallites which form large angles with the direction of extension at the beginning of the deformation will at first be "compressed", but later on the distance widens between

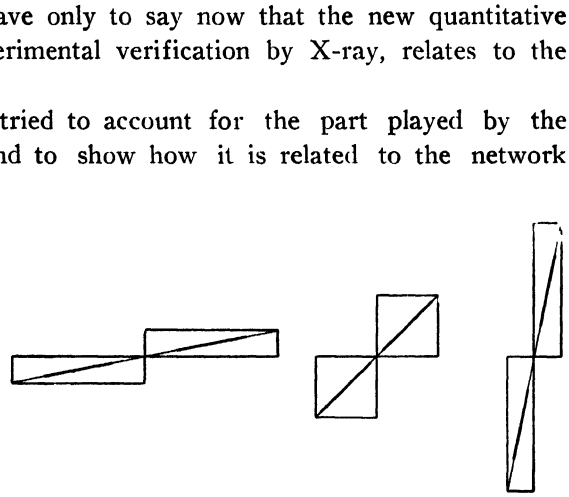


Fig. 162. Diagram showing affine deformation around two successive crystallites. First the distance between the rodlets on the diagonals narrows but, as elongation proceeds, it widens (according to *O. Kratky*).

[37] *P. H. Hermans, O. Kratky* and *R. Treer,* Kolloid-Z., 96, (1941) 30.
[38] With the correct v_a values, there is even less agreement
[39] *B. Baule* and *O. Kratky,* Z. physik. Chem. B. 52, (1942) 142

the string of crystallites. In these movements, then, the amorphous components are either compressed or extended. Over a whole chain of crystallites there may be adjustment amounting to equilibrium.

Although affine deformation, itself, does not impose any limit upon extensibility, such a limit is set nevertheless, owing to the restricted extensibility of the amorphous components by which the crystallites are interconnected.

It was in this way that *Kratky* attempted a synthesis of the models of the first and second "critical cases". The "sine assumption" for the relative velocity of rotation of the chain links, introduced without sufficient foundation in the second critical case, was now replaced by the rotational function called for by affine deformation. Furthermore, the chain is supposed to have extensible "hinges". In the chain model of the second critical case the maximum extension was 2; in the more comprehensive picture it becomes greater, thanks to the intrinsic extensibility of the amorphous components. There is no incompatability, therefore, between this picture and the fact that the extensibility of model filaments has sometimes been observed to exceed $v = 2$ (up to $v = 3$). *Baule* and *Kratky's* investigations[40] also contain a few calculations respecting the average stretch of the amorphous components all according to the degree of extension, which produced values of the correct order of magnitude.

2.7. *Additional Remarks on the General Significance of the Theory of Affine Deformation*

Kratky's work, which was dealt with in the foregoing section, is undoubtedly invaluable to the theoretical treatment of the deformatory mechanism of micellar systems, but it is by no means the last word on the subject. In particular, he treats the deformation of the amorphous regions rather cavalierly and quite formally. As we shall see later on, although the theory of affine deformation is roughly valid for the orientation of the crystallites, it is by no means so quantitatively; there are other important factors — which we have not yet considered — governing the movement of the crystallites.

One fundamental point, however, of immeasurable importance brought to light by *Kratky's* work is the effect upon orientation of the changes in volume that take place during extension.

It is worth noting that, in point of fact, the principle of affine deformation with reference to the orientating tendency of cellulose gels — qualitatively, at any rate — is to be found as far back as in the elegant investigations carried out many years ago by the American research worker *W. A. Sisson*[41]. He repeatedly demonstrated that the orientation both of the crystallite axes and of the A_0 planes is wholly determined by the *relative changes in the dimensions of the gel,* irrespective of whether the transformations resulted from deformation or changes in the degree of swelling. *The crystallite axes*

[40] *B. Baule* and *O. Kratky*, Z. physik. Chem., B. 52, (1942) 142.
[41] *W. A. Sisson*, J. Phys. Chem., 40, (1936) 343; 44, (1940) 513.

always orientate in the direction of the greatest relative elongation of the gel dimensions, the A_0 planes perpendicularly to the direction of the greatest relative shortening thereof. Thus, when an isotropic filament is extended, the crystallite axes will align in the direction of the extension, and the A_0 planes tangentially to the fibre axis. Any change in volume that may take place during extension will favour both tendencies.

If a filament previously stretched in the swollen state is allowed to dry freely, i.e., without exerting any tension upon it, its shrinkage is anisotropic. Its relative change in length is less than its shrinkage in diameter. It remains to be seen — and this is an important question — whether any change in orientation occurs as a result of drying. According to *Kratky* et al [42], to whose publication reference has already been made more than once, very little change, if any, is observed during drying. This has recently been confirmed by an investigation carried out in the author's laboratory, where a more accurate technique was employed [43].

This shows that *Sisson's* rules are only correct if externally applied tensions act on the gel during its deformation.

It is clear from *Sisson's* investigations that, wherever orientation has been observed to result from shrinking (or swelling), free development of the shrinkage (or swelling) has been hampered in some way, *a sure sign of external tensions.*

Thus the enquiry into the mechanism of the shrinkage of a gel neither under tension, nor interfered with, is a problem unto itself as yet to be tackled. In the same category is the shrinkage of an isotropic gel.

The diagram reproduced in Fig. 161 constitutes but a first approach to this problem.

§ 3. THEORIES RESPECTING RUBBER-LIKE SUBSTANCES AND LINEAR POLYMERS GENERALLY

3.1. Introductory Remarks

Cellulose being likewise a substance with flexible chain molecules, we cannot, when considering its properties, ignore those theories which were developed in regard to other linear polymers. We saw in the first part of this book that, in their physical behaviour dilute cellulose solutions resemble solutions of other substances built up of linear macro molecules; also that the theory of statistically kinked chain molecules provides a quantitative explanation of this behaviour. If we turn to the chapter in *K. H. Meyer's* book [44] on the mechanical properties of rubber, we find a survey of the principal substances possessing similar elastic properties to those of rubber and, at the end of a long list of polymers, "swollen cellulose and cellulose derivatives". It is further stated that, in the rubber-like state, all the substances examined are amorphous.

[42] *P. H. Hermans, O. Kratky* and *R. Treer,* Kolloid-Z., 96, (1941) 30.
[43] *P. H. Hermans* et al, J. Polymer Sci., 2, (1947) 632.
[44] *K. H. Meyer,* Die hochpolymeren Verbindungen, Leipzig 1940, p. 136.

P. H. Hermans [45] also pointed out certain striking analogies between model filaments and rubber in their behaviour under deformation. The question therefore naturally arises as to whether the deformatory behaviour, in particular, of the amorphous components of cellulose can be explained in terms of the kinked chain-molecule hypothesis.

3.2. Mechanism of Deformation of Rubber-like Substances

The pronounced extensibility of rubber-like substances is known to be due to the presence of long main valence chains of considerable inner mobility (flexibility thanks to the more or less free rotation around the covalent single bond). In the isotropic state, the chains tend to assume the, statistically, most probable kinked shape. On being extended, the chains gradually straighten out and align; that is to say, they orientate in the direction of extension. The unfolding of the kinked chains is largely responsible for the pronounced extensibility — which is of the order of 400—600 per cent. and over. Statistically, the straighter configuration assumed by the chains upon extension is less probable than the original one. Thus, with extension the entropy of the system decreases.

The reason for the reversibility of extension (elasticity) is that, when the external strain is released, the chains, impelled by internal heat motion, spontaneously tend to revert to the more kinked and unordered state with higher entropy.

With bodies of ideal rubber-like elastic properties (as almost realized in moderately vulcanized Hevea rubber), it is assumed that the mechanism of deformation and recovery is entirely governed by these changes in entropy and that factors of energy do not come into play [46]. Thus the force of recovery is of a totally different nature from that in a steel spring, in which case potential energy is accumulated during extension and is released again in the recovery. The molecular spring represents an entropy spring.

For the coils to unfold freely, is must be assumed that in the rubber-like elastic state not only are the chains flexible, but neighbouring links of the chains must be capable to glide past each other almost as easily as the molecules in a liquid which is tantamount to saying that there is little cohesion, as is actually found with hydrocarbons. This ease of reciprocal movement is reminiscent of *W. Kuhn's micro-Brownian movement.* This does not mean, however, that, as in a fluid, the molecules in their entirety can move and shift mutually with ease. Interchange of position between entire molecules — *Kuhn's macro-Brownian movement* — is extremely difficult, not to say impossible. Were this not so, the passing of one orientated molecule past another in the extended state would lead to rapid flow of the substance. Within a given time

[45] *P. H. Hermans,* Proc. Acad. Sci., Amsterdam, 43, (1940) 1032; Cellulosechemie, 18, (1940) 97; Naturwiss., 28, (1940) 264; J. Phys. Chem., 45, (1940) 827.

[46] Moderately vulcanized rubber actually does behave like this. It is in this respect immaterial whether, according to *R. Houwink,* (Z. physik Chem., A 183, (1938) 209), energy effects of opposite sign and neutralizing each other in that case play any part.

of relaxation, the state of stress produced by extension would be annulled and the opportunity for elastic recovery lost. The stretched chains must in some way be prevented from gliding. In the case of vulcanized rubber, either the *cross links* (bridges) between the chains, which are formed during vulcanization or mere mechanical molecular entanglements (Fig. 166) acting as *junction points*, arrest gliding [47]. There are comparatively few places where these cross links are formed.

The extension of properly vulcanized rubber is fully reversible. There are uninterrupted chains of atoms connected by primary valence bonds between the clamped ends of the object in its stretched state. Objects of this kind contain a continuous network of chains firmly interlinked by sporadic *junction* points. These, and these alone, exhibit perfectly reversible extensibility [48]. *The network pre-exists in the isotropic object;* upon extension, it is merely deformed and its coiled "strings" unfold.

Figs. 112 and 115 (p. 294 and 296) represent the mechanical behaviour of flowing and non-flowing substances of rubber-like nature, the former reproducing the flowing and the latter the non-flowing system.

The mechanism of deformation of substances possessing ideal rubber-like properties is a relatively easy subject to deal with and interpret by exact theory, for the reason that cohesion may be ignored. In this respect the system resembles ideal gases, the expansion and compression of which are likewise governed by changes in entropy alone. The results of the thermodynamic analysis of these materials are familiar. The stress in an extended object increases with increasing temperature; it becomes warmer as it is being stretched. (It is exactly the reverse with a steel spring).

For the same reason the case of the ideal rubber-like substance lends itself pre-eminently to the theoretical treatment in terms of uncoiling processes in molecular chains and their physical consequences. It is for that particular reason that it interests us here as an ideal model for these processes. Later we shall have to consider the complications involved when cohesion can no longer be ignored or, as in cellulose, becomes very strong. Swollen cellulose will perhaps provide us with the easier task, as the cohesive forces within it are far less powerful than in unswollen cellulose.

The problem has to be tackled statistically because of the great variety of shapes which molecular chains are liable to assume. *W. Kuhn*, chiefly [49], and also *W. Kuhn* and *F. Grün* [50], evolved the exact principles. Further contributors

[47] This statement applies only to the first phase of extension. At higher degrees of extension, an important part in this respect is undoubtedly played by the crystallization which then sets in.

[48] Condition for "perfect elasticity" according to *J. M. Burgers*, First Report on Viscosity and Plasticity, Acad. Sci., Amsterdam 1935, p. 98.

[49] *W. Kuhn*, Kolloid-Z., 68, (1934) 2; 76, (1936) 258; 87, (1939) 3; Z. angew. Chem., 49, (1936) 858; 51, (1938) 640; 52, (1939) 289.

[50] *W. Kuhn* and *F. Grün*, Kolloid-Z., 101, (1942) 248; see also *W.* and *H. Kuhn*, Helv. chim. acta, 28, (1945) 1533; 29, (1946) 71.

were *M. L. Huggins*[51], *F. H. Müller*[52] and *J. J. Hermans*[53]. At the present juncture we shall concern ourselves only with those results of their work which relate to orientation, that is to say to geometrical factors. Resilience in conjunction with the average chain length between two junction points, and breaking tension, will be considered elsewhere.

3.3. Orientation in Molecular Felt and Net-like Structures

α *Formulation of the Problem.*

The affinity between the present problem and the questions which occupied us in the preceding sections is manifest.



Fig. 163. Deformation of a convoluted chain molecule.

We are reminded of *Kratky's* chain when we look at the extension of a coiled chain as shown in Fig. 163. And at the same time we have to ask ourselves in what way the orientation Θi of the individual chain links A is distributed against the direction of extension. As the chain may assume any of many shapes, we cannot rely on there being no retrograde links.

Let us consider a network of such chains linked by junction points. Each chain will begin and end in a junction point and we are then faced with the second question, viz., how do the positions of the junction points change when the system is stretched?

If we can answer these two questions, we shall also be able to discover the disposition of the chain links Λ and thus their average orientation all according to the degree of extension.

There is no strict and general answer to the first question. Numerous factors are involved in the movement of the chain links; it would be necessary to know more about its scope, how it is affected by neighbouring chains, etc. These factors depend upon the particular substance and the temperature, among other things. Some of these difficulties are obviated in the model of ideal rubberlike substances: It is assumed that neighbouring chains do not interfere with each other and that the disposition of the chain links is entirely subject to the laws of mere chance. This was *Kuhn's* point of departure and is likewise at the root of *J. J. Hermans'* and other author's theories.

Our first task is to make clear to ourselves what we mean by "chain link". The most obvious course is to imply by the term the smallest rigid part of the chain. In paraffin chains this is the connecting line between two neighbouring carbon atoms. Although that is not the monomeric residue in cellulose (since the glucose groups itself is likewise capable of deformation) but, for the sake of simplicity, we shall nevertheless call the monomeric residue the smallest link of the chain.

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[51] *M. L. Huggins*, J. phys. Chem., 43, (1939) 439; J. appl. Phys. 10, (1939) 700; 14, (1943) 246.
[52] *F. H. Müller*, Kolloid-Z., 95, (1941) 181, 307.
[53] *J. J. Hermans*, Kolloid-Z., 103, (1943) 210. For other authors see footnote 57.

β *F. H. Müller's Views.*

F. H. Müller[54] tried to base a theory on the simple assumption that every monomeric residue alters its direction in accordance with the principle of affine deformation (that is to say, as *Kratky* assumed in his first critical case for the crystallites). Thus every monomeric residue moves independently of its neighbours, like a rodlet embedded in a plastic medium.

In this picture maximum orientation is reached only with infinite extension, for it takes no account of the restriction whereby extensibility ceases when the molecule is stretched to the full. *F. H. Müller* endeavoured to adjust the theory by means of several supplementary qualifying clauses. In this attempt he considered the linking of the chains to form a network and the limitation of extensibility thereby entailed.
According to *Kuhn's* calculations (see below), in the isotropic state the average distance between the end points of a molecule (and, therefore, between the junction points of a network) is proportional to $\sqrt{P}$, where P is the number of monomeric residues in the chain (degree of polymerization). In the stretched state the length of the chain is bP. Accordingly, the maximum extensibility is

$$v_{max} = \frac{bP}{b\sqrt{\tfrac{1}{3}P}} = c\sqrt{P} \quad \ldots\ldots\ldots\ldots \quad (7.5)$$

The factor $\frac{1}{3}$ is required because the connecting line between the molecular terminal points does not always lie exactly in the direction of extension, as illustrated in Fig. 163, but is statistically distributed in all directions.
Müller's calculation is then designed to produce complete orientation at this degree of extension.

His ultimate result is that, all according to the degree of extension, birefringence must for the most part increase l i n e a r l y. This is confirmed by experiments with polyvinylchloride resin and polystyrene. The birefringence of rubber also increases roughly linearly up to a degree of extension of approximately 2[55]. *F. H. Müller* states that the steepness of the ascent depends upon the degree of polymerization of the chains considered; the direction constant of the curve is, he says, proportional to $P^{-\frac{1}{2}}$.

Müller's calculations are not very satisfactory. He does not confine himself to the ideal rubber-like substance and has to resort to the result of *Kuhn's* statistics for the distance between the molecular terminals in the isotropic state. The assumption of affine distortion of the individual monomeric residues is not a very satisfactory foundation to go upon.

Müller does not commit himself at all to the second question, i.e. the altered position of the junction points.

Before turning to *W. Kuhn's* more exact calculations, we must briefly mention a few additional suggestions brought forward by *F. H. Müller.*

According to formula (7.5), the familiar degrees of polymerization of rubber-like objects would correspond to a maximum degree of extension of 30—50, whereas usually an extension of 10 has been observed to be the highest reversible one. Though possessing a similarly high degree of polymerization, other substances show still lower values for maximum stretch. *Müller* lays this

[54] *F. H. Müller,* Kolloid-Z., 95, (1941) 181, 307.
[55] Complications of a different nature are involved in degrees of extension above this: *P. A. Thiessen* and *W. Wittstadt,* Z. physik. Chem., B. 41, (1938) 33.

difference at the door of the statistical cross-linking of the chains, hence the network structure. This makes the deformation of a thread molecule to be as shown in Fig. 164 and not like that represented in Fig. 163.

What determines the deformatory properties is the number of chain links between the junction points, and not the total number in the "molecule". According to the hypothesis expressed approximately in formula (7.5), the former should be roughly 100—200 at a maximum degree of extension of 10.

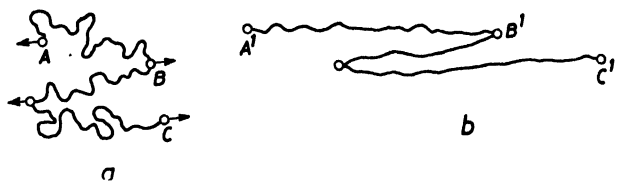


Fig. 164. Diagram showing the deformation of a chain belonging to a network structure up to the maximum possible extension (according to *F. H. Müller*).

The more junction points there are in the network — or the more irregular is its pattern — the less extensible will the material be. The extension of the net shown in Fig. 165a can only take place up to the position illustrated in Fig. 165b in which the shortest continuous chains have been stretched. In this state the average orientation of all chain links in the network is by no means complete. These views remind of *Kratky's* (see Fig. 160).

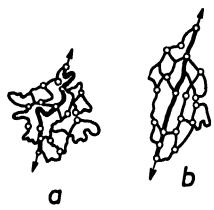


Fig. 165. Network structure with numerous junction points, a) unextended, b) after maximum extension. The net is to be conceived spatially. (After *F. H. Müller*).

Let us say now what we shall say again when we consider cellulose, viz., that further extension of the net shown in Fig. 165b is quite conceivable. Then, however, the shortest chains would break, followed by the next shortest and so on until there is complete rupture. Further extension forced in this way will start the internal destruction of the structure. If the junction points do not derive their being from natural chemical cross links, but from cohesive forces — the power of attraction of which is generally lower by nearly one order of magnitude — one could imagine certain junction points (orientated suitably, in this sense, in relation to the direction of extension) tearing asunder. Fresh ones would then be formed in different places (cf. Fig. 158, p. 408).

We shall have to reckon, says *F. H. Müller,* not only with junction points as hitherto understood, but also with molecular entanglements — or molecules hooked together — serving a similar purpose. Space in an unswollen substance is undoubtedly far more densely packed than in the diagram of Fig. 165. Other chains will then run through every "mesh". Some of them will run to and fro and when the material is stretched, gather into loops (Fig. 166a), while others will envelop the chain forming the mesh; the latter cannot disentangle themselves. The substance can be stretched only so far as the entanglement

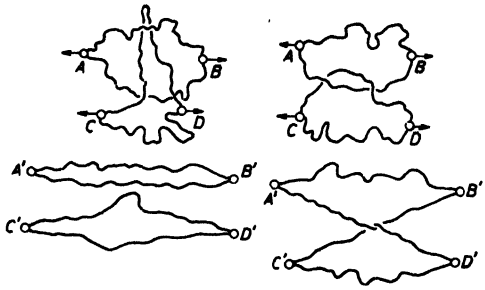


Fig 166. Entanglement (right) and interpenetration (left) of two meshes; above: unextended; below: extended. (According to *F. H. Müller).*

permits (Fig. 166, to the right). The interpenetration does not, according to *F. H. Müller,* seriously limit extensibility. The maximum elongation of a single mesh is of the order of $b\sqrt{P}$ to bP; the enclosed surface prior to extension will be about the square of $\sqrt{P}$ and is at most transformed to a surface bP. Thus is does not become smaller during extension. As before, therefore, the same chains may pass through the mesh[55a]. If the substance shows signs of macro-flow, it means that the junction points partially dissolve with growing extension, when, of course, the value P also changes, depending, in a way peculiar to the material, upon the degree of extension, the temperature or the state of swelling. It explains the complicated behaviour of many high polymers when subjected to deformation.

So long as some of the junction points or entanglements hold, the substance is capable of reverting to its original shape when released from strain. Once true flow has set in, none of the junction points will be in their original positions.

γ *The Views of W. Kuhn and J. J. Hermans*

W. Kuhn's theory regarding the coiled thread molecule relies on the mobility (free rotation) of the individual chain links with respect to each other and on the assumption that the molecular shape is subject to the laws of chance [56].

The totality of molecular configurations in a substance will therefore correspond to the state of maximum entropy. The shape of the molecule is not affected by other factors and the molecule is free in its movements. Actually, therefore, it is an ideal case, such as that of a single thread molecule in a solvent. The results, however, are largely applicable to less ideal cases as well, for it is now suggested that the same freedom of movement of the chains may also be assumed in ideal rubber-like substances.

Kuhn introduced the idea of *"statistical chain elements"* to enable him to tackle the problem of the most probable shape of a chain molecule statistically. This statistical chain element is the shortest part of a molecular chain, containing just enough chain links for the relative orientation of the two terminal links to be considered as independent and thus to be governed by mere chance. In a paraffin chain a section of this kind might contain 5 to 6 CH_2 groups. The number of chain links in the statistical chain element depends,

[55a] Also see *P. J. Flory,* Chem. Rev., 35, (1944) 51.

[56] It is immaterial whether the rotation around the main valence bonds be "free" or whether it necessitate overcoming certain potential barriers. The only essential is that the rotation per second should be sufficiently frequent; i.e. that the potential barrier should be overcome often enough (by means of energy quanta transmitted by the heat motion).

of course, upon the relative mobility of the successive chain links (i.e., upon the "flexibility" of the chain).

If we again consider the monomeric residue as a chain link and allocate ν residues to the statistical chain element, then the molecule is divided upon into $N = P/\nu$ *Kuhn* chain elements (Fig. 167) The configuration of the molecule is now furthermore described by the orientation of the chain elements and to these is ascribed an average length A. If the length of a monomeric residue is b, then always $b<A<\nu b$.



Fig. 167. Diagram showing the subdivision of a chain molecule into statistical chain elements according to *W. Kuhn*.

The most probable shape of a chain molecule left to itself is in the mean less straightened than that represented in Fig. 167. The most likely distance between the molecular terminals is

$$r = A\sqrt{N} \qquad (7.6)$$

The connecting line between the end points of the chain is further represented as vector r according to size and direction (Fig. 168). (Hence in a network structure the r vectors also represent the connecting lines between the junction points of the network).

W. Kuhn and *F. Grün*[57] now tackled the problem of deformation, formulated in Section 3.3.a, in the following manner. They first consider the initial state of a single chain and the most probable spatial distribution of the individual chain elements A (Fig. 163) with reference to the vector r. They find that the spatial distribution of the chain elements is not generally isotropic, even when the molecule is free to assume its most probable configuration. Thus, contrary to *Kratky's* chain, the chain molecule is an anisotropic system even when it is within an isotropic substance. Since, however, the molecules in the isotropic substance are distributed without any order at all, the anisotropies of the individual chain molecules neutralize each other completely.

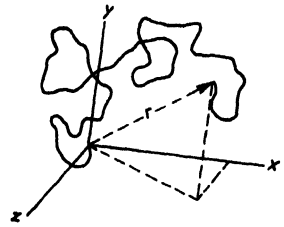


Fig. 168. The connecting line between the terminals of the molecule represented as vector r.

The next step is to calculate the anisotropy of the chain molecule according to the size of r.

By the elementary application of statistics, the most probable spatial distribution of the angles Θ (Fig. 163), with a prescribed length r of the chain, may be derived from the equation:

$$dN = \frac{e^{\alpha}}{2} \sin\Theta \, d\Theta \; e^{\beta \cos\Theta} \qquad (7.7)$$

where α and β are constants determined by:

$$\int_0^{\pi} \frac{e^{\alpha}}{2} \sin\Theta \, d\Theta \, e^{\beta\cos\Theta} = N; \quad \int_0^{\pi} \frac{e^{\alpha}}{2} \sin\Theta \, d\Theta \, e \cos\Theta \, e^{\beta\cos\Theta} = \frac{r}{A} \qquad (7.8)$$

[57] *W. Kuhn* and *F. Grün*, Kolloid-Z., 101, (1942) 248. Essentially the same results were obtained by *F. T. Wall*, J. Chem. Phys. 10, (1942) 132, 485; 11, (1943) 527; also see the critical review by *L. R. G. Treloar*, Trans. Faraday Soc., 39, (1943) 36; 40, (1944) 59.

For small values of $\frac{r}{NA}$ we find $\beta = \frac{3r}{NA}$ An analysis of eq. *(7.7)* shows that small values of the angle are more frequently represented than the larger. (This also determines the anisotropy of the single molecule).

It is now assumed that every chain element A is, optically, a uniaxial system and is therefore polarized with symmetry of rotation, the axis of which lies in the longitudinal direction of A. If the polarizability of the chain element is α_1 in this direction and α_2 perpendicularly to it, the anisotropy of the whole system can be expressed by these values with the aid of the ascertained spatial distribution of the chain elements. For the whole molecule resembles in its behaviour a system that is polarized with symmetry of rotation, notably with the axis in the r direction. If its polarizabilities $\parallel$ and $\perp$ to r are equal to γ_1 and γ_2, we get:

$$\gamma_1 - \gamma_2 = (\alpha_1 - \alpha_2)\ (1 - \frac{3}{2}\overline{sin^2\ \Theta})\ N \qquad (7.9)$$

a formula entirely analogous to formula (4.22) on p. 234; $\overline{\sin^2\ \Theta}$ stands for the (average sine square of the angle of orientation of all the chain elements)^2.

Where $\frac{r}{NA}$ is small, the approximate value is found by averaging, i.e., integrating $(1 - \frac{3}{2} sin^2\ \Theta)$ dN (see equation 7.7), viz.,

$$\gamma_1 - \gamma_2 = \frac{3}{5}(\alpha_1 - \alpha_2)\ \frac{r^2}{NA^2} \qquad (7.10)$$

The value $\frac{r}{NA}$ represents the proportion between the actual length of the coiled molecule and its length after complete alignment of all the chain elements A, and is therefore a relative measure for the "stretch" of the coil. The relation is more complicated than equation (7.10) for larger values of $\frac{r}{NA}$. In the isotropic state of the material, equation (7.6) shows r^2 to be on an average $= NA^2$; therefore

$$(\gamma_1 - \gamma_2)_{iso} = \frac{3}{5}(\alpha_1 - \alpha_2) \qquad (7.10a)$$

Thus the anisotropy of a single molecule is then $\frac{3}{5}$ times that of the statistical chain element, irrespective of the degree of polymerization.

Equation (7.10) gives the anisotropy of a single molecule with $\frac{r}{NA}$ stretch. This answers the first of the questions formulated at the outset in Section 3.3.α. The statistical treatment circumvents the difficulty of stating how each individual chain link is orientated when the molecule is stretched, and the anisotropy of the chain is known in dependence upon its total length.

The next case to consider is that of the chains combining to form a network. For purposes of calculation, the vectors r can now be substituted for the chains between the junction points and thus we come to the second question, viz., what alterations in dimensions and orientation do vectors r undergo when the network is stretched?

Kuhn and *Grün* again invoked the principle of affine deformation, obviously for lack of any more plausible assumption. They therefore presumed that vectors r change their orientation in the same way as the rodlets in *Kratky's* first critical case do; but, *in contradistinction to the rodlets, vectors r undergo* changes in length as well as in position, which is to say that the affine deformation comes to bear upon the junction points of the network. By integration the anisotropy of the network, subject to the degree of extension, can once more be calculated. With moderate degrees of extension, the anisotropy of the polarizability β of the material is then found to be

$$\beta_{\parallel} - \beta_{\perp} = \frac{I}{5}(\alpha_1 - \alpha_2)\left(v^2 - \frac{I}{v}\right) \qquad (7.11)$$

By arithmetrical progression we get:

$$v^2 - \frac{1}{v} = 3\gamma + \gamma^3 - \gamma^4 + \gamma^5 - \gamma^6 + \gamma^7 - \qquad (7.12)$$

where $\gamma = v - 1$ represents the specific elongation $\frac{\Delta l}{l}$ of the chain.

The fact that the member γ^2 is omitted proves that equation (7.11) has an almost linear character up to fairly high values of v. If, however, the anisotropy is plotted against $\gamma = v - 1$ instead of against $v^4 - v^{-1}$, the initial slope of the curves, according to eq. (7.12) becomes three times greater.

For very small degrees of extension ($\gamma \ll 1$) we find:

$$\beta_{\parallel} - \beta_{\perp} = \frac{3}{5}(\alpha_1 - \alpha_2)(v - 1) \qquad (7.13),$$

i.e., taking (7.10a) into account,

$$\beta_{\parallel} - \beta_{\perp} = (\gamma_1 - \gamma_2)_{iso}(v - 1) \qquad (7.14)$$

The anisotropy of the material is then equal to the product of the specific degree of extension $v-1$ and the average intrinsic anisotropy of the molecules in their most probable configuration.

With the aid of equation (7.11) we can ascertain the shape of the curve representing the anisotropy of polarizability and, consequently, also the birefringence as a function of the degree of extension[58]. $\frac{I}{5}(\alpha_1 - \alpha_2)$ being a material constant, we have only to plot $v^2 - \frac{I}{v}$ against v. This curve is reproduced in Fig. 169; its course, in relation to the axis of extension, is somewhat *convex*, to some extent similar to that for *Kratky's* second critical case (cf. Figs. 151 and 154). Thus, qualitatively, the two chain models — *Kratky's* simple one of hinged, linked, rigid rodlets, and *Kuhn's* chain molecule obeying the laws of statistics — produce similar results.

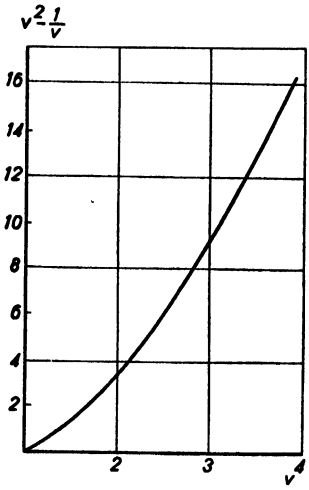


Fig. 169. The optical anisotropy as a function of the degree of extension for the ideal rubber-like elastic body as suggested by *W. Kuhn* and *F. Grün*. (Formula 7.11; the ordinate gives $n_{\parallel} - n_{\perp}$ up to a constant).

The constant in *Kuhn* and *Grün's* formula (7.11) refers to the

[58] When there is little difference between $n_{\parallel}$ and $n_{\perp}$, $n_{\parallel} - n_{\perp}$ is known to be proportional to $\beta_{\parallel} - \beta_{\perp}$.

anisotropy of the statistical chain element and we do not know what relation this bears to the anisotropy of the monomeric residue. Unfortunately, therefore, this cannot be derived from the initial slope of the curve in the o point. At best we might estimate the order of magnitude.

The affine deformation upon which *Kuhn* and *Grün* based their theory relies upon pure geometry and has no foundation in physics. A short while ago, *J. J. Hermans*[59] endeavoured to evolve a theory from the physics of the matter. He points out that in actual fact it is not that vectors r suffer deformation, as if they lay embedded in a viscous medium with nothing further to do save passively to surrender; it is just the reverse: the strain attacks the network and the medium, whatever it may be, (the swelling medium in the case of swollen objects) is indirectly involved in the deformation.

J. J. Hermans then states that a certain tension exists in a molecule extended to length r (Fig. 170). Consequently, a given torsional moment L acts upon every chain element,

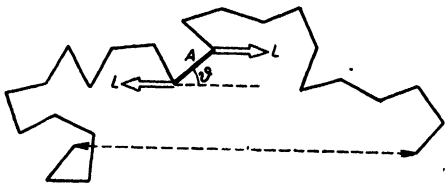


Fig. 170. Torsional moment upon the statistical chain element A resulting from the tension prevailing in the molecule (according to *J. J. Hermans*).

corresponding to a potential energy of the chain element and distributed among the chain elements of the chain in conformity with the *Maxwell-Boltzmann* distribution. A force in the direction r also acts upon the molecular terminals. These forces keep each other in equilibrium.

Now if stress is brought to bear in x direction, every molecule receives an added force at its terminals which is related to that applied to the cross-section of the material. *Hermans* then goes on to treat the problem as being that of an equilibrium of diffusion in a field of force and in this way finds quantitative relations between tension, optical anisotropy and degree of extension, represented by rather complicated equations:

$$v = \varrho\sqrt{\pi} + \frac{1}{\phi_e}; \qquad \beta_{//} - \beta_{\perp} = \frac{2}{5}(\alpha_1 - \alpha_2)\, G\left[\varrho^2 + \frac{\varrho}{\sqrt{\eta}\,\phi\,(\varrho)}\right] \qquad (7.15)$$

where ϱ is an auxiliary, ϕ a function of ϱ and G the total number of elews per cm³.

The form of the resultant relation between birefringence and degree of extension will be seen in Fig. 171. We thus get again a similar curve to that of Fig. 169. Up to $v = 2$ the curve, is practically linear.

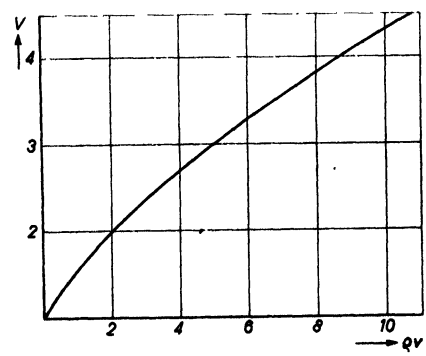


Fig. 171. Birefringence depending upon the degree of elongation for the ideally rubber-like body as suggested by *J. J. Hermans*.

J. J. Hermans states that for slight degrees of extension:

$$n_{//} - n_{\perp} = \frac{4}{45}\,\frac{\pi}{\pi - 2}\,\frac{(n^2+2)^2}{n}\,(\alpha_1 - \alpha_2)\, G_0 \quad (\nu - 1) \qquad (7.16)$$

[59] *J. J. Hermans*, Kolloid-Z., 103, (1943) 210.

and *Kuhn* and *Grün* have

$$n_{/\!/} - n_{\perp} = \frac{2\pi}{15} \frac{(n^2+2)^2}{n} (\alpha_1 - \alpha_2)\, G_0\, (v-1) \qquad (7.17)$$

where $n = \frac{1}{3}(n_{/\!/} + n_{\perp})$ and G_0 = the number of coils per cm³ in the unextended material. The numerical constants in these two equations are found by calculation to be 9.25 and 5.24. Hence *J. J. Hermans* finds the birefringence to increase more rapidly than do *Kuhn* and *Grün.*

If G_0 could be determined by experiment, one could, by comparing it with the number of monomeric residues per cm³ known from the density of the substance, also come to know the number N of monomeric residues per coil, and this would provide a measure for the degree of cross-linking. The anisotropy of the statistical chain element α_1—α_2 being unknown, optical measurements cannot be employed for this purpose. By means of relations, likewise deduced, between extension and stress, *J. J. Hermans* was nevertheless able to calculate G_0 from experimental data produced by *F. H. Müller*[60] and gives roughly 30 statistical chain elements per coil for rubber, ≈ 30 for polystyrene and ≈ 15 for polyvinyl chloride. So this corresponds to approximately 80—150 chain links, very low numbers compared to the degree of polymerization. Thus there is a *fairly high degree of cross-linking* even with these substances and, as the instance of polyvinyl chloride bears out, it may be expected to increase with growing cohesion. As may be inferred from the above equations, the birefringence, subject to the degree of extension, will then also rise more steeply, since with increasing degree of interlinking the number G_0 of coils present per cm³ will likewise grow larger.

When applying speculations of this kind, therefore, to the deformation of the amorphous components of *cellulose,* it will have to be borne in mind that there will be *high degrees of interlinking* and *coils with only a few chain elements.* We shall then be faced with the difficulty that the calculations made by *W. Kuhn* and *J. J. Hermans* are based on the assumption of a very large number of chain elements per coil. Hence the theory has yet to be extended to encompass coils with a finite number of chain elements, and to this we shall revert in Chapter XI.

[60] *F. H. Müller,* Kolloid-Z., 95, (1941) 181, 307.

CHAPTER VIII

THE STRUCTURE OF THE PRIMARY GEL

§ 1. DEGREE OF SWELLING OF THE PRIMARY GEL

1.1. General Remarks

It was pointed out in Chapter IV, § 2 and Chap. V, § 2, that, relatively speaking, the degree of swelling of the primary gel resulting from the coagulation of viscose in a concentrated solution of salt, is very high. With normal viscose containing 8 per cent. of cellulose, the ratio of the volume occupied by one g of cellulose in the gel and in the viscose is roughly as 2 to 3. This means that the molecules come but little nearer to each other during gelatination, and this fits into the general picture which we formed of the process in the sections referred to. It will now be interesting to know how the degree of swelling of the primary gel is affected by the composition of the viscose and by that of the coagulating bath. We shall see presently that this primary degree of swelling is intimately connected with the deformatory properties of the gel.

1.2. Effect of the Concentration of the Spinning Bath

Fig. 172 shows the degree of swelling $(q_1)_X$ of freshly spun isotropic xanthate filaments (which were spun in the manner described in Chap. V, § 1, as model filaments from viscose with 8 per cent. of cellulose in a bath of ammonium sulphate), subject to the

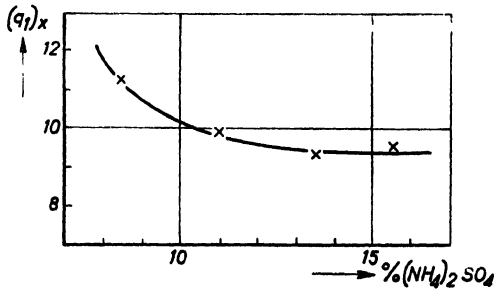


Fig. 172. Degree of swelling $(q_1)_X$ of primary xanthate gels from viscose with 8 per cent. cellulose content depending upon the concentration of the ammonium sulphate spinning bath.

concentration of the spinning bath[1]. It will be noted that the degree of swelling is virtually constant in the range of 12 to 17% by weight of ammonium sulphate (sp.gr. 1.07—1.10). Only with far more dilute solutions does the degree of swelling increase.

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[1] In $(q_1)X$ the index 1 denotes the isotropic state and X the xanthate state.
[2] *E.Hubert, A. Matthes* and *K. Weisbrod:* Kolloid-Z. 98, (1942) 193.

E. Hubert, A. Matthes and *K. Weisbrod*[2] tested freshly spun rayon for degree of swelling depending upon the composition of a spinning bath consisting of solutions of sulphuric acid and sodium sulphate. They found a curve similar to that represented in Fig. 172 for the effect of the concentration of salt, that of the acid being constant. The effect of the sulphuric acid concentration produces a remarkable curve with a maximum and a minimum, for which evidently far more complicated factors are responsible than can be comprehended at a first glance.
This matter is, altogether, somewhat intricate; for, it is not the degree of swelling of the primary gel that is being measured, but that of an *F* state after some orientation which is likewise not constant owing to variation of the composition of the spinning bath.
Rayons (both copper and viscose) spun by the funnel process have an appreciably higher degree of swelling than ordinary viscose rayon. This, too, may have something to do with the low concentration of the spinning baths used.

1.3. Effect of the Cellulose Concentration and the Degree of Polymerization of the Cellulose

We shall now produce some examples to demonstrate the effect of the composition of the viscose. We shall first take a series of nine different viscoses. As the experimental evidence obtained with these will be referred to several times in the following pages, a few introductory details may be useful.

The cellulose content and the average degree of polymerization were varied in this series. The fact that the viscosity must be kept within reasonable limits at once imposes a certain restriction; thus a high average degree of polymerization could only be combined with a low cellulose content, and vice versa. In all cases the *molar* concentration of the other constituents and the xanthate ratio were kept constant for spinning. The content of "free" alkali -- in the form of NaOH — was 0.78 mol/litre, that of the stoichiometrical salt mixture Na_2CO_3 + 2 Na_2CS_3 0.29 mol/litre, and the sulphite content was 0.013 mol/litre. Thus the composition of the "solvent" was exactly the same for all nine viscoses [3].

Altogether, five different *DP* ($\sim$650, $\sim$400, $\sim$280, $\sim$200, $\sim$180) and five cellulose concentrations (2, 4, 6, 8, 10%) were chosen, combined as shown in Table XLII. The first column of the table gives the viscoses, numbered consecutively, the second column the cellulose content *C* (in per cent. by weight), the third the average degree of polymerization *DP* and the fourth the total alkali *A* (in per cent. by wt. as commonly recorded in practice [4]). The fifth column gives the specific gravity of the viscose, the 6th and 7th the

[3] Wishing to study the effect of the composition of the viscose upon the primary degree of swelling of model filaments, one may also vary the concentration of the spinning bath within the range of 12 to 17 per cent. of ammonium sulphate (§ 1.2). Variations of this kind are often an advantage when viscoses of somewhat different specific gravities are spun.
[4] This implies NaOH + Na_2CO_3 + Na_2CS_3 (possibly + Na_2SO_3) expressed as per cent. by weight NaOH. Whereas the percentage of free NaOH in mol/litre was constant in the whole series, the total alkali content customarily recorded is, of course, not.

viscosity η of the viscose in poises (from steel ball test) and the characteristic viscosity constant $[\eta]$ calculated as described in Chap. II, § 2.2, while finally column 8 gives the xanthate ratio (the γ number) at which the model filaments were spun, this being kept constant in so far as was possible.

TABLE XLII

Data respecting Composition, Specific Gravity, Viscosity and XR of a Series of Nine Experimental Viscoses, Cellulose Content and DP being Varied and Molar Composition of the Solvent being Constant

1 Viscose No.	2 *C* % by wt.	3 *DP*	4 *A* % by wt.	5 Sp.gr.	6 η (Poises)	7 $[\eta]$	8 *XR*
1	1.9	650	5.3	1.08	9.1	5.85	0.33
2	4.1	400	5.4	1.09	24.7	3.33	0.39
3	4.0	280	5.4	1.09	7.8	2.65	0.40
4	6.1	400	5.6	1.10	187	3.45	0.39
5	6.0	280	5.3	1.10	22.1	2.25	0.40
6	6.0	200	5.6	1.10	7.8	1.75	0.35
7	8.0	280	5.5	1.11	85	2.30	0.37
8	7.8	200	5.5	1.10	26	1.80	0.39
9	10.5	180	6.1	1.13	61	1.58	0.42

Viscose 1 was made of cotton linters, the remaining eight being produced from a normal sulphite wood pulp [5].

In Table XLIII we find the degrees of swelling $(q_1)_X$, $(q_1)_F$ and $(q_1)_R$ found for the three main states of swelling *X*, *F* and *R* of the isotropic material (for this cf. Chap. V, § 2). The cellulose concentration and *DP* are repeated in the second and third columns, while the last column shows the ratio of the volume occupied by 1 g cellulose in the xanthate gel, to that in the viscose, denoted as "relative gel volume" [6].

In later references to the viscoses in Table XLIII we shall designate them by their cellulose content and *DP*. Thus viscose No. 1 will be referred to as (1.9—650), viscose No. 2 as (4.1—400), etc.

[5] The DP was measured by careful nitration of material obtained from viscoses 5, 7 and 9 and by determination of the viscosity of the nitrates in very dilute acetone solution based upon a *Staudinger Km* constant of 11×10^{-4}. The *DP* of the other viscoses was calculated via $[\eta]$. (The *Km* constant found from these data is 8.9×10^{-4}, which is far higher than that recently recorded by *G. Jayme*, viz., about 4×10^{-4}, a discrepancy which yet remains to be explained).

[6] The concentration of the spinning bath was as follows: With the 2 per cent. viscose, 10% by wt., with the 4%, 12% by wt., with the 6%, 13.5% by wt. and with the 8% and 10%, 15.5% by wt. $(NH_4)_2SO_4$. Thus, with viscoses 2 to 9 it remained within the limits mentioned above in § 1.2.

TABLE XLIII

Degree of Swelling of the Primary Isotropic Gel Subject to the Composition of the Viscose

$(q_1)_X$ as xanthate; $(q_1)_F$ after decomposition of the xanthate; $(q_1)_R$ in re-swollen state

Viscose No.	C % by wt.	DP	Degrees of Swelling			Relative Gel Volume.
			$(q_1)_X$	$(q_1)_F$	$(q_1)_R$	
1	1.9	650	29.0	11.2	2.21	0.47₅
2	4.1	400	16.0	6.8	2.29	0.56₅
3	4.0	280	16.1	7.8	2.16	0.54₅
4	6.1	400	10.5	5.4	2.14	0.55
5	6.0	280	13.1	5.9	2.30	0.68
6	6.0	200	13.4	7.0	2.10	0.69₅
7	8.0	280	9.75	5.0₅	2.33	0.67
8	7.8	200	10.5	4.9₅	2.21	0.71
9	10.5	180	8.1	4.6	2.31	0.73₅

It is clear from Table XLIII and from the diagram in Fig. 173 that:

1) *DP* being constant, the primary degree of swelling $(q_1)_X$ decreases as the concentration of cellulose increases.

2) The concentration of the cellulose being constant, $(q_1)_X$ decreases as the *DP* increases. The latter effect is most marked in the more concentrated viscoses and appears to become almost imperceptible with increasing dilution.

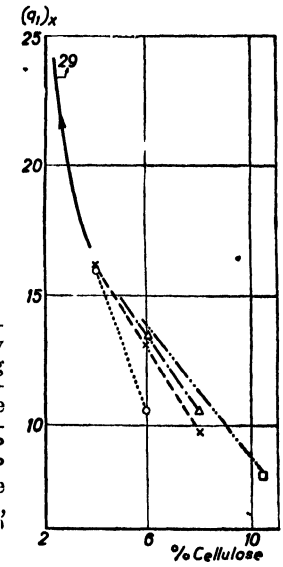


Fig. 173. Degree of swelling of the primary xanthate gel, depending upon the cellulose concentration and upon the average degree of polymerization; o DP 400; x DP 280; Δ DP 200; □ DP 180. The curve meets the ordinates at 2 % cellulose, $(q_1)_X$ = 29 and DP 650 (Table XLIII)

According to Chap. IV, § 2, high *DP* and high concentration both favour low distance order (order in the smallest regions) in the viscose, and it seems reasonable to suppose that the better the low distance order in the liquid, the more junction points (centres of crystallization) will be formed during primary coagulation and the more compact will be the structure of the primary gel frame.

Supposing the structure of the gel frame to be as formerly suggested, viz., well-parallelized regions forming the nodal points of a network and the less well-ordered regions — or regions without any order at all — containing more or less kinked molecular chains constituting the strings of the net, then, under deformation, we may expect that the more junction points there are and

the more compact the systems, the more rapidly will orientation take place subject to the degree of extension. We shall see in Chapter XII that this rate of orientation actually is to a large extent dependent upon the degree of swelling $(q_1)_X$.

If we look at Table XLIII and see the degrees of swelling $(q_1)_F$ of the fresh cellulose filaments obtained upon the decomposition of the xanthate gel, we shall see that as a rule these too rise and fall with $(q_1)_X$ and, therefore, obey the same rules[7]. Roughly, however, they amount to only half $(q_1)_X$, which means that the average distance between the particles becomes $\sqrt[3]{}$ 0.5 or 0.8 times smaller. The explanation might be that the primary junction points in the xanthate gel still contain xanthate groups and water of constitution and are consequently more interspaced than after the decomposition to cellulose (cf. Chap. IV, § 3).

If the gel is now dried and then re-swollen in water there is no longer a n y correlation w h a t e v e r between degree of swelling $(q_1)_R$ and $(q_1)_X$ and, according to Table XLIII the former is about 2.2—2.3 for all the viscoses. During the process of drying the net frame of the primary gel contracts very considerably and a variety — both in number and kind — of new points of contact — a "spectrum" of secondary junction points — are formed between the cellulose chains (cf. Chapt. IV, § 5). Mere re-swelling in water will no longer disperse many of these new junction points. In all instances the secondary junction points are so numerous that they completely dominate the character of the swelling, usurping the influence exerted by the position and distribution of the primary junction points. We shall see below, however, that *the character of the primary gel reasserts itself, even in these objects, when deformation is applied.*

1.4. Effect of the Concentration of Alkali

Since, as experiments with three viscoses containing 8 per cent. of cellulose and 0.78, 1.5 and 2.1 mol/litre of free NaOH have demonstrated, the concentration of the alkali is virtually immaterial, we shall not devote any time to it here[8].

1.5. Effect of the Xanthate Ratio of the Viscose

It is interesting to note that the degree of swelling $(q_1)_X$ of the primary xanthate gel is not influenced by the *XR* during spinning. Table XLIV records the results of relevant experiments carried out with a viscose containing 8% of cellulose ($DP \sim 200$), 6.2% of total alkali and 39% of carbon bisulphide (as referred to cellulose), spun in the same bath at various degrees of ripeness.

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[7] *E. Hubert, A. Matthes* and *K. Weisbrod* (Kolloid-Z. 98, (1942) 193) tested freshly spun rayon for degree of swelling depending upon the composition of the viscose. They state that increased cellulose concentration lowers, whereas increased alkali concentration raised the degree of swelling; also that wood-pulps of high α-cellulose content (especially linters) produce low, while normal wood-pulps produce higher degrees of swelling. Hence these data refer to orientated *F* states and appear in the main to agree with the above evidence. The degree of orientation not having been established, however, direct unqualified comparison is not permissible.

[8] This, of course, only applies to model filaments spun in ammonium sulphate and not to practical spinning of rayon, where the alkali content does have some influence.

TABLE XLIV

Effect of the Xanthate Ratio upon the Degree of Swelling of the Isotropic Gel

C % by wt.	XR	Ripeness according to Hottenroth	$(q_1)_X$	$(q_1)_F$	$(q_1)_R$
8	51	24	9.8	4.8	2.33
8	36	9.3	10.1	4.8	2.24
8	12	1.1	9.9	5.7	2.20

It will be seen that, between XR 12 to 51, $(q_1)x$ is virtually constant, whereas $(q_1)F$ becomes larger with decreasing XR. Thus the ratio $(q_1)F/(q_1)X$ rises with increasing degree of ripeness of the viscose. Fig. 174 exemplifies the dependence of $(q_1)F/(q_1)X$ upon the xanthate ratio of the viscose [9].

For $XR = 0$ the curve can without difficulty be extrapolated to $(q_1)F/(q_1)X = 1$.

The volume of the primary gel — i.e., the "openness" of the primary net — is quite unaffected by the xanthate decomposition in the viscose, reacting only to the concentration of cellulose; on the other hand, in the subsequent decomposition of the xanthate gel, there is all the less decrease in volume as it contains fewer xanthate groups. This bears out the interpretation of this decrease in volume suggested above.

Again, the degree of swelling $(q_1)_R$ is scarcely affected at all by the XR.

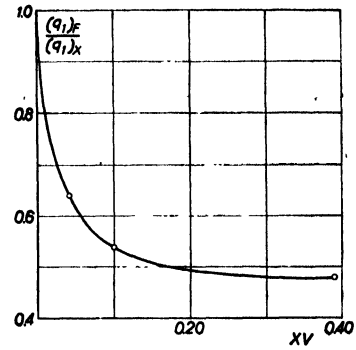


Fig. 174. Ratio of the degree of swelling $(q_1)_F$ of the fresh isotropic cellulose gel to the degree of swelling $(q_1)_X$ of the primary xanthate gel, depending upon the xanthate ratio, XR, of the viscose.

§ 2. CHANGES IN VOLUME WHEN SWOLLEN ISOTROPIC FILAMENTS ARE EXTENDED.

2.1. Xanthate Filaments and Fresh Cellulose Filaments

When highly swollen isotropic X and F filaments are extended they lose very considerably in volume. In the extension test large amounts of swelling fluid are squeezed out of the filament [10], which is precisely what one would expect to happen to a network structure when subjected to deformation. When a regular, mathematical net (Fig. 140) closes up, the volume would eventually fall to zero. We must spend a little time on the quantitative aspect of this phenomenon.

If we consider the relative decrease in the degree of swelling depending upon the extension, that is the value q_3/q_1 as a function of v_3 [11], we find the

[9] The determinations of the xanthate ratio used in this figure do not refer to those indicated in Table XLIV for the viscoses, but to xanthate determinations applied to the X filaments themselves at the moment when the volume was measured. (At that moment the XR of the X filaments was a little lower than that of the original viscose.)

[10] *P. H. Hermans:* Cellulosechemie 19, (1942) 117, 122.

[11] For this nomenclature see Chap. V, § 3.2. The degree of extension of the filament when clamped is denoted by v_2, while that remaining after release and recovery (taking place during the tests) is denoted by v_3.

striking rule that almost exactly the same curve is obtained for all the viscoses listed in Table XLIII [12]. This is reproduced in Fig. 175. As a rule, the curves for model filaments produced from different viscoses vary slightly in length. The terminal point is governed by the maximum extensibility of the filaments, being always a little lower for F filaments than for X (see next Section). Fig. 175 was drawn for an average case. It will be seen that the volume of the X filaments is liable to drop to approximately a third of the initial volume.

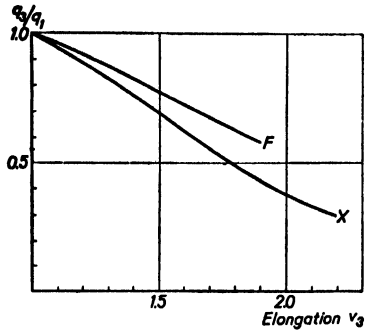


Fig. 175. Relation between degree of swelling q at the end of the elongation and degree of swelling q_1 in the original isotropic state for X and F filaments, depending upon the degree of elongation. (The curves hold for all the viscoses of Table XLIII)

The fact that the relative change in volume accompanying initial degrees of swelling as different as those given in Table XLIII is almost the same for all, is a revelation of the *close relationship between deformation and volume* which apparently exists in these systems.

Another noteworthy fact is that X and F filaments produce almost identical curves. Apparently the reduction of the degree of swelling to about half, which occurs in the transition from the X to the F state, has no effect in this regard. This would seem to agree with the proposition put forward in Chap. IV, § 3 and § 5, to the effect that this shrinkage is subject to a different mechanism from that governing the further shrinkage of the F filament (cf. next Section).

A characteristic connection between X and F state may also be inferred from the fact that points are obtained likewise falling almost on the curve when filaments extended in the X state are degraded to F filaments after the extension.

2.2. *Reswollen Filaments*

The picture presented by R filaments is totally different. Table XLIII shows the initial degree of swelling always to be approximately the same. When these filaments are extended (under water) there is invariably seen to be an increase followed by a reduction in volume. Of this Fig. 176 affords a typical example in the case of viscose No. 4 (6—390) of Table XLIII.

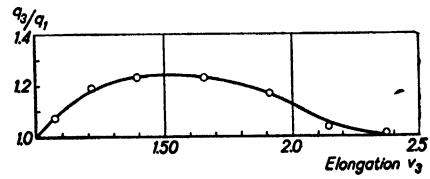


Fig. 176. Ratio between the degree of swelling q_3 at the end of the elongation and degree of swelling q_1 in the original isotropic state for R filaments, depending upon the degree of elongation.

One would be tempted to interpret the maximum in the volume curve as

[12] Only viscose No 9, where the initial degree of swelling was the lowest, produces a slightly flatter curve. The curve for X filaments is here about midway between the two curves in Fig. 175.

follows: According to the hypothesis propounded, the network structure contracted considerably, its strings folding up (or coiling), under the operation of isotropic drying, and a spectrum of new junction points was formed, which restrain the degree of swelling when the material is re-swollen. Upon its extension in this state, some of these junction points — notably those at that end of the spectrum where there is little cohesion — are dissolved owing to the internal tensions and displacements brought about by the deformation. As a result, the degree of swelling increases slightly. (Compare the diagram in Fig. 161 [13]). As extension proceeds, however, the "drawing together" of the net becomes more obtrusive and the volume again decreases. As Fig. 177 may illustrate (viscose No 5 of Table XLIII; 6—270), *X*, *F* and *R* filaments tend towards roughly the same ultimate volume when extended.

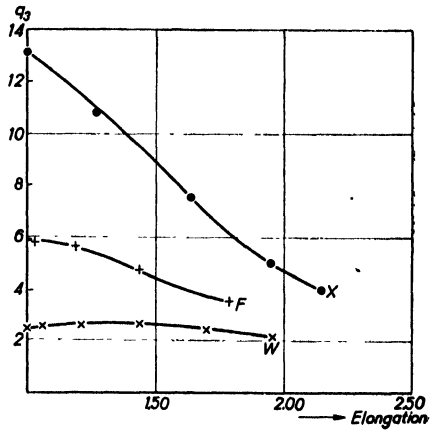


Fig. 177. Degree of swelling q after elongation, depending upon the degree of elongation, for X, F and R filaments.

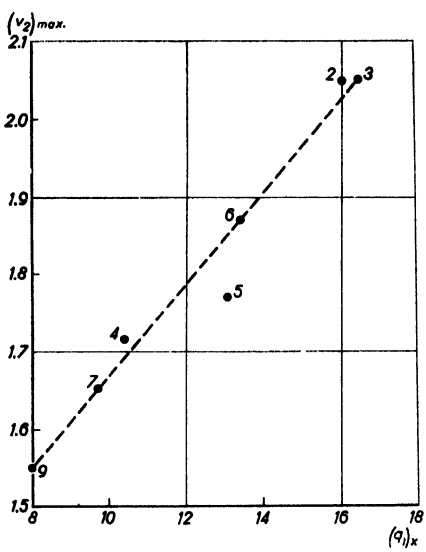
The following facts would seem to bear out this general account. If it is valid, there would be reason to believe that the more the network structure had shrivelled while drying, the further would the maximum in Fig. 176 have shifted to the right and the higher would it stand. The "straightening out" of the involuted strings of the net then demands a relatively higher degree of extension and, accordingly, relatively more junction points will be dispersed. Now this expectation is corroborated by the facts. *Both the degree of extension at maximum volume and the level of this maximum run parallel to the primary degree of swelling* $(q_1)_X$ *of the original xanthate gel.*

Fig. 178 reproduces the degree of extension $(v_2)_{max}$, at which the maximum occurs in the volume curve, for seven of the varieties of viscose presented in Table XLIII, subject to $(q_1)_X$; Fig. 179 shows the relative increase in volume q_2/q_1 in this maximum value [14]. The correlation of the two values with $(q_1)_X$ is unmistakable. Thus in this respect the *R* filaments decidedly "remember" the degree of swelling of the primary gel from which they originated [15].

[13] This might be put somewhat differently. One might say that, looking at the figure, it is clear that, when a net thus involuted is deformed, there will at first be some relaxation.

[14] In this case the degree of extension and volume were measured in the clamped material (hence without recovery), which is why the index 2 was used. The relative increase in volume of the *R* filament, which is measured in this way, is a little greater than that measured as a funcion of v_s.

[15] Older examples of the gels' "memory" of the primary degree of swelling were cited from the literature in Chap. IV, § 6.



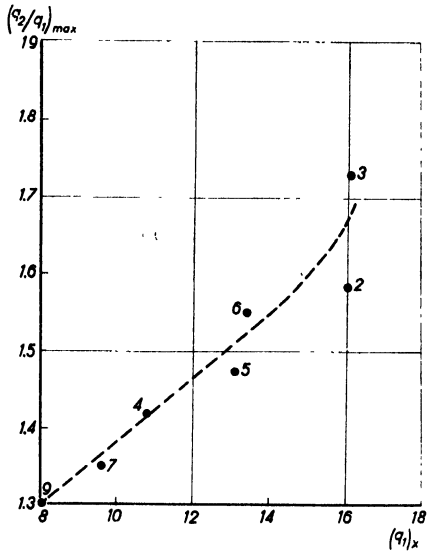


Fig. 178 and Fig. 179. Degree of elongation (v_2)**max** and relative increase in volume q_2/q_1 in the maximum of the volume curve of R filaments as a function of the degree of swelling $(q_1)x$ of the primary gel. (The numbers in the Figures correspond to the viscose numbers of Table XLIII).

Extrapolating the curves in Figs. 178 and 179 to $(q_1)_X = 1$, it will be found that $(q_2/q_1)_{max}$ and $(v_2)_{max}$ likewise become equal to unity for this fictitious primary degree of swelling.

The swelling of commercial artificial fibres in water bears no direct relation to the degrees of swelling represented in Fig. 176. It does correspond, on the other hand, to the swelling of model filaments which have been preliminarily extended to a given degree in the xanthate state, then decomposed and dried. Testing these filaments for degree of swelling subject to the degree of preliminary extension, this will be found to decrease a little — viz., from $q = \sim 2.2$ to ~ 1.8 — with increasing preliminary extension; which agrees with the fact often observed in practice that highly orientated filaments usually swell somewhat less than those not so highly orientated. This may mean that more (or stronger) secondary junction points are formed in well orientated substances during the first process of drying; but in this sense no pronounced correlation with the primary degree of swelling $(q_1)x$ can any longer be detected.

2.3. *Additional Remarks*

Borrowing from colloid-chemical terminology, the expulsion of water upon the extension of highly swollen gels might be described as a form of s y n e r e s i s. The loosely knit primary network structures of the gels contain a large amount of uncombined swelling medium, which is to some extent mechanically enclosed, as in a sponge.

It has already been pointed out that the high degrees of swelling we are considering are not e q u i l i b r i a of s w e l l i n g (p. 408). Nevertheless, provided there be no extension, their durability is almost unlimited.

The presence of fairly large voids filled with water may also be inferred from the fact that much of the water is easily replaceable by organic liquids if imbibition is first applied with a liquid miscible with water, such as alcohol

or acetone, and then with "lyophilic" liquids. *P. H. Hermans* and *A. J. de Leeuw*[16] have described experiments of the kind. They also noticed that, after subsequent evaporation of the organic liquid (particularly with benzene or hexane), chalk-white filaments are often obtained, which obviously contain numerous minute voids filled with air; they then exhibit an abnormally high volume (up to twice the volume in the *D* state). These are known as "Air filaments"[17]. In this case the net frame has remained open to some extent. In the absence of sufficient water in the gel the involuting tendency of the net strings is apparently impeded and the state of densest packing cannot be attained. (For this see Section 4.1). Similar phenomena in other gels (e.g. gelatin gels) were described in detail and explained in the same way in the previous century by *O. Bütschli*[18].

§ 3. RELATION BETWEEN DEGREE OF SWELLING AND EXTENSIBILITY

3.1. Extensibility of Isotropic Filaments in the Four Main States of Swelling

Table XLV gives, as the mean value of several tests, the extension at break of the isotropic filaments in the four main states of swelling for the nine viscoses covered by Table XLIII (As always, the D state refers to 65% rel. humidity in desorption).

TABLE XLV

Extension at Break of Isotropic Model Filaments in the Four Main States of Swelling, Spun from Viscoses Variously Composed. (The numbers of the viscoses refer to Tables XLII and XLIII)

Viscose No	Cell %	*DP*	Extension at Break				$(q_1)_X$
			X	*F*	*R*	*D*	
1	1.9	650	1.99	1.75	2.26	1.02	29.0
2	4.1	400	2.43	2.17	2.65	1.25	16.0
3	4.0	280	2.20	1.96	2.58	1.22	16.1
4	6.1	400	2.89	2.27	2.99	2.26	10.5
5	6.0	280	2.44	2.06	2.59	1.93	13.1
6	6.0	200	2.12	1.86	2.55	1.33	13.4
7	8.0	280	2.46	2.14	2.59	2.14	9.75
8	7.8	200	2.25	2.06	2.52	1.85	10.5
9	10.5	180	2.24	1.92	2.33	2.01	8.1

With few exceptions, all varieties of isotropic filaments are extensible up to above 100 per cent. These data do not reveal any relationship between extension at break (*E B*) and initial degree of swelling q_1, but the following should be noted:

1. *E B* increases always in the order of *D-F-X-R*. (We shall have more to say about this in Section 3.2).

[16] *P. H. Hermans* and *A. J. de Leeuw:* Kolloid-Z. 82, (1938) 58.
[17] Filaments of this kind invariably also enclose considerable amounts of the organic solvent.
[18] *O. Bütschli* 1898. Untersuchungen über Strukturen. Leipzig 1898.

2. Whatever the concentration of cellulose, $E\,B$ increases together with increasing DP.
3. At a given DP, $E\,B$ increases as the concentration of cellulose increases. Viscose No. 4 (6.1—400) displays the optimum.

For the time being we shall accept points 2 and 3 as empirical facts and shall not attempt to explain them. Something must be said, on the other hand, respecting the very poor extensibility of some of the viscoses in the D state. These are the viscoses containing 2 per cent. and 4 per cent. of cellulose, as also the viscose of 6 per cent. cellulose content with the lowest DP. At the same time, these are the viscoses with the highest primary degree of swelling $(q_1)_X$. Thus, according to earlier interpretations, the gel in the dry state here underwent the highest degree of involution, or coiling.

A possible explanation for the low extensibility in the D state is that the chains are particularly strongly interlinked or entangled in the amorphous regions. As extension proceeds, migration — microflow (cf. p. 299) — becomes necessary and in these cases the corresponding resistance is so great, owing to the many junction points and linkages, that the strain exceeds the breaking tension and the process of extension therefore comes to an end prematurely. If, on the contrary, the frictional resistances are diminished by swelling, extension will proceed with as little hindrance as in the case of less involuted networks, as is demonstrated by the "normal" extensibility of the R filaments of these viscoses in Table XLV.

Extended in the D state, however, the other D filaments also show peculiar signs of fairly radical internal processes; for, as they extend, the filaments, which are at first as clear as crystal, gradually become untransparant and turbid, often even chalky white as seen from above. Seen through the microscope, there are then visible innumerable very fine lateral fissures at the limit of optical resolving power; these evidently fill with air and thus impart turbidity to the material. When looking through them, they have a peculiar brown colour [19].

P. H. Hermans and *A. J. de Leeuw* [20] state that, after the extension of these opalescent filaments, a slight increase in volume of the order of ten per cent. is to be observed. It looks as though the same process as that which takes place in the extension of re-swollen filaments is imminent, but is prevented from coming to fruition for obvious reasons.

3.2. Extensibility of Isotropic Cellulose Filaments as a Function of Regain

P. H. Hermans and *P. Platzek* [21] report interesting facts that emerge when the extensibility of a given isotropic filamentous material is tested as a function of its regain.

Let us look again at Fig. 161, which is reproduced below as Fig. 181. Now,

[19] *A. Herzog* (Die Kunstseide 16, (1934) 128) made similar observations with "Rosshaar" from viscose and with other artificial fibres. Analogous phenomena are occasionally met with in other high polymers (see, for instance, *Halle:* Kolloid-Z. 69, (1934) 329.
[20] *P. H. Hermans* and *A. J. de Leeuw:* Kolloid-Z. 82, (1938) 58.
[21] *P. H. Hermans* and *P. Platzek:* Kolloid-Z. 97, (1941) 329.

if the diagram there given represents the true facts as to the extension and contraction of the gel framework in principle, we have a right to expect that an isotropic filament produced from a given primary gel will be more extensible in proportion as its selected degree of swelling is lower. But it must, of course, be presupposed that, at all the degrees of swelling involved in the investigation, the filament will be able to attain to the same state of orientation, so that the conditions to the right of Fig. 181 — at the end of the extension — be identical, all according to its longitudinal stretch.

Although the schema represented in Fig. 181 is admittedly very primitive, this conclusion which we draw from it appears, in fact, to be correct. If we consider true cellulose gels only — that is, ignoring the xanthate gels — it will already be clear from Table XLV that *F* filaments are always less extensible than the less swollen *R* filaments. The investigations referred to above were then extended to isotropic filaments which had been conditioned at different relative humidities. The solid curve A in Fig. 180 shows the result (*E B* in dependence upon the degree of swelling). The material used consisted of model filaments made of industrially produced viscose containing 8 per cent. of cellulose. The point at the extreme right on curve A represents the *F* filaments, then the *R* filament follows from right to left and, finally, a series of observations relating to various conditioned filaments. The last point corresponds to the *D* filament (65% rel. h.)[22].

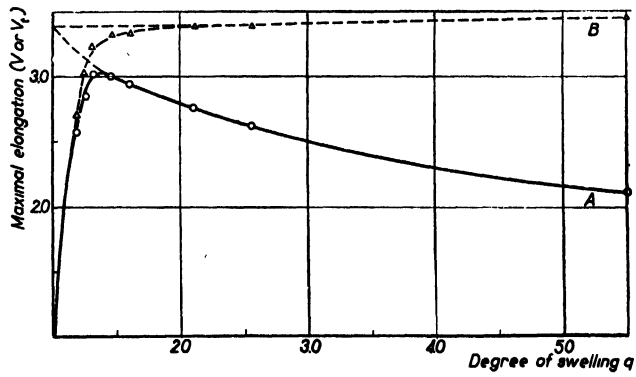


Fig. 180. Maximum extensibility of isotropic cellulose filaments as a function of the degree of swelling. Curve A: Extension at break found experimentally. Curve B: Maximum degree of elongation v_t.

It will be seen that the extensibility does in fact steadily increase in inverse ratio to *q*, reaching a maximum at *q* 1.3—1.4. With yet drier filaments the extensibility again begins to diminish. The curve can readily be extrapolated to the 0 point of the system of co-ordinates, which means to say that the filament is no longer extensible at all in the bone-dry state ($q = 1$). This is borne out experimentally. Dry isotropic filaments are as brittle as glass and scarcely extensible at all.

Something rather different obviously takes place to the left of the extensibility maximum — which coincides with 25—30 per cent. regain. Here we get

[22] As an exception, the degree of swelling *q* referred in this case to the bone-dry state.

what *E. Hubert, A. Matthes* and *K. Weisbrod* [23], in another connection, denoted as *"Trockenstarre"* (drying rigidity), for which see next Section. Lack of sufficient water impedes microflow and leads to premature break, the lower the water content, the sooner. (As we saw in the preceding Section, the more "crumpled" the gel frame is during drying, the earlier will this break occur).

Were it not for this "Trockenstarre", the fully dry filament would possess approximately 3.4—3.5 extensibility, in conformity with the extrapolation of the curve to the left of the maximum. We may therefore say that the *D* filaments of particularly low *E B*, which we find in Table XLV, lie further down on the left branch of the curve in Fig. 180.

With the aid of Fig. 181 it will now readily be understood that the extensibility of a given gel must diminish in inverse ratio to $q^{\frac{1}{3}}$; for, assuming the extended network to have the same orientation and length in both states of swelling, extensibility is governed only by its ratio to the isotropic initial length, and this is in direct proportion to $q^{\frac{1}{3}}$.

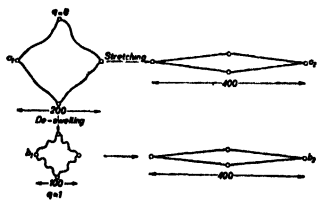


Fig. 181. Diagram showing the extension and shrinkage of a network structure in the swollen state (above) and the unswollen state (below). (Repetition of Fig. 161).

Thus if, for reasons to be given directly, we say that the extensibility (extrapolated from Fig. 180) of the dry filament is 3.47, the extensibility v_{max} for a degree of swelling q would, if our diagram is correct, be equal to $3.47 \times q^{-\frac{1}{3}}$. In Table XLVI the result is set out in comparison with the observed extensibility. The two actually do agree approximately.

TABLE XLVI

Observed and Computed Maximum Extensibility of Isotropic Cellulose Filaments as a Function of the Degree of Swelling; also Observed Extensibility v_t referred to the Dry State

q	vmax computed	vmax observed	vt (max) observed
1	(3.47)	—	—
1.45	3.07	3.01	3.33
1.59	2.97	2.95	3.34
2.10	2.71	2.77	3.40
2.55	2.53	2.62	3.40
5.50	1.97	2.10	3.47

Fig. 182 reproduces the result of an actual extension test upon a swollen isotropic filament.

[23] *E. Hubert, A. Matthes* and *K. Weisbrod:* Kolloid-Z. 98, (1942) 193.

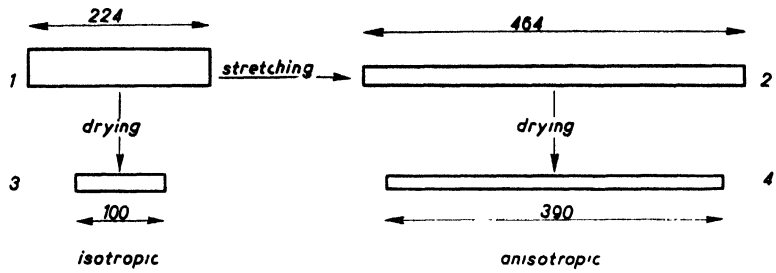


Fig. 182. Result of an actual extension test (filament lengths in mm). While the unextended filament (left) is drying, isotropic shrinkage takes place, whereas the elongated filament shrinks anisotropically. The longitudinal ratio of 4 to 1 represents the degree of elongation v_t.

This time the example refers to an isotropic X filament (1) of 224 mm length and q being 11.2. After extension (2) the filament has become 464 mm long; hence v is 464 : 224 = 2.07. The filament now being strongly orientated it exhibits high anisotropy of swelling. Therefore, on drying (4), it contracts little in length, this becoming 390 mm. (In the diagram of Fig. 181 the same length was assumed). If the isotropic filament (1) is now also converted to the dry state (3), its length becomes $224 \times q^{-\frac{1}{3}} = 100$ mm.

Thus by extension in the swollen state to $v = 2.07$, the filament has been lengthened by 3.9 as compared to the dry state. A *"degree of extension referred to the dry state"*, which we shall denote as v_t can be classified with every degree of extension in the swollen state (cf. Chapter IX for further details).

Hence the v_t which has occurred in Fig. 181 in the extension from a_1 to a_2 is the ratio of the length of b_2 to that of b_1. If the principle of the schema is valid and if we presume that for all degrees of swelling at maximum extension the same orientation is attained, then all objects of the same origin extended to the maximum should by rights have the same length in the dry state. That means, however, that, irrespective of the degree of swelling at which extension takes place, the degree of extension v_t will always be the same. In other words: $(v_t)_{max}$ would remain constant in all the degrees of swelling of a shrinking primary gel. The values of v_t determined experimentally are given in the last column of Table XLVI. In Fig. 180 they are connected by the dotted curve B. It can be seen that v_t really is far less dependent upon the degree of swelling than v and that it becomes virtually constant above $q \sim 2$.

These results lend further support to the principle of the schema in Fig. 181. This means that apparently *at all degrees of swelling above about $q = 1.5$, the same network structural frame with fixed junction points persists,* "folded up" more or less according to the degree of swelling; also that only microflow, no macroflow, takes place during deformation in all the states of swelling we have been considering.

Let it be said that the *xanthate state falls outside this category.* Although its degree of swelling is still roughly twice as high as that in the *F* state, its extensibility is also considerably higher (Table XLV). There must, therefore, be some other essential difference between the *X* and *F* states beyond that which is embodied in their different degrees of swelling[24]. We shall see later that an appreciably higher orientation is attained at the end of the extension in the *X* state than in the *F* and *R* states. Hence the assumption of identical final states cannot be applied to this case.

§ 4. THE DEGREE OF SWELLING AFTER RESWELLING SUBSEQUENT TO DRYING

4.1. *Thermal Treatments. The "Trockenstarre"*

The supposed structural changes taking place during the shrinkage of the primary gel were discussed in the foregoing. The far lower degree of swelling (of the order of 100 per cent.) upon reswelling in water after the first process of drying (*R* state) was attributed to the formation of a number of new junction points immune to the solvent power of water. These come into being when the network is compressed as it shrinks, at the places where the chain molecules approach each other in suitable positions and at sufficiently close quarters.

Were by some means the molecular chains permanently maintained in fully extended configuration and parallel alignment during the process of contraction, a cellulose monocrystal would undoubtedly be formed at the end of the shrinkage. The hypothesis of the primary network structure and also of the involution of the net during shrinkage lead to the very opposite. Instead of complete recrystallization, the resultant can at most be limited recrystallization in scattered minute regions, or expansion of the spectrum of the junction points.

The theory of the network structure also makes it plain that the possibility of compression must be remote and that it could never advance to the density of the crystalline cellulose. Three factors are involved:

1. The geometric arrangement of the chains does not allow the attainment of the condition of densest packing.
2. In the process of shrinking the chains in the amorphous regions are forced to coil in a manner inimical to their most probable shape.
3. The process of shrinkage presupposes permanent slight relative displacements of the monomeric residues. As the regain decreases, these become more and more constrained owing to the increasing number of junction points formed. Even that part of the junction point spectrum which has no noticeable binding power in the presence of water now comes into action.

[24] The reader is reminded that we have before assumed a different mechanism for the shrinkage of *X* to *F* from that for the further contraction of the *F* state (Chap. IV § 3 and § 5). In the former case the character and the spatial requirements of the junction points change above all; in the latter the process of folding up then begins.

We saw in Part II, Chap. III § 2 that isotropic model filaments dried in the ordinary way reach a density of 1.512 and, therefore, a specific volume of 0.662. The latter is five per cent. greater than that of crystalline cellulose. In well orientated fibres, i.e. with favourable geometric arrangement, the density reached is 1.519, which means to say a specific volume of 0.659, about $^1/_2$% lower.

It is obvious that, the more the gel shrinks while drying, the more water-resistant junction points will be formed and the lower will be the degree of swelling when the material is re-swollen. This may therefore be looked upon as some measure for the shrinkage attained.

E. Hubert, A. Matthes and *K. Weisbrod*[25] have shown by extensive and fundamental investigations that the degree of swelling of artificial fibres can be largely controlled by varying the conditions of drying. They found that rapid dehydration (high temperature, low rel. humidity) produces fibres of higher degree of swelling than slow, careful drying low temperatures, high rel. hum.). They cite 2.36 and 1.85 degrees of swelling as extreme cases[26].

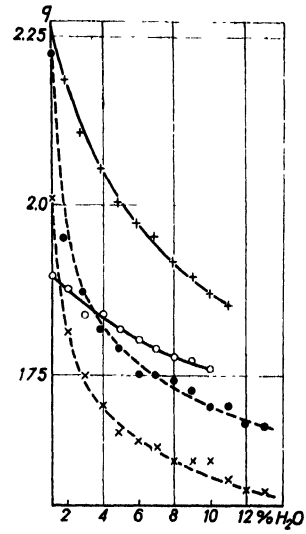


Fig. 183. Alteration in the degree of swelling of four different viscose fibres when re-swollen in water after repeated drying down to 12% regain and re-wetting under identical conditions (after *Hubert, Matthes* and *Weisbrod*). Full curves: Dried at 60° and 20 % rel. hum. Broken curves: Dried at 60° and 60 % rel. hum.

If a fibre is repeatedly dried and moistened under identical conditions, its swelling power diminishes slightly every time after it has been dried; the trend is evidently towards a minimum value, which is all the lower as drying is slower. Some examples are given in Fig. 183. As artificial fibres in use as finished products are constantly being washed and dried, their swelling capacity continues to diminish little by little.

Hubert, Matthes and *Weisbrod* offer the following explanation. Shrinkage can only take place in the presence of a certain minimum quantity of water, but the rate of dehydration is always greater than that of shrinking. Consequently the gel prematurely falls into a kind of *"Trockenstarre"*. Every time the gel has been moistened and dried again, it has an opportunity of pushing its reconstruction a step further. Obviously the cycle would have to be repeated over and over again before the minimum swelling power can be reached. We discussed in the preceding Section how the "Trockenstarre", checking internal flexibility, is also manifested in the extensibility of the gels.

Hubert, Matthes and *Weisbrod* also tried "steaming" as a device whereby they studied the decline in swelling power. By treating regenerated fibres with saturated steam at 100°, they succeeded in lowering the degree of swelling in the *R* state to 1.45 — 1.50 (corresponding to a regain of 50—55 per cent.) in one to two hours. This effect is n o t produced by heating swollen fibres

[25] *E. Hubert, A. Matthes* and *K. Weisbrod:* Kolloid-Z. 98, (1942) 193.

[26] The swelling values reported by *Hubert, Matthes* and *Weisbrod* have here been converted to degrees of swelling (as referred to the dry state) in accordance with formula (3.5) on page 209.

in water to the same temperature and the experiment is only successful when every precaution is taken to prevent the formation of liquid water [27].

We find similar effects with model filaments. In this case completely dried filaments need only be placed in saturated water vapour of 100° — or, curiously enough, merely in boiling water — to produce advanced "shrinking". But heating filaments previously swollen in the cold to 100° does not produce the effect.

Evidently, by a combination of high temperature and optimum water content, these treatments contrive to overcome the "Trockenstarre", as it were, and further compression of the structure is able to take place. Table XXI (page 202) is there to show that these operations actually do somewhat increase the density of the bone-dry fibre.

***Hubert, Matthes* and *Weisbrod* also report the exceedingly interesting fact that it is also possible to procure the minimum swelling power — and that immediately — by soaking dry fibres in liquid ammonia and allowing the latter to evaporate from the fibre. Apparently the ammonia serves as an excellent "softener", since it is also capable of paralyzing a considerable portion of the junction point spectrum. A closer enquiry into the effect of liquid ammonia upon the properties of cellulose gels should certainly be rewarding.**

The swelling value 50—55 (q = 1.45 — 1.50) appears really to be a defined critical value. The influence of the orientation upon this critical value has not yet been investigated.

The degree of swelling of cotton fibres is at about q = 1.38 (swelling value 45). Thus, although artificial fibres almost attain the degree of swelling of cotton in the minimum swelling, their sorption is by no means reduced correspondingly. Their isotherms of sorption are only a little below those of the unsteamed objects [28]. Hence steaming barely changes the percentage of "amorphous" components. In the main, the facts go to show that steaming only slightly increases the "water-resistant junction points".

As was stated before, the extent of swelling in water in its last phase is not determined by the percentage of amorphous components, but obviously by entirely different factors. One of them is probably the reversion of the chains of the amorphous components to more plausible configurations, which drying forced them to abandon. This process certainly would be seriously hampered by even a few additional junction points.
The fact that there is virtually no more heat effect in this last phase of swelling supports this view. (Cf. what was said respecting this matter on page 192).

4.2. Other Swelling Media

It is evident that higher degrees of swelling may again be attained by using swelling media able to dissolve more junction points than is water. An example may be found in a publication by *P. H. Hermans* and *A. J. de Leeuw* [29]. An isotropic, air-dry filament swelled in water to q = 2.15. After being treated with 2 n. sodium hydroxide, the filament reached 4.77 degree

[27] It is clear from other, unpublished, experiments that there is a certain optimum water content of the fibre at which the experiment is most successful.
[28] *P. H. Hermans:* Contribution to the Physics of Cellulose Fibres, Amsterdam—New York, 1946.
[29] *P. H. Hermans* and *A. J. de Leeuw:* Kolloid-Z. 82, (1938) 58.

of swelling and, after the caustic soda had been washed out with water, its degree of swelling was 2.85.

E. Hubert, A. Matthes and *K. Weisbrod*[30] have given examples of a like nature. As they used orientated objects, however, the effects they found are interwoven with those of swelling retraction (for which see § 5).

The same investigators reported the interesting fact that the degree of swelling of freshly spun rayon is reduced by sodium hydroxide of lower concentrations. This phenomenon still awaits an explanation.

4.3 The Influence of Deformation

Interesting things happen when isotropic model filaments, whose degree of swelling has been lowered by steaming, are extended in their re-swollen state. With these, too, the curve representing the volume in dependence upon the degree of extension has, in the main, the same shape as that given in Fig. 176 for the *R* state. It shows, however, that the stretched filaments swell up much more after intermediate drying than before they were extended, and the more so in proportion as they have been further extended. The reduction in swelling capacity brought about by steaming is for the most part wiped out after extension above 100 per cent. Filaments such as these swell up more by 25 per cent. than before they have been elongated.

This corroborates the view already propounded that *a proportion of the junction points are mechanically dissolved during extension in the R state,* while it also supports the assumption that the reduced swelling capacity brought about by steaming is to be ascribed to an increase in the number of junction points. These additional junction points formed in the already folded-up net appear to be the first to be destroyed when deformation is applied.

§ 5. SWELLING RETRACTION

P. H. Hermans and *A. J. de Leeuw*[31] apply the term *"swelling retraction"* to that phenomenon by which cellulose filaments, when allowed to swell up in a freely relaxed state after they have been elongated, undergo spontaneous recovery, which partially nullifies the imparted elongation. It was briefly discussed in Part II, Chap. VI § 4.3 (p. 291) and even there it was said to be a common occurrence. It always takes place when a fibre orientated by extension in some or other state of swelling is raised to a higher degree of swelling than it possessed at the end of the extension. For instance, *X* filaments extended in a 2 n. ammonium sulphate solution exhibit retraction when laid in a more dilute salt solution — say 0.5 n. sodium sulphate solution. They then become shorter and thicker.

Filaments extended in the *F* or *R* state retract when placed in 1 n. caustic solution, those extended in the *D* state when allowed to swell in water, and so on.

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[30] *E. Hubert, A. Matthes* and *K. Weisbrod:* Kolloid-Z. 98, (1941) 193.
[31] *P. H. Hermans* and *A. J. de Leeuw:* Kolloid-Z. 81, (1937) 300.

P. H. Hermans[32] has shown that this retraction is a *partial reversal of the* deformation. All the properties depending on the degree of extension, such as degree of swelling, anisotropy of swelling and birefringence, are regressive in exact proportion to the shortening of the fibre. Hence a retracted fibre is indistinguishable from one of the same degree of extension which has been extended only. Fig. 184 shows how the volumes of directly extended X filaments and of those retracted after swelling in 0.5 n. sodium sulphate solution and then again replaced in the original ammonium sulphate solution, fall on the same curve as a function of their elongation v (with reference to the isotropic state). Thus the reduction in volume which took place during extension is nullified upon retraction in proportion to the shortening of the fibre. Exactly the same applies to the anisotropy of swelling and the birefringence, as was demonstrated in the publication above referred to.

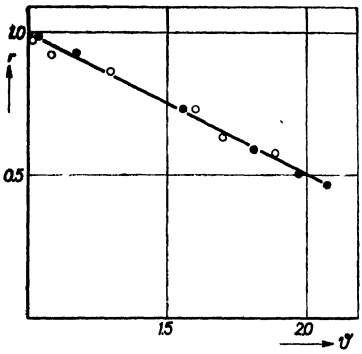


Fig. 184. Relation r of the degree of swelling of elongated (●) and retracted (o) X filaments, respectively, to the degree of swelling in the unextended state, as a function of the extension (degree of elongation).

Retraction also takes place if filaments extended in the swollen state are first dried and afterwards re-swollen, if and when the subsequent swelling is pursued to higher figures than that at which the extension took place. Fig. 185 provides an example. Here the filaments were elongated in the F state, then dried and briefly re-swollen in 2 n. sodium hydroxide. Once again, the birefringence of the retracted objects, plotted against the degree of extension v_t [33], lies on the same curve as that of the birefringence of the filaments extended merely. In this example the retraction was particularly marked, which will be apparent from the numerical data of Table XLVII, corresponding to Fig. 185. As a rule, the further the objects are allowed to swell, the greater will the retraction be.

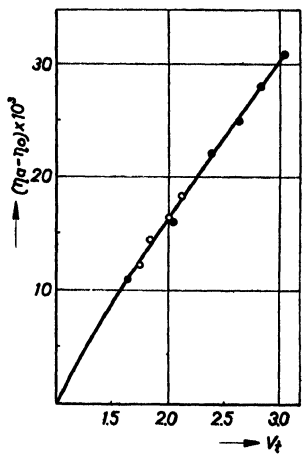


Fig. 185. Birefringence in the air-dry state of F filaments elongated at $q = 6.8$ as a function of the degree of elongation vt, before (●) and after (o) retraction in 2 n. NaOH with interposed drying. (The points of retraction were determined for the four highest degrees of elongation).

[32] *P. H. Hermans:* Cellulosechemie 19, (1942) 117.
[33] For this cf. p. 439.

TABLE XLVII

Degree of Extension and Birefringence before and after Retraction for the Four Farthest Extended Filaments of Fig. 185

Before retraction		After retraction	
vt	$(n_a - n_o) \times 10^3$	vt	$(n_a - n_o) \times 10^3$
2.40	22.2	1.66	12.3
2.65	24.9	1.84	14.6
2.85	27.9	2.02	16.5
3.06	30.8	2.13	18.4

Examples are cited in the publication referred to above of the birefringence of X filaments being reduced from 0.024 to 0.001 and from 0.040 to 0.005 as the result of allowing them to swell very much indeed; so that the filaments had become almost isotropic. (It must be admitted that recovery was not quite complete even in these extreme cases).

Exactly similar phenomena of retraction have also been observed in nitrocellulose filaments and have been quantitatively measured [34]. These facts point to the *reversibility, in principle, of the process of deformation,* which, provided the degrees of swelling and the retractions be not excessive, is quantitatively demonstrable in all its manifestations.

The following explanation is suggested. The network gel frame assumes different configurations under the stress of deformation. When tension is relaxed, there is only partial elastic recovery, owing to new junction points formed between the chain molecules which impede recovery. The position of these new junction points with reference to the spectrum of possible cohesions naturally depends upon the degree of swelling at which the extension took place. Only if the extended object is subsequently immersed in a medium possessing greater swelling capacity can these new junction points be partially dissolved, this proportion depending upon the swelling power of the new medium. The recovery then also proceeds proportionally.

There is good reason to explain the recovery tendency in similar terms to those used to describe the elasticity of rubber-like substances. Deformation alters the configuration of the chains in the amorphous components, which is no longer the same as the most probable one in the isotropic state. If not prevented by the newly formed junction points, the chains tend to reassume their original configurations and, as a result, the configuration of the whole net frame shows a strong bias towards the original.

The recovery of cellulose upon retraction after swelling is comparable to that of rubber or poly-styrene stretched in the cold, when heated (further details in Chap. XV). Here newly formed junction points are dissolved by raising the temperature; in the former case by swelling. In both instances cohesion is weakened. *R. Houwink* [35] labelled the former

[34] *H. R. Kruyt, D. Vermaas* and *P. H. Hermans:* Kolloid-Z 99, (1942) 244, 251; 100, (1942) 111.

[35] *R. Houwink:* Physikalische Eigenschaften und Feinbau von Natur — und Kunstharzen, Leipzig 1934, p. 133 ff.

phenomenon "thermorecovery". To distinguish the recovery brought about by certain external interferences from that occurring spontaneously with time (such as elastic after-effects and relaxations), the author selected the term "retraction" and, therefore, "thermoretraction" is perhaps a preferable term.

Fig. 184 affords another example of the close relationship between deformation and degree of swelling in swollen objects, which provides a strong argument in favour of the network structure of the gel frame. The phenomena of retraction give us weighty clues to the character of the mechanism of recovery, generally, and also, therefore, to that of deformation. If, as was formerly assumed, true flow (macroflow) were to take place in the latter through, let us say, "micels" gliding past each other, this reversibility of the deformation would be incomprehensible. This "memory" of previous states, which is again manifested, and the urge to revert to them, points to mere microflow and, at the same time, *to the necessity of stressing the conceptions of macromolecular structure, or molecular mechanism in the theory of deformation.*

It should be added that the shortening of rayon filaments when swelling in sodium hydroxide, which *W. Weltzien*[36] investigated and has since used for practical tests ("swelling analysis"), is a retraction after swelling. In the spinning of rayon, deformation takes place at high degrees of swelling; therefore, the finished fibre does not retract when swollen in water. If, however, swelling is forcibly increased by the use of sodium hydroxide as the swelling medium, a portion of the junction point spectrum established during spinning is ultimately dissolved and a typical retraction follows.

The shrinking of rayon filaments stretched in the air-dry state when swollen in water is likewise a form of retraction following swelling (cf. Fig. 109). For a more comprehensive treatment of shrinkage phenomena in rayon, see Chapter XVII, p. 506.

[36] *W. Weltzien*, Melliands Textilber., 7, (1926) 338; compare also *O. Faust* and *K. Litmann*, Cellulosechemie, 7, (1926) 166.

CHAPTER IX

ON THE CHOICE OF A RATIONAL STANDARD OF ELONGATION FOR THE DEFORMATION OF SWOLLEN OBJECTS

§ 1. INTRODUCTORY REMARKS

Before we proceed to deal with the phenomena of orientation and the mechanism of deformation, it is necessary that we should have clearly in our minds exactly what we mean by *degree of extension.* In the case of swollen objects, this is less simple than it might seem at first sight, and its importance in this sphere of research is coming increasingly to the foreground.

In the preceding chapters we have already come across three different ways of defining the degree of extension and these we shall now consider more closely.

§ 2. SWELLING IN RELATION TO THE STANDARD OF ELONGATION

The most obvious standard of elongation is the "relative extension" v, i.e., the relation between the length of the stretched and the original filament. Sometimes the value $\gamma = v-1$ is used, which we might term the "specific extension".

Let us concentrate on degrees of extension referred to the isotropic state as the initial state. If l_1 is the length of the isotropic filament, l_2 the length to which the filament is stretched and l_3 the length of the filament after its release, then by v_2 and v_3 we can express the degrees of extension of the filament before and after release, viz.,

$$v_2 = l_2/l_1 \qquad v_3 = l_3/l_1 \qquad (9{\cdot}1)$$

The degree of extension is intended to denote the change in length resulting from deformation. Now if the elongation of swollen filaments at the same time involves a change in degree of swelling (which it usually does; see Chapter VIII, § 2), this must be taken into account; for, a change in degree of swelling itself also involves a change in the linear dimensions of a body. The relative extension, as defined above, is only a correct standard of elongation when the degree of swelling undergoes no change.

To obtain a correct standard of elongation *we must refer the initial and the final length to one and the same degree of swelling.* Let us consider an

isotropic filament of q_1 degree of swelling and of l_1 length which is elongated to a filament the degree of swelling of which is q_3 and the length l_3 (see Fig. 186, where the degree of swelling is plotted, against the length of the filament).

The common "experimental degree of elongation" is then denoted by $v_3 = l_3/l_1$. A more rational measure of elongation, however, is that by which the length l_3 of the elongated filament is compared with the length $(l_{iso})_3$ which the isotropic filament would have at the degree of swelling q_3. This length is, of course,

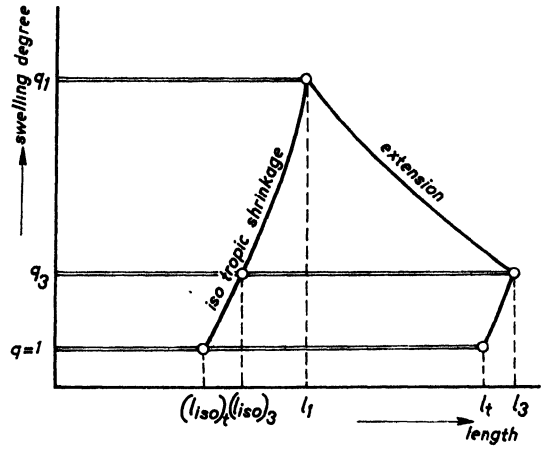


Fig. 186. Diagram showing the changes in length and degree of swelling as concomitants of elongation and drying.

$$(l_{iso})_3 = l_1 \, (q_3/q_1)^{\frac{1}{2}} \tag{9.2}$$

and the standard of elongation is therefore

$$v_a = l_3/(l_{iso})_3 = (q_1/q_3)^{\frac{1}{3}} \, l_3/l_1 \tag{9.3}$$

Taking equation (9.1) into account, this becomes:

$$v_a = \left(\frac{q_1}{q_3}\right)^{\frac{1}{3}} v_3 \tag{9.4}$$

This expression is identical to that occurring in the theory of affine deformation as stated by *B. Baule, O. Kratky* and *R. Treer* (see page 411). If the volume decreases during elongation, then $v_a > v_3$; if it increases, then $v_a < v_3$.

An alternative is, however, to set the standard of elongation against some other degree of swelling, the most obvious being $q = 1$ (the "dry" state). We then get an expression for the degree of elongation v_t as referred to the dry state, which was introduced in Chap. VIII, § 3.2 (page 439). This is found by allowing both the elongated and the isotropic filament to dry. The length of the former then becomes $l_t = l_3/\lambda$ (where λ is a factor indicating the longitudinal shrinkage of the anisotropic filament), while the length of the isotropic filament, of course, becomes $(l_{iso})_t = l_1 \cdot q_1^{-\frac{1}{3}}$. We then get $v_t = l_t/(l_{iso})_t$.

$$v_t = \frac{v_3}{\lambda} \cdot q_1^{\frac{1}{3}} \tag{9.5}$$

This degree of elongation has the advantage of always being easily deducible from the experiment (also see Fig. 182). If the volume decreases during elongation, v_t is always $> v_3$ and, if it increases (as with *R* filaments, see p. 432), v_t may become $< v_3$.

We learn the following from these elementary considerations: *If the degree of extension is to be rationally defined in experiments with swollen filaments, it is necessary to indicate to what degree of swelling it is referred.* This is an important point which has hitherto been too much neglected.

§ 3. ON THE CHOICE OF THE STANDARD OF ELONGATION

It cannot be said without qualification that either v_a or v_t is the most rational standard of elongation for the description of deformation. As will become plainer further on (Chapter XI), it depends upon the theoretical standpoint from which one views a given case and upon the phenomena one wishes to examine.

At a first glance, v_t would seem to be the obvious choice. This was suggested by *P. H. Hermans* and *P. Platzek* [1] and was regularly used later on. The following are the arguments in favour of it:

1. The gauge is the dry state of the fibre, which is also the normal state in practice.
2. The implication of this degree of elongation is a very real one. It defines the effect of an elongation v_s in the swollen state upon the length of the dry state (see Fig. 182).
3. This degree of elongation is not founded on any theory at all. Diagrammatically, v_t fits in well with the schematic theory of the network structure as explained in Chapter VIII, § 3.2, with reference to Fig. 181, as will be clearer still later on. On the other hand, the degree of elongation v_a is more at home in Kratky's theory of affine deformation, if applied to the movement of the crystallites (Chapter VII, § 2.6), a theory which claims v_a to be the rational standard.

As a rule the experiment will have to be the criterion by which to decide which standard of elongation is the most rational for the description of the phenomena. It will be evident that, for elongations in the non-swollen (dry) state, both v_a and v_t become identical with v_s.

§ 4. RELATION OF V_T TO THE ANISOTROPY OF SWELLING

By definition, the anisotropy of swelling $Q = B/L$, where B and L are the specific lateral and longitudinal swelling (see equation (6.9) on page 394). One can then write the degree of swelling q_s after elongation as follows:

$$q_s = (1 + L)\ (1 + B)^2 \qquad (9.6)$$

Thus the contraction factor $\lambda = 1 + L$, introduced § 2, is governed entirely by q_s and Q. (The mathematical relation, however, requires the solution of a cubic equation). If $Q > 1$ (which it is in practice, almost without exception) because $B > L$, λ will always be less than $q_s^{\frac{1}{3}}$, and it follows from (9.4) and (9.5) that then v_t will always be greater than v_a.

[1] *P. H. Hermans* and *P. Platzek*, Kolloid-Z. 87, (1939) 296.

§ 5. EXAMPLE OF THE PRACTICAL APPLICATION OF THE DEGREE OF EXTENSION V_T. THE PHENOMENON OF DRYING RETRACTION.

Consider a series of elongations (cf. p. 389) of *R* filaments of q_1 degree of swelling. After being elongated, they are measured and dried in the air. They are then re-swollen in boiling water and dried again[2]. During this shrinkage their anisotropy of swelling, *Q*, is measured.

With the aid of equation (9.6), the specific longitudinal shrinkage *L* of the filaments is calculated from the degree of swelling q_3 at the end of the elongation, and *Q*. The degree of extension *vt* can then likewise be computed in accordance with eq. (9.5).

Besides this, *vt* is also determined experimentally by measuring the length of the filament after the first drying process. The result of a series of such measurements is given in Table XLVIII.

TABLE XLVIII

For the Retraction during Drying of Elongated R Filaments; v_2 Degree of Extension in the Clamped State, v_3 Degree of Extension after Release

v_2	v_3	Q	q_1	q_3	vt found.	vt calculated.
1.25	1.09	1.04	2.25	2.45	1.04	1.06[5]
1.50	1.22	1.15[5]	2.33	2.75	1.13	1.18[5]
1.75	1.39	1.61	2.26	2.78	1.35	1.41
2.00	1.67	3.8	2.17	2.72	1.90	1.89
2.25	1.96	7.4	2.17	2.57	2.39	2.36

The table shows us that:

1. With low degrees of extension the calculated *vt* value is lower than v_3. The reason is that increase in volume takes place during the elongation (see § 2).
2. With low degrees of extension, moreover, the *vt* value found experimentally is a little below the calculated value. This is because of a remarkable additional shortening of the filaments during the first shrinkage after elongation, which we shall denote as *drying retraction*. A further manifestation of it is a wholly anomalous anisotropy of swelling during the first shrinkage, often becoming < 1. (Longitudinal shrinkage $>$ lateral shrinkage.)

Nitrocellulose filaments that had been swollen in alcohol have also clearly displayed this type of retraction during the first drying[3].

It has been discovered that this, as also the retraction after swelling, entails partial *retrogression of orientation*. This can mean but one thing, viz., that during drying some of the new junction points formed during elongation are torn apart again owing to the internal stresses set up — resistance of the frame to folding — as drying proceeds, especially in the last phases; and this leads to retraction.

This phenomenon is especially pronounced after elongation in the *R* state[4]. We have discussed it in some detail, as allowance has always to be made for it when applying exact orientation measurements to filaments elongated in the *R* state and then dried, and ascertaining the necessary correction by the above procedure. This correction relates to the value of v_3 to be inserted, which must be a little lower than the experimental value.

Elongated filaments that have been steamed, as suggested by *Hubert, Matthes* and *Weisbrod*, after the first drying, or swollen in boiling water (Chap. VIII, § 4), are stabilized and exhibit neither retraction nor anomalous anisotropy of swelling as they dry.

Drying retraction occasionally takes place in practice as well, when rayon shows a tendency to shrink; but it has hitherto never been recognised as such. (Cf. Chap. XVII).

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[2] This was empirically found to be the most reliable procedure. If swelling takes place in cold water, Q is distorted in the following swelling and shrinking processes by phenomena of retraction, which it is not after this operation. (See below.)

[3] *H. R. Kruyt, D. Vermaas* and *P. H. Hermans:* Kolloid-Z. 99, (1942) 244.

[4] It may also be observed after the elongation of filaments in the *X* or *F* state, but far less obtrusively.

§ 6. THE ELONGATIONS V_T AND V_A DEPENDENT ON THE EXPERIMENTAL ELONGATION V_3.

It is necessary that we take a glance at the experimental interrelationship between elongations vt and va dependent on the "experimental" elongation v_3. Our example will be experiments with model filaments produced from viscose No 5 (Tables XLII and XLIII) and elongated in three main states of swelling. Fig. 187 shows the experimentally determined course of vt in dependence upon elongation v_3 for extension in the *X*, *F* and *R* states. The dash-and-dot curve represents it for *R* filaments as found when drying retraction is not taken into account. Whereas vt for *X* and *F* filaments is always greater than v_3, we find $vt < v_3$ with *R* filaments for low degrees of elongation up to about $v_3 = 1.20$. (The dotted line represents $vt = v_3$). As previously stated, this is due to the initial increase in volume which takes place when *R* filaments are elongated. The figure, moreover, affords an impressive illustration of the fact that relatively moderate elongations in the swollen state lead to far higher degrees of extension as compared to the dry state. E.g., for $v_3 = 1.8$ the elongations as referred to the dry state amount to 2.22, 3.10 and 3.96 for *R*, *F* and *X* filaments respectively.

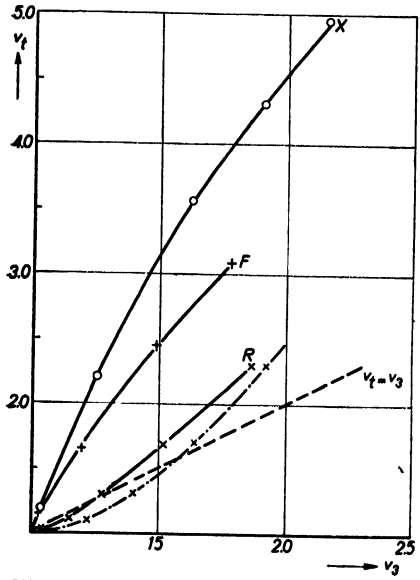


Fig. 187. Experimentally determined vl referred to the dry state as a function of the degree of elongation v_3 for X (o), F(+) and R(x) filaments. (The dash-and-dot line represents the curve for R filaments obtained when no correction is made for the drying retraction). Observed in isotropic model filaments spun from viscose No 7 (Tables XLII and XLIII).

In Fig. 188 we see the relation between v_3 and va for the same objects. The standards of elongation on the ordinates were chosen in the same way as in Fig. 187. Here too a correction must be made for the drying retraction of *R* filaments, as has been done in fig. 187. The dotted curve again represents $va = v_3$.

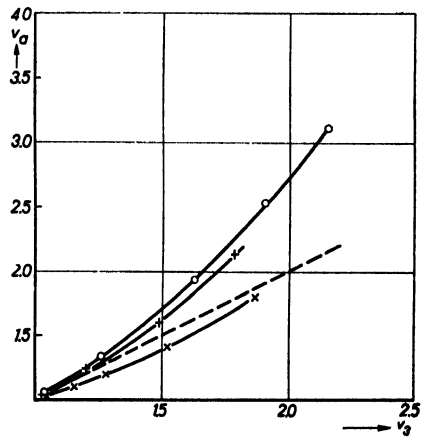


Fig. 188. The degree of elongation va as a function of the degree of elongation v_3 for X(o), F(+) and R(x) filaments.

We see, firstly, that the observations for *X* and *F* filaments fall practically on the same curve. As $v_a = v_3 \sqrt[3]{\frac{q_1}{q_3}}$, this means that the relative decrease in volume occurring in the elongation of *X* and *F* filaments follows an almost exactly identical course. We have already seen this in Chap. VIII § 2.1 (see Fig. 175).

Secondly, we see that the character of the curve for *R* filaments is different. As in this case elongation at first produces an increase in volume, $v_a < v_3$, the greatest difference is at the maximum volume and then subsides. As in this instance q_3 remains greater than q_1, the curve lies below the broken line up to the end point of the elongation[5].

[5] With *R* filaments produced by a different method, q_3 sometimes ultimately becomes smaller again than q_1 in which case the curve cuts the broken straight line.

We present the degrees of swelling and elongation for the example of viscose No 5 in Table XLIX.

TABLE XLIX

Degrees of Swelling and Elongation, also Anisotropy of Swelling Q for X, F and R Filaments of Viscose No 5 (Table XLII)

	q_1	q_3	v_2	v_3	va	vt	Q
X filaments	12.3	11.8	1.25	1.04	1.06	1.15	1.26
	13.0	10.8	1.50	1.25	1.33	2.12	4.2
	13.0	7.9s	1.75	1.62	1.91	3.47	11.5
	13.2	5.6s	2.00	1.89	2.50	4.24	19
	13.3	4.5	2.25	2.19	3.12	4.98	21.5
F filaments	6.1	5.8	1.25	1.03	1.04	1.12	1.21
	5.9s	5.4	1.50	1.20	1.24	1.63	2.55
	5.8	4.7	1.75	1.49	1.60	2.44	7.2
	5.8	3.5	2.00	1.79	2.09	3.08	12
R filaments	2.26	2.44	1.25	1.02	1.00	1.02	1.0
	2.34	2.73	1.50	1.14	1.08	1.09	1.0
	2.30	2.84	1.75	1.27	1.19	1.30	1.4s
	2.36	2.96	2.00	1.52	1.41	1.69	2.7
	2.20	2.52	2.25	1.83	1.75	2.24	4.9

(Degree of extension v_2 is the elongation before elastic recovery.)

It will be seen that, the lower the reference degree of swelling, the higher do the values become for the degrees of extension, with the exception of v_2. In other words: vt is always larger than va and, if $q_3 < q_1$, also va larger than v_3.

CHAPTER X

EXPERIMENTAL EVIDENCE RELATING TO THE ORIENTATION OF MODEL FILAMENTS UPON DEFORMATION

§ 1. INTRODUCTORY REMARKS

The researcher into the fundamentals of the elongation process must be equipped with experimental data showing how the orientation of isotropic filaments is affected by stretching. These data were collected in the author's laboratory from model filaments, all spun in the same way from the differently compounded viscoses mentioned in Chap. VIII, § 1.3 to § 1.5 (p. 427 to p. 430). It is upon this material that this and the two following chapters are based.

For the sake of clarity, we shall confine ourselves in this Chapter mainly to the discussion of the evidence obtained from experiments with model filaments from viscose of one particular composition, these being typical of all model filaments. In Chapter XI we shall deal with the attempts so far made to interpret this material in the terms of some theory, and in Chapter XII we shall consider what effect variation of the composition of the viscose has upon the phenomena.

Although the theoretical interpretation is still in its initial stages, the outlook holds potential promise of clarifying the subject. The author therefore deemed it to be in the interests of its further development that these matters should be dealt with in some detail here.

Our first point in this Chapter will be the orientation of the crystalline component, being that which can most reliably be derived from X-ray data. This method does not, however, provide us with particulars as to the orientation of the non-crystalline portion of the fibre and the evidence has therefore to be supplemented by information furnished by other physical methods of investigation.

§ 2. ORIENTATION OF THE CRYSTALLINE COMPONENT DERIVED FROM X-RAY DATA

2.1. Experimental Objects and Method

Isotropic model filaments are elongated progressively in the four main states of swelling (see p. 386) and are then examined by X-rays [1]. The first discovery is that *the drying of stretched filaments involves no, or only slight (at a first*

[1] Cf. Part II, Ch. V, § 2, p. 251.

approximation, negligible) change in orientation. This important fact, already hinted at by *O. Kratky* et al [2], was later confirmed by investigations made in the author's laboratory [3]. In Section 2.3 we shall consider what this implies. The swollen filaments, then, need only be examined in their dry state to discover how orientation is affected by elongation. The first experiments by *Kratky* and co-workers [2] to this end were discussed in Chap. VII, § 2. They were later repeated with greater precision by the present author and his collaborators, the material being filaments made from three of the viscoses (Nos. 2, 5 and 9) mentioned in Table XLIII (p. 429), the cellulose concentration being 4, 6 and 10% respectively. Both the distribution and the average orientation of the A_0 (101) and A_3 ($10\bar{1}$) planes of the crystallites, as also the overall orientation factor f_X were determined, allowance being made for the influence of the (021) planes. (cf. Part II, Chap. V, § 2, p. 256)[4].

2.2. *Experimental Results*

To provide an example, the whole gamut of degrees of elongation [5] and orientation factors is set out in Table L for the filaments produced from one of the three viscoses (No. 5). (For the connotation of the various degrees of elongation see Chapter IX, § 2). The orientation factor f_X for the crystalline substance was calculated from the average square sine of the angles of orientation of the A_0 and A_3 planes in conformity with the equation:

$$f_X = 1 - \frac{3}{2}\,(\overline{\sin^2 \alpha_0} + \overline{\sin^2 \alpha_3}).$$

(See formula (5.5) on p. 255). The table also includes the optical orientation factor f_O derived from measurements of the birefringence, and the f_O / f_X ratio, to which we shall revert presently [6].

TABLE L

Data for the Evaluation of the X-Ray Diagrams of Model Filaments Orientated by Elongation in Three Main States of Swelling

v_2 = Degree of elongation in the swollen state, clamped [7].
v_3 = Ditto after release and elastic recovery.
v_a = Equivalency degree of elongation according to *O. Kratky.*
v_t = Degree of elongation as referred to the dry state.
f_X = Orientation factor (X-ray).
f_O = Orientation factor (optical).

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[2] *P. H. Hermans, O. Kratky* and *R. Treer,* Kolloid-Z. 96, (1941) 30.
[3] *P. H. Hermans, J. J. Hermans, D. Vermaas* and *A. Weidinger,* J. Polymer Sci, 2, (1947) 632.
[4] *P. H. Hermans,* J. Polymer Sci. 1, (1946) 389; *P. H. Hermans, J. J. Hermans, D. Vermaas* and *A. Weidinger,* ibid 1 (1946) 393; 2, (1947) 632.
[5] v_3 and v_a are corrected for drying retraction.
[6] The filaments having been measured in the standard atmosphere, the value 0.043 was used for the birefringence with ideal orientation; f_O was obtained from the ratio between the observed double retraction $\wedge$ and 0.043 (vide Part II Chap. IV, § 6 5).
[7] As v_2 indicates, the isotropic filament was subjected on a yarn testing dynamometer to elongations increasing by 25 per cent. The residual elongation after elastic recovery was then v_3.

Experiment No	*Degrees of elongation*				*Magnitudes of orientation*				
	v_2	v_3	*va*	*vt*	$\overline{\sin^2\alpha_0}$	$\overline{\sin^2\alpha_3}$	*fx*	*fo*	*fo/fx*
X filaments									
1	1.25	1.04	1.06	1.15	0.294	0.331	0.06[3]	0.03[5]	0.55[5]
2	1.50	1.25	1.33	2.12	0.147	0.287	0.37	0.27[5]	0.74[5]
3 *	1.75	1.62	1.91	3.47	0.055	0.127	0.73	0.61	0.83[5]
4	2.00	1.89	2.50	4.24	0.024	0.049	0.89	0.79	0.89
5 *	2.25	2.19	3.12	4.98	0.019	0.030[5]	0.90	0.90[5]	1.00
F filaments									
6	1.25	1.03	1.04	1.12	0.283	0.327	0.08[5]	0.03[5]	0.41
7	1.50	1.20	1.24	1.63	0.210	0.291	0.25	0.18[5]	0.74
8 *	1.75	1.49	1.60	2.44	0.069	0.177	0.63	0.44	0.70
9	2.00	1.79	2.09	3.08	0.044	0.151	0.78[5]	0.64	0.81[5]
R filaments									
10	1.25	1.02	1.00	1.02	—	—	—	—	§
11	1.50	1.13	1.08	1.09	0.333	0.326	0.01[3]	0.03	§§
12	1.75	1.26	1.19	1.30	0.250	0.301	0.17[5]	0.09	0.54
13 *	2.00	1.54	1.41	1.69	0.129	0.256	0.42[5]	0.22[5]	0.53
14	2.25	1.8[illegible]	1.75	2.24	0.079	0.170	0.69	0.42	0.61

§ Nearly isotropic. §§ Uncertain owing to excessive relative errors.

The average orientation $\overline{sin^2 a_0}$ and $\overline{sin^2 a_3}$ for the paratropic lamellar and lateral planes are derived from the photometrically determined intensity curves. These have already been illustrated for experiments 3 and 5, marked with an asterisk, in Fig. 82, p. 257. By way of example, Fig. 189 shows the corresponding curves for experiment numbers 8 and 13. Both the numerical values for the mean square sines and the illustrations show that the orientation of the A_3 planes lags far behind that of the A_0 planes right up to the highest degrees of elongation, as reported for the first time by *O. Kratky* and co-workers and explained by them in the sense of the "affine deformation" theory (Chap. VII, § 2.6).

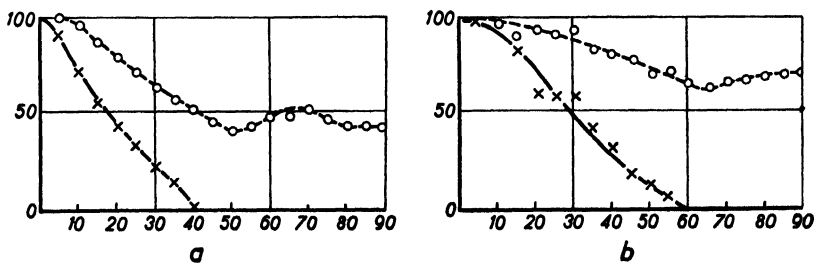


Fig. 189. Distribution of intensity along the *Debye - Scherrer* orbit of the A_0 interference of the lamellar plane (full curve) and of the superimposed A_3 and 021 interferences (broken curves). a) for F filaments at $v_3 = 1.49$ (experiment No 8, Table L). b) for R filaments at $v_3 = 1.54$ (experiment No 13, Table L).

W. A. Sisson described the quicker orientation of the A_0 planes as "minor orientation tendency" which, with cellulose objects, almost invariably occurs side by side with the "major orientation tendency", i.e., the orientation of the crystallite axes. The intensity curves reproduced in Figs. 82 and 189 for A_3 include the interference 021, the maximum of which is at 60° and which is seen as separated from A_3 in the case of Fig. 82a only. The 021 interference has been deducted from the $\overline{sin^2 a_3}$ values given in Table L.

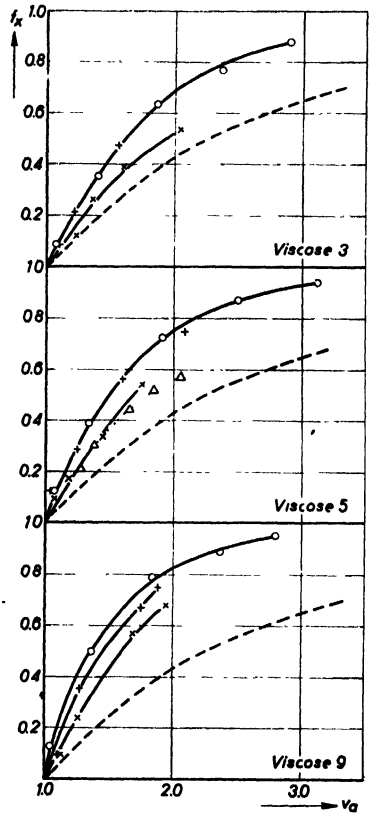


Fig. 190. Orientation factor f_x of crystallites plotted against the elongation v_a for model filaments spun from three different viscoses with cellulose concentration increasing from 3 to 9. Dotted curve corresponds to the theory of affine deformation.

It will be seen from column f_x in Table I, that xanthate filaments attain to the highest orientation when elongated (f_x = 0.90). The maximum values for F and R filaments are f_x = 0.78[5] and 0.69.

We get the same general picture with the filaments from viscoses 2 and 9.

The values of f_x are plotted against the degree of elongation v_a for all three viscoses in Fig. 190[8].

2.3. *Comparison with the Theory of Affine Deformation*

According to *Kratky's* theory of affine deformation, assuming that the crystallites are simply carried along with the amorphous matrix in which they are embedded (see Ch. VII § 2.6, p. 410), all the f_x values, when plotted against v_a should fall on one single curve, since in this theory v_a is an "equivalent degree of elongation" (cf. p. 411).

We see in Fig. 190 that neither the curves for X, F and R filaments from one and the same viscose, nor the curves representing the different viscoses fulfil this condition. We see, too, that in all instances orientation proceeds more rapidly than the theory requires (compare the theoretical curves). The result is the same, of course, if we compare the experimental and theoretical curves for the course of $\overline{sin^2 a_0}$ and $\overline{sin^2 a_3}$, i.e., the average angles of orientation of the lamellar and of the side planes 101 and $10\bar{1}$ (see Fig. 191).

[8] The plotted values of f_x are corrected ones (taking into consideration the general relation between f_x and f_0 referred to in the next Section.)

It is the $10\bar{1}$ plane that deviates most; this, according to the theory, should lag still further behind the lamellar plane. There is only a qualitative agreement in the general shape of the curves[9] and with the fact, predicted by the theory, that the orientation of the 101 planes runs ahead of that of the $10\bar{1}$ planes. Yet the latter fact need not necessarily be characteristic of an affine deformation, since there are other conceivable mechanisms in which the lamellar plane of the crystallites is a favoured point of attack.

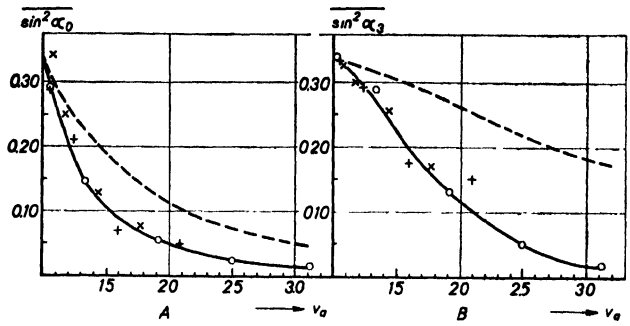


Fig. 191. Course of the average orientation of the lamellar plane A_0 (left) and of the lateral plane A_3 (right) as a function of the degree of elongation v_a. Full curves observed; broken curves according to the *Kratky* theory of affine deformation.

Another fact we gather from Fig. 190 is that the discrepancies between fact and theory are the more marked in proportion as the cellulose content of the viscose from which the filaments are produced is higher. That this is not due to the lower degree of swelling of the *X* and *F* filaments from the more concentrated viscoses, but is *an intrinsic property of the gel*, may be gathered from the fact that the same may be noted of re-swollen *(R)* filaments, the degree of swelling of which is virtually the same for all viscoses. Were the theory of affine deformation applicable, the method by which the filaments had been produced would make no difference to the result.

The conclusion we have to draw is that *this theory does not satisfactorily account for the process of orientation.* Thus the degree of elongation v_a does not fulfil the conditions of an "equivalent degree of elongation"; but neither do the degrees of elongation v_s and v_t of Table I.

We saw above that the orientation of the stretched filaments scarcely changes at all while they are drying. This goes to show that *the drying process is quite outside the category of an affine deformation.* Let us take Fig. 192 to illustrate this fact.

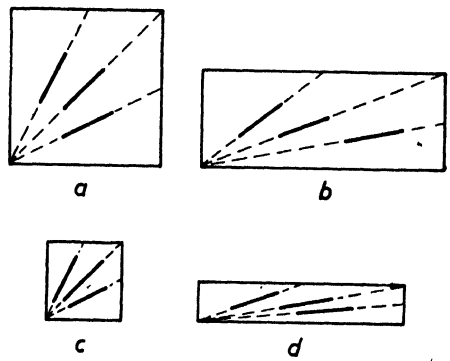


Fig. 192. Diagram showing change in length and orientation of molecular vectors upon elongation and drying.

[9] The ostensible conformity of the shape of the orientation *distribution* curves with the theory, found by *B. Baule, O. Kratky* and *R. Treer* (Z. physik. Chem. B 50, (1941) 255), likewise fails to hold good and merely resulted from the fact these authors omitted to allow for the (021) plane (vide *Hermans* et al, J. Polymer sci. 2 (1947) 632.)

This diagram shows how three rodlets of arbitrarily chosen orientation in an isotropic gel (a) would change their position upon elongation (b). If this stretched gel is then dried (d), its relative change in diameter is greater than in length (anisotropic shrinkage). If the principle of affine deformation also held good for the process of shrinking, this would imply a considerable increase in degree of orientation[10]. (No change in orientation would occur, of course, if the isotropic body (a) were dried isotropically (c).)

A further argument for rejecting the theory is that, although it takes into consideration the observed changes in volume, it is incapable of explaining, let alone predicting, their occurrence.

The failure of this theory is not surprising, when all is said. According to our picture of the structure of gels, the crystalline gel component does not consist of individual particles embedded in a matrix, it acts, rather, as a system of permanent junction points in a coherent network structure formed by both the crystalline and non-crystalline components. It would seem that the problem can only be solved by considering the properties of the network as a whole, focussing particular attention on the amorphous portion, which is predominant in quantity. This network will presumably have the character, more or less, of a molecular network consisting of interlinked chains kinked at random (vide Chap. XI).

§ 3. ORIENTATION ACCORDING TO OPTICAL MEASUREMENTS

As previously explained (Part II, Chap. IV, p. 229), the birefringence of a fibre is a measure of the average orientation of all monomeric glucose residues, or, to put it differently, for the average orientation of the crystalline and amorphous components.

The optical orientation factor f_O can be calculated from the measured double refraction. The measurements now to be referred to are always with reference to the bone-dry filaments, as the birefringence of swollen filaments is difficult to analyse. (This means, therefore, that the optical orientation factor is likewise assumed not to change during drying.)

Seeing that the orientation factor f_X deduced from the X-ray diffraction refers to the crystallites only, we need not be surprised if the optical orientation factor f_O has a different value. We have seen before that, in the case of artificial fibres, f_O is always less than f_X which we interpreted as meaning that the average orientation of the amorphous portion lags behind that of the crystalline component (p. 261).

We see in Table L (p. 454) that this always happens when model filaments are stretched. The f_O / f_X ratio is given in the last column and it will be observed that this is less than unity, but increases with the degree of elongation.

[10] It was shown by computation in the publication by *Hermans* et al, cited above, that this improvement in orientation ought to have been very clearly manifested in the experiments with model filaments.

P. H. Hermans et al[11], scrutinizing comprehensive material relating to all the model filaments produced from viscoses 3, 5 and 9, have discovered that a general, uniform relationship exists, within the margin of experimental error, between f_O and f_X which is represented by the curve in Fig. 193. This enables us also to obtain the orientation factor f_X of the crystallites from double refraction measurements, which is a welcome simplification, seeing that optical measurements are far easier to carry out than X-ray measurements. A useful aid is the empirical formula.

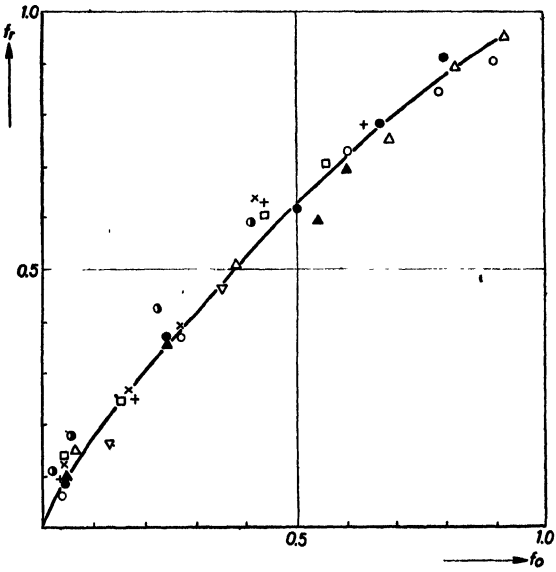


Fig. 193. Graph showing the general relation between the orientation factor f_X of the crystalline component and the optical orientation factor f_O derived from birefringence.

$$f_X = f_O + 0.125 \sin f_O \pi \qquad (10.1)$$

The inference from the foregoing would seem to be that the linkage between the movements of the amorphous and those of the crystalline components during deformation is always of the same nature, regardless of the degree of swelling of the gel and the technique employed for its production.

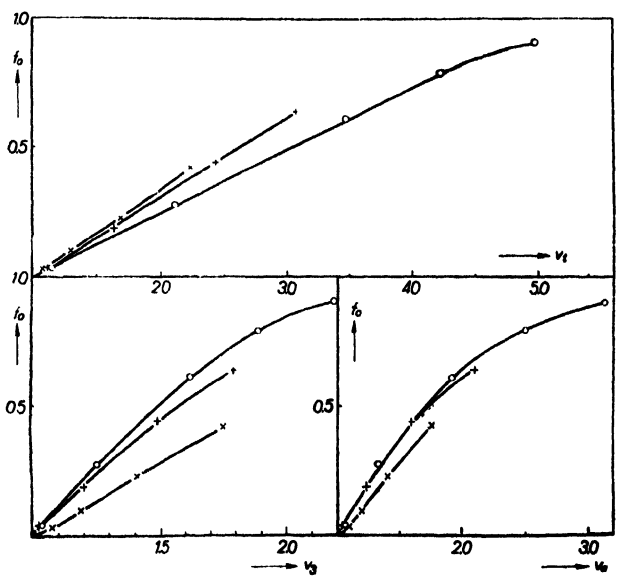


Fig. 194 The optical orientation factor f_O (Table L) as function of the degrees of elongation v_t, v_s and v_a. None of these degrees of elongation is an equivalent one.

Finally, the f_O values found for viscose 5 are plotted in Fig. 194 against the degrees of elongation v_s, v_a and v_t. We see that for a considerable part of the way the f_O — v_t curves are linear, deflecting a little at high degrees of extension only.

The same was found

[11] *P. H. Hermans, J. J. Hermans, D. Vermaas* and *A. Weidinger*, J. Polymer Sci. 2, (1947) 332.

with the filaments of all the other viscoses examined. The practical advantage this offers is that, up to $v_t \sim 4$, the curves can be represented by the equation.

$$f_o = c_o\ (v_t - 1) \qquad (10.2)$$

With the help of the slope constant c_o we can then see how the birefringence runs with the degree of elongation v_t.

Another fact which emerges from Fig. 194 is that none of the three degrees of elongation v, v_a or v_t is an "equivalent degree of elongation" for f_o. In the case of filaments from viscose of high cellulose concentration, however, the $f_o - v_t$ curves almost coincide for F and R filaments.

It should be stated in conclusion that, the higher the cellulose concentration of the viscose, the greater is the slope of the f_o curves (as also that of the f_r curves in Fig. 190). For further details the reader is referred to Chapter XII.

§ 4. ORIENTATION ACCORDING TO SWELLING ANISOTROPY

The theoretical grounds for the anisotropy of swelling having not yet been satisfactorily established, we must be careful to regard the determination of this quantity as affording merely adventitious information.

At one time, *P. H. Hermans* and *P. Platzek*[12] had found that v_t was an equivalent degree of elongation for the anisotropy of swelling of X, F and R filaments, but it was discovered later that the matter is not quite so simple as that; v_t is only an equivalent degree of elongation if the filaments have been spun from a viscose of high cellulose concentration and if the swelling anisotropy is measured during first drying, after elongation. The statement no longer holds good for filaments spun from more dilute viscoses.

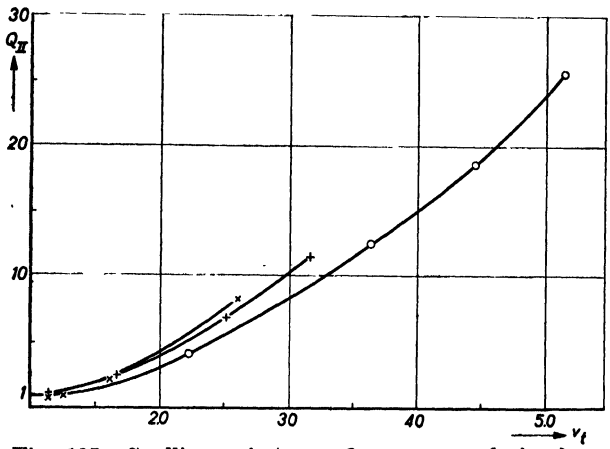


Fig. 195. Swelling anisotropy Q_{II} on second shrinkage as a function of vf for X (o), F (+) and R (x) filaments. This correlates qualitatively with the course of fo (Fig. 194).

The actual state of affairs becomes plainer if the swelling anisotropy Q_{II} is measured during the second drying after the filaments have been re-swollen in water. This is a better measure, because it lies on the linear part of Fig. 146 (see p. 394). The degree of swelling is then lower. The Q_{II}-v_t curves thus obtained for viscose No. 5 of Table XLIII (p. 429) are reproduced in Fig. 195. Comparing this with Fig. 194, we see that we now have qualitative

[12] *P. H. Hermans* and *P. Platzek*, Kolloid-Z. 87, (1939) 296.

correlation with the optical v_t curves. Seeing that both the swelling anisotropy and f_o will reflect, before all, the orientation of the amorphous component, this may be welcomed as a satisfactory result.

The course which the curves follow does not fall into line with formula (6.8) on page 394 and the mechanism of the swelling is without doubt entirely different from that then assumed.

It has been found empirically that the quantity $Q_{II}^{\frac{1}{2}} - 1$ runs linearly with v_t up to degrees of elongation of about 4 (Fig. 196). We can, therefore, write

$$Q_{II}^{\frac{1}{2}} - 1 = c_Q (v_t - 1) \qquad (10.3)$$

The course of these curves can, therefore, be represented with the help of the constant of direction c_Q.

This proves to apply to all filaments, irrespective of the composition of the viscose from which they are spun. At a first approximation, $c_Q = 2\, c_o$ and we thus get (see formula 10.2) the empirical equation

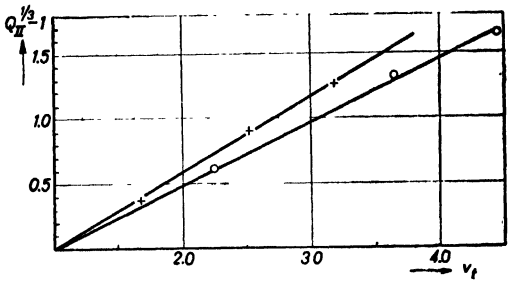


Fig. 196. Linear relation between $Q_{II}^{\frac{1}{2}} - 1$ and v_t for X (o), F (+) filaments. The constants of direction of the curves are 0.49 and 0.59 respectively.

$$Q_{II} = 1 + 2.0\, f_o \qquad (10.4)$$

which relates anisotropy of swelling to optical orientation factor[13].

We would add that Q_{II} may be regarded at a first approximation as being equal to the differential swelling anisotropy Q_{diff} of Chap. VI, § 2.

[13] The equation holds good only with *X* and *F* filaments. The determination of Q_{II} in *B* filaments is often disturbed by retraction.

CHAPTER XI

HYPOTHESES AS TO THE MECHANISM OF THE DEFORMATION OF CELLULOSE GELS

§ 1. INTRODUCTORY REMARKS

The experimental results reported in the preceding Chapter make it perfectly clear that all the theories hitherto propounded respecting deformation fail us. The evidence goes to show that the movement of the crystallites does not fit in with the theory of affine deformation, that there must be some interconnection between the movement of the crystallites and that of the amorphous substance and, finally, that orientation depends for its progress upon the composition of the viscose from which the gel is produced.

In the next Section we shall see that the molecular networks possess properties which could account for the phenomena observed in cellulose gels. We look upon the gel as a network of molecular chains kinked at random, in which the crystalline regions serve as junction points; that is to say, a structure resembling that presented in diagram in Fig. 165, while the junction points are conceived to be like those suggested by *Hermann* and *Gerngross* as represented in Fig. 16 (p. 30).

§ 2. DEFORMATION OF MOLECULAR NETWORK STRUCTURES

2.1. Kuhn and Grün's Theory Modified

It will be convenient first to consider a molecular network such as that upon which the theory of the deformation of rubber is also based nowadays. The deformation of this molecular network has been dealt with quantitatively by *Kuhn* and *Grün* (see Chap. VII § 3.3. α, page 421). As was explained on page 423, this theory amounts to the assumption of an affine deformation of the junction point pattern.

At a first view it might seem hazardous to transfer to cellulose gels hypotheses which rely on ideal elastic rubber-like substances, but several arguments may be advanced in extenuation. Firstly, we are concerned with swollen gels, the cohesive forces in the amorphous portion of which may be considered to be weak. Secondly, as long as the cellulose molecules are in solution, their configuration may be taken to be governed by *Kuhn's* statistics. Then, when coagulation takes place, they become locally interlinked by a process of partial

crystallization, the statistical shape of the chains in the amorphous portion being preserved, to a certain extent, at least.

Under the strain of deformation, the changes in the configuration of the chains will then, admittedly, not be governed by entropy factors only, but will also be to some extent subject to factors of energy. We may nevertheless venture upon comparison with rubber-like substances if we bear in mind that the latter factors will operate, spatially, in an entirely random fashion in accordance with the laws of chance, at all events at the beginning of the deformation.

Under such conditions the relation between deformation and orientation (as e.g. birefringence-strain curves) may remain very similar to that in rubber-like networks. The relations between deformation and stress, however, will change completely. In the following we shall therefore focus attention on the former.

The theory developed for this by *W. Kuhn* and *F. Grün*[1] was worked out for deformation with constant volume. As we are now interested in swollen gels, the volume of which does not remain constant, we shall have to adapt the theory accordingly. Furthermore, *Kuhn* and *Grün* assume that the degree of coiling of the chains is normal in the isotropic non-swollen state (i.e., that it corresponds in that state to random kinkiness as produced by the laws of chance). If the network then swells isotropically, the chains will be stretched and, therefore, they will uncoil to some extent (cf. Fig. 161, page 410).

Where isotropic gels produced from a solution by coagulation are concerned, *the network is formed in the swollen state;* hence in this case we shall have to assume "normal coiling" in the primary gel and not in the dry gel. During isotropic shrinkage the degree of coiling will then increase (cf. Fig. 161 p. 410) and the result is what may be termed supercoiling. (Changes in the configuration of the chains as the reverse of those taking place on stretching). We shall give the symbol q_0 to the swelling degree of the primary gel at which coiling is normal.

Now the theory propounded by *Kuhn* and *Grün*, modified to allow for changes in volume[2], shows that both the degree of swelling q_0 of the primary gel and the changes in volume during deformation have a bearing on the course of the orientation.

From equation (7.11) on page 423 it follows that, according to *Kuhn* and *Grün*, the optical anisotropy Δ at elongation v is

$$\Delta = k\ (v^2 - \frac{1}{v}) \qquad (11.1)$$

where k is a constant. The modified theory leads to the equivalent equation:

$$\Delta = k\ (\frac{q_i}{q_0})^{\frac{2}{3}}\ (v_f^2 - \frac{q_f}{v_f}\cdot\frac{1}{v_f}) \qquad (11.2)$$

[1] *W. Kuhn* and *F. Grün*, Kolloid-Z. 101, (1942) 248.

[2] *P. H. Hermans* and *D. Vermaas*, communicated at the *Gen. Discussion on Swelling and Shrinking*, held by the Faraday Soc., London 1946, and other unpublished work.

where k is the same constant, q_i the initial swelling degree of the isotropic gel, q_f the final swelling degree of the stretched gel and v_f the final relative elongation.

This equation is quite general and covers any change in shape of the gel, as, by way of example, the case of isotropic shrinkage. In this case the relative change in length is, of course, $v_f = (q_f / q_i)^{\frac{1}{3}}$. Substituting this in (11.2), one finds $\Delta = 0$; in other words, there is no change in orientation upon drying.

The equation (11.2) also shows that *the optical anisotropy at a given elongation v_f is always in inverse ratio to the 2/3 power of the primary swelling degree q_0* no matter at what degree of swelling q_i the elongation is carried out.

If, mentally, we replace the molecular chains by the vectors r which connect their initial and terminal points (see Fig. 168, p. 421), we can think of all these vectors as substituted by one mean vector with the mean angle of orientation (cf. p. 233). The diagram of Fig. 197 now shows how the size and direction of the mean vector change upon affine elongation of the swollen isotropic gel and while this is drying, both in the isotropic and in the elongated state[3]. (The corresponding changes in length of the macroscopic object are indicated by the symbol l in the figure).

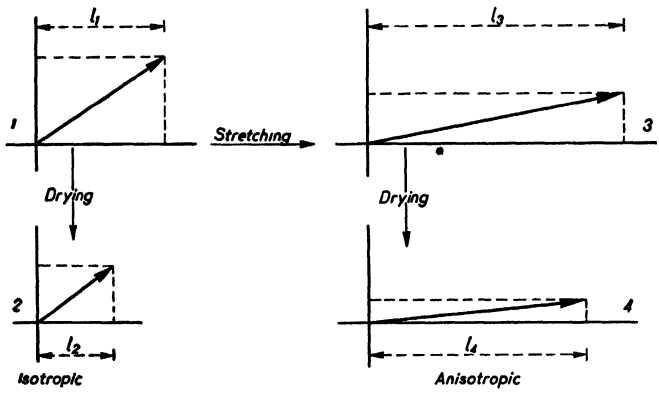


Fig. 197. Diagram of vectors representing states 1 to 4.

The applicability of equations (11.1) and (11.2) is subject to the following conditions:

1. The molecular chains must contain a large number of statistical chain elements.
2. Affine deformation of the net must actually take place.
3. The degrees of elongation must not be excessively high.

If there is any departure from these conditions, the anisotropy versus elongation curves are apt to change, but even then the swelling factors occurring in (11.2) may be expected to manifest themselves approximately as indicated by the formula. Indeed, the primary touchstone for the theory must be the effect of the changes in degree of swelling indicated by formula

[3] By means of this simplified notion of the "mean vector" (which allows to avoid lengthy mathematical considerations) it is even possible to derive formula (11.9) by elementary geometrical reasoning.

(11.2). It will also be necessary to watch carefully what happens at low degrees of elongation i.e., the initial slopes of the anisotropy curves.

2.2. The Various Degrees of Elongation in the Light of the Theory

The interrelationship of the various degrees of elongation discussed in Chapter IX now at once becomes clear from formula (11.2) for the case of affine deformation of a molecular network. For elongation v, with the volume constant, $q_i = q_f$ and we thus get

$$\Delta = k \left(\frac{q_i}{q_0}\right)^{\frac{2}{3}} (v^2 - v^{-1}) \qquad (11.3)$$

As shown on p. 423, we can, by approximation, use $3\gamma = 3\,(v-1)$ for small degrees of elongation, and thus obtain:

$$\Delta = 3kq_0^{-\frac{2}{3}} \cdot q_i^{\frac{2}{3}} (v-1) \qquad (11.4)$$

Comparison with equation (11.1) stated by *Kuhn* and *Grün* will show that *the orientation as a function of the degree of elongation v will proceed the more rapidly as q_i is larger*[4], this applying to all isotropic gels of q_i degree of swelling (which have been formed by isotropic swelling or shrinkage *from a given primary gel* of q_0 degree of swelling).

With model filaments, however, there is no such thing as elongation with the volume remaining constant. If the degree of swelling changes from q_i to q_f one uses (11.2). This equation may also be written thus:

$$\Delta = kq_0^{-\frac{2}{3}} \cdot q_f^{\frac{2}{3}} \left[\left(\frac{q_i}{q_f}\right)^{\frac{2}{3}} v_f^2 - \left(\frac{q_i}{q_f}\right)^{-\frac{1}{3}} v_f^{-1}\right]$$

and, because $v_a = v_f\,(\,q_i / q_f\,)^{\frac{1}{3}}$ (see Chap. IX, p. 448), this becomes:

$$\Delta = kq_0^{-\frac{2}{3}} \cdot q_f^{\frac{2}{3}} (v_a^2 - v_a^{-1}) \qquad (11.5)$$

Here we see that, when change of volume takes place, the degree of elongation v_a does the duty of the conventional degree of elongation v. For low degrees of extension we then get

$$\Delta = 3kq_0^{-\frac{2}{3}} \cdot q_f^{\frac{2}{3}} (v_a - 1) \qquad (11.6)$$

It will be observed that, with a given value q_0 of the primary gel, the value of Δ depends upon the degree of swelling q_f of the stretched filament.

Let us now consider the case of a swollen isotropic filament of q_1 degree of swelling and l_1 length which is first elongated to l_3 length and then dried, its length then becoming l_4 and its degree of swelling equal to 1 (see diagram in Fig. 197); then in the general formula (11.2) $v_f = l_1/l_4$ and further $q_i = q_1$, and $q_f = 1$. We then get

$$\Delta_t = kq_0^{-\frac{2}{3}} \cdot q_1^{\frac{2}{3}} \left(v_f^2 - \frac{1}{q_1 v_f}\right)$$

or, written differently:

$$\Delta = kq_0^{-\frac{2}{3}} \left[\left(q_1^{\frac{1}{3}} v_f\right)^2 - \left(q_1^{\frac{1}{3}} v_f\right)^{-1}\right] \qquad (11.7)$$

[4] This is always found in cellulose gels; cf. *P. H. Hermans*, Kolloid-Z. 98, (1942) 62 and Fig. 154, p. 405.

Thus the quantity $q_1^{\frac{1}{3}} v_f$ serves as the rational degree of elongation for the dry filament. Now this quantity is no more and no less than the degree of elongation v_t previously defined; for, in the process of stretching from 1 to 2 (see diagram in Fig. 197), the conventional degree of elongation v_3 is equal to l_3/l_1. While drying is going on from 3 to 4 there is some contraction, represented by $l_4 = l_3/\lambda$ (cf. page 448). We thus have

$$q_1^{\frac{1}{3}} \cdot v_f = q_1^{\frac{1}{3}} \cdot \frac{l_4}{l_1} = q_1^{\frac{1}{3}} \cdot \frac{l_3}{l_1} \cdot \frac{1}{\lambda} = q_1^{\frac{1}{3}} \cdot v_3 \cdot \frac{1}{\lambda} = v_t$$

(see formula (9.5) on page 448). Thus formula (11.7) becomes:

$$\Delta_t = k q_0^{-\frac{1}{3}} (v_t^2 - v_t^1) \qquad (11.8)$$

and, for small degrees of elongation,

$$\Delta_t = 3k q_0^{-\frac{1}{3}} (v_t - 1) \qquad (11.9)$$

Hence the theory indicates v_t as being the rational degree of elongation for the anisotropy measured in the dry filament, the condition being that the drying process shall likewise take place in conformity with the principle of the affine deformation of the network.

If we now think of anisotropic shrinkage of a similar type to that which occurs when cellulose elongated in the swollen state is dried (shrinkage in diameter > shrinkage in length), we shall at once recognize the advantage of the network theory. In the case of rigid rodlets participating in affine deformation (see p. 410), there must then be considerable improvement in orientation during drying. We learn from the experiment that the orientation does not change. According to the network theory, this is quite possible. We see in the diagram of Fig. 197 that, although the *orientation* of the molecular vectors *increases* while the anisotropic filament is drying (which would lead to increased anisotropy), the vectors at the same time become *shorter*, as the result of which their intrinsic anisotropy diminishes. The two factors may cancel each other out and *this can only be if the shrinkage in diameter exceeds the shrinkage in length.* In the next Section this will be verified quantitatively.

We have seen in the foregoing that the degrees of elongation v_a and v_t introduced in Chapter IX, have a well-defined meaning in the network theory. It follows from formula (11.9) that, for small degrees of elongation, the anisotropy Δ must be a linear function of v_t since q_0 is a constant for a given gel. The slope of the curve representing Δ as a function of the degree of elongation must be in inverse ratio to $q_0^{\frac{1}{3}}$. *Hence, the higher the degree of swelling of the primary gel, the more slowly will orientation proceed with stretching* (provided equal values of k be assumed).

Formulas (11.4) and (11.5) show that this also applies to degrees of elongation other than v_t. Qualitatively, this is in line with the behaviour of cellulose gels (see Fig. 190 and Chap. XII).

Formula (11.4) exhibits exactly the reverse for isotropic gels of different degrees of swelling q_i all *obtained from the same primary gel,* viz., quicker

orientation in proportion to the higher degree of swelling q_i. This, too, is always observed in cellulose gels.

It is clear, then, that the theory of a molecular network is capable of accounting for several traits of cellulose gels which are otherwise inexplicable.

2.3. *Drying and Anisotropy of Swelling*

In the preceding Section we saw that the network theory admits shrinkage and swelling of an anisotropic filament without entailing changes in its anisotropy, provided the consequent changes in length l and diameter b conform to certain conditions. We may most conveniently start from formula (11.9) on our path of enquiry. We now express the degrees of swelling and degrees of elongation as length and diameter of the filament. Let the indices 1, 3 and 4 be used for the isotropic, the elongated and the dry state respectively (see Fig. 197). Then:

$$v_3 = l_3/l_1 \qquad q_i = \tfrac{1}{4}\pi l_1 b_1^2$$
$$v_4 = l_4/l_1 \qquad q_f = \tfrac{1}{4}\pi l_3 b_3^2$$

Substituting this in formula (11.2), we get for the anisotropy Δ_3 in the stretched swollen state 3:

$$\Delta_3 = k\,(l_3^2/l_1^2 - b_3^2/b_1^2) \qquad (11.10)$$

where k' is a constant.

The condition that the anisotropy shall not change while the filament is drying is:

$$l_3^2/l_1^2 - b_3^2/b_1^2 = l_4^2/l_1^2 - b_4^2/b_1^2 \qquad (11.11)$$

The values found by experiment, calculated from length and diameter measurements of model filaments spun from viscose 5 (Table XLIII) are tabulated in Table LI.

TABLE LI

Change in orientation of the amorphous material on drying

Experiment No	$\frac{l_3^2}{l_1^2} - \frac{b_3^2}{b_1^2}$	$\frac{l_4^2}{l_1^2} - \frac{b_4^2}{b_1^2}$	$\frac{\Delta_4}{\Delta_3}$
X filaments			
1	0.16	0.14	0.87
2	0.92	0.89	0.97
3	2.26	2.26	1.00
4	3.39	3.36	0.99
5	4.52	4.40	0.97
F filaments			
6	0.12	0.11	0.92
7	0.68	0.61	0.90
8	1.66	1.62	0.98
9	2.83	2.69	0.95
B filaments			
11	0.52	0.20	0.38
12	1.09	0.57	0.52
13	1.86	1.34	0.72
14	3.14	2.79	0.89

If formula (11.11) were to work out, the figures in the last column should have the value 1. We see that they have, approximately, for X and F filaments, but for R filaments they are appreciably lower, which implies distinct *diminution in orientation during drying.* Now this is exactly what does happen in first drying of R filaments (and *only* of R filaments) This is the *drying retraction* which we fully discussed in Chapter IX § 5 (page 450). Hence this phenomenon is predicted by the network theory on the ground of the changes in dimensions observed during drying.

When the R filaments are re-swollen and again dried, their behaviour reverts to the normal.

2.4. *The Absolute Slope of the Orientation Curves in Relation to the Length of the Chains between the Junction Points*

All the equations in § 2.2 producing the rate of orientation as a function of elongation contain the constant k. According to what appears on page 422 this has the value

$$k = \frac{3}{5}\,(\alpha_1 - \alpha_2)\,\frac{r_o^2}{NA^2} \qquad (11.12)$$

where $(\alpha_1 - \alpha_2)$ = anisotropy of the statistical chain element, r_0 the average length of the molecular vectors in the net, A the length of a chain element and N the average number of chain elements between the junction points. It follows from (11.12) that the slope of the anisotropy curves will be slighter in proportion as N is larger, and vice versa. *Kuhn* and *Grün's* theory assumes that N is large. Upon closer analysis we now soon learn that this cannot be so in cellulose; indeed, it is already implied by the limited extensibility of the isotropic filaments. For the maximum extensibility v_{max} of a molecular network the theory gives roughly:

$$v_{max} = \sqrt{\frac{3\pi}{2}}\,N = 2.17\,\sqrt{N} \qquad (11.13)$$

If we remember that the highest v_a values observed are about 3, we shall find that approximately $N = 2$. We get a figure of the same order of magnitude if we estimate N on the basis of formula (7.11) put forward by *Kuhn* and *Grün* (p. 423), or of formula (7.17) suggested by *J. J. Hermans* (p. 425).

The formulas worked out by *Kuhn* and *Grün* do not apply to such small values of N and we shall have to be prepared for some appreciable quantitative discrepancies.

This is where new calculations made by *J. J. Hermans*[5] may help us. These calculations were based on a mathematical approach suggested by *H. A.*

[5] *J. J. Hermans,* J. Colloid Sci. 1, (1946) 235; Paper presented at the *Gen. Discussion on Swelling and Shrinking,* Trans. Faraday Soc. 42B, (1946) 160.

Kramers for adapting the theory to chains with a small number of statistical chain elements, to which we shall be reverting in greater detail in § 3. Fig. 198 shows how, according to this theory, the orientation factor as a function the degree of elongation must run for various values of N. The curves are

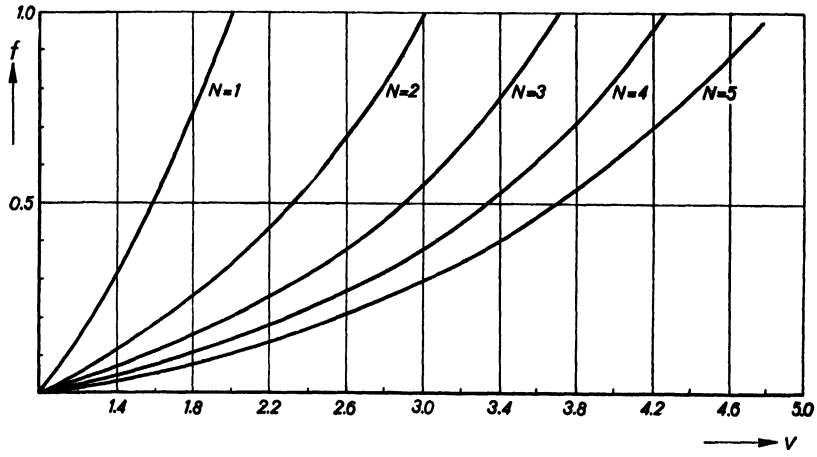


Fig. 198. The short chain theory. The orientation factor f as a function of the degree of elongation for various values of N (number of statistical chain elements per chain).

convex with respect to the axis of elongation, the curve for the case of $N = 1$ being identical to the curve for the "second borderline case" propounded by *Kratky* (Chap. VII § 2.3, page 401, and Figs. 152 and 154, curve II). In fine, the obvious conclusion to be drawn is that between the junction points in cellulose gels there are chains with only a few statistical chain elements of the order of $N = 1$ to 3.

It should be added that the above rough outline of the comparison between the theory and the experiment is based on the optical orientation factor, which is not likely to be very different from that of the amorphous substance. We have already seen that the orientation of the crystallites (represented by the X-ray orientation factor f_x) progresses more quickly still. For crystallites behaving as stated by *Kratky's* theory of affine deformation, the slope constant of the f_x—v_a curve should amount to 0.60 at the start. Actually it is about twice that figure.

We have also seen (Fig. 193) that the movement of the crystallites appears to be coupled to that of the amorphous component in obedience to a fixed rule. No quantitative theory has, however, been propounded yet to account for this fact.

§ 3. THE THEORY EVOLVED BY J. J. HERMANS FOR SHORT CHAINS

3.1. Fundamental Features of the Theory

We found in the preceding section that the coils in the molecular network must be far shorter than they are assumed to be in *Kuhn* and *Grüns'* theory. Naturally, therefore, this theory accounts for only some of the features of the experimental evidence at all satisfactorily and fails in other respects.

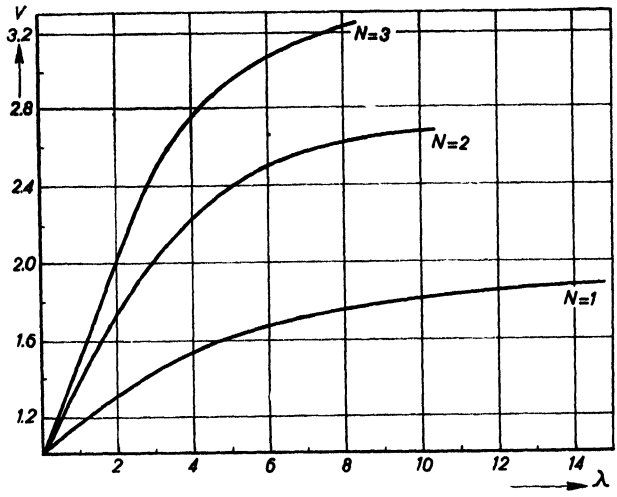


Fig. 199. Short chain theory. Relation between degree of elongation v and the parameter λ as a function of N.

J. J. Hermans[6] has since tried to work out a theory for short chains on the basis of similar physical principles. This theory opens up several new points of view and has proved particularly succesful in explaining the stress-strain diagrams (Chap. XIII). In this Section, therefore, it will only be briefly dealt with.

Instead of relying on the principle of affine deformation, *J. J. Hermans* asks what change in configuration the coiled chains (again considered as free and independent from each other) will undergo if a force p is brought to bear upon every end-point of the chain. This force corresponds to a potential energy $-px$, where x represents the projection of the molecule upon the direction of elongation. The number of chains with a given x then becomes $e^{px/kT} = e.^{\lambda x}$ In the calculation, the quantity λ represents a parameter; it is proportional to the total tension P, calculated with reference to the original cross-section of the object. If α_0 and α are the angles formed by a chain element with the X axis before and after elongation, then the degree of elongation becomes.

$$v = \frac{\overline{\cos \alpha}}{\overline{\cos \alpha_0}} \qquad (11.14)$$

where the bars indicate that mean values were determined by integration over all molecules. The theory produces a different curve v as a function of λ for every number of N of chain elements per chain (see Fig. 199). The orientation factor fam can be calculated by determining $\overline{\sin^2 \alpha}$:

$$fam = 1 - \frac{3}{2} \overline{\sin^2 \alpha} \qquad (11.15)$$

and is then again found as a function of λ. By eliminating λ one obtains the orientation factor f_{am} in dependence upon v. This has already been shown in Fig. 198.

The curve for $N = 1$ virtually coincides with that for *Kratky's* second borderline case (page 399)[7]. Now, however, the so-called retrograde chain elements have also been taken into account.

3.2. *Changes in Volume during Elongation*

The short chain theory does not take into account the change in degree of swelling during elongation, but itself dictates the course the volume shall follow. It is therefore at once conceived as applying to swollen objects. The change in volume follows from $\overline{\sin \alpha}$, which is determined by the average

6 *J. J. Hermans:* J. Colloid Sci. 1, (1946) 235. Trans. Faraday Soc. 42B, (1946) 160.

7 This is comprehensible, since it had already been pointed out in the footnote on page 401 that, with variation of the function of rotation, always the same curve is obtained for the rodlets.

lateral size of the object. Fig. 200 represents the result, including the observations for X, F and R filaments. It will be seen that, according to the theory, steady decrease in volume takes place only with values of $N \backsim 1$ and that higher values of N lead to a maximum curve. This initial increase in volume is a typical effect which is inevitable with the elongation of molecular chains kinked at random; but it will be manifested only in swollen objects elongated in the swelling liquid. (In the case of dry rubber, the cohesion between the molecules prevents the volume from increasing, as need hardly be said.) In Fig. 200 the volume curves for X and F filaments are located more or less as the theory for $N = 1$ requires, at all events qualitatively.

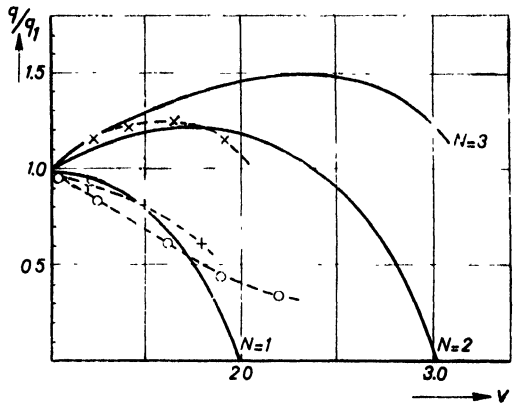


Fig. 200. Relative change in volume resulting from elongation according to the short chain theory for various values of N (full curves). Experimental curves for X, F and R filaments are broken.

Contrary to our former practice, we shall not now concern ourselves with the effect of changes in volume, as such, upon orientation. We have seen that even drying does not affect orientation (§ 5.2) and now, therefore, simply assume that the still remaining deviations of the actual volume curves from the theoretical have no influence upon the orientation.

3.3. *The Course of Orientation*

To compare the course of the orientation with the theory, then, let us simply plot f_{am} for X, F and R filaments against the experimental degree of elongation v_3[8]. The result is given in Fig. 201.

It will be observed that the curves virtually coincide with those for $N = 1$, $N = 1.15$ and $N = 2.2$[9].

It may, at first, seem strange that the value of N increases from X to R filaments, but on further reflection we shall recognize, precisely in this fact, a link with former views.

The theory considers molecules of normal degree of coiling in the initial state for $r^2 = NA^2$ (see formula 7.6 on page 421). If our former views were correct, there should, however, be an enhancement of this normal degree of coiling from X to R filaments in isotropic shrinkage (cf. Fig. 161). It can

[8] The orientation factor f_{am} is that of the amorphous substance, which is derived from f_o and f_x by a method of approximation not described here, but not differing much from f_o. It makes scarcely any difference to the general conclusions if the argument is based on f_o.

[9] Since we have to do with mean values, the figures for N need not be whole numbers.

now be demonstrated that a molecule more than normally coiled behaves like a normal molecule with a larger number of chain elements N''. If the degrees of swelling are q' and q'', we get the equation [10].

$$\frac{N''}{N'} = \left(\frac{q'}{q''}\right)^{\frac{2}{3}} \qquad (11.16)$$

This formula does not hold good exactly until $N > 3$. For smaller values of N, corrections have to be allowed for, which we shall not enter into here, but which have been made in Table LII (p. 473). Thus the lower the initial degree of swelling in the isotropic state, the higher will N be found to be.

If we plot f_{am} against v_t instead of against v_3 (Fig. 202), it means that we are referring the process of elongation to the dry state, where the dry isotropic state is the initial condition, in which case the

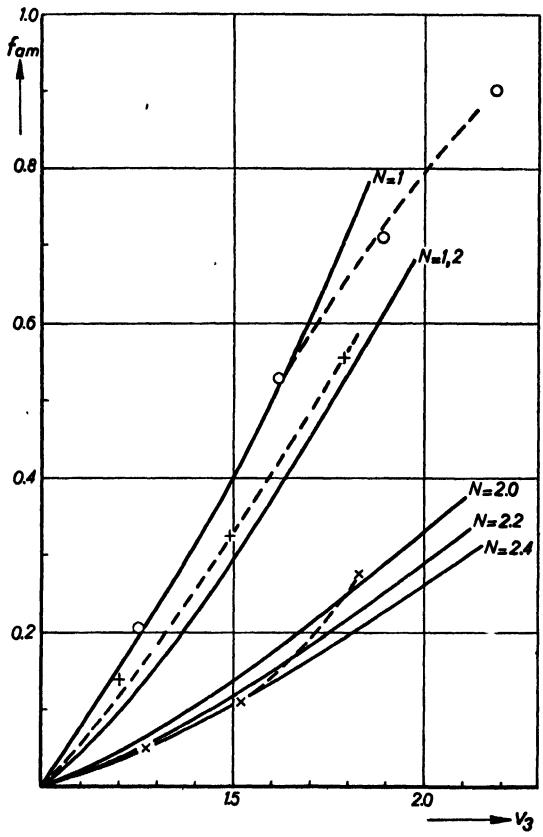


Fig. 201.
Orientation factor f_{am} as a function of the degree of elongation v. Dot and broken curves represent actual observations; full curves according to the short chain theory for the given values of N.

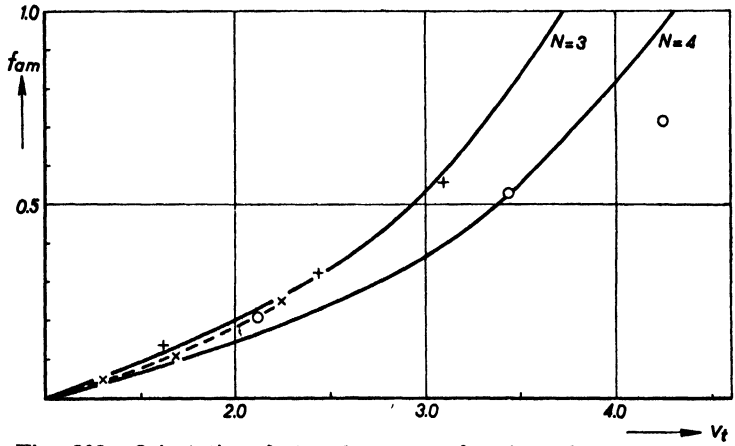


Fig. 202. Orientation factor f_{am} as a function of the degree of elongation v_t, as compared with Fig. 201.

[10] This also follows both from *J. J. Hermans'* and *Kuhn's* theory. In the former case discrepancies occur only with very small degrees of elongation.

N values should be higher than in Fig. 201. It is evident from the theoretical curves in Fig. 202 that this is so. We thus find for X, F and R filaments the values 4, 3.0 and 3.3 for N. It now remains to be seen whether formula (11.16) also holds good quantitatively when allowing for the necessary corrections for $N < 3$. That it does approximately will be clear from Table LII.

TABLE LII

Values of N according to Fig. 202 Compared to the Values Calculated in conformity with Formula (11.16)

	q'	q''	N'	N'' (calcd)	N'' (Fig. 202)
X filaments	13.1	1	1	4.6	4
F filaments	5.9	1	1.15	3.5	3.0
R filaments	2.35	1	2.2	3.7	3.3

In the transition from xanthate to cellulose, the chemical character of the chains changes somewhat, involving minor modifications of A and N and, therefore, of the degree of kinkiness (page 480). This may possibly account for the generally less satisfactory correlation in the case of X filaments (cf. Fig. 202).

The departures from the theory, which are seen to occur at high degrees of elongation in Figs. 201 and 202, argue for, rather than against it, since a theory of that kind would scarcely be likely to continue to apply towards the end of the theoretical extensibility (for which also see § 5).

The experimental material is now seen from another angle. We now link up, on the one hand with *Kratky's* theory of the second borderline case and, on the other, with the formerly developed, newer views respecting a network structure of molecular chains kinked at random. As has already been said, we shall reconsider the theory of short chains when we discuss mechanical properties.

§ 4. THE PERCENTAGE OF CRYSTALLINE SUBSTANCE

P. H. Hermans[11] states that an upper limit for the percentage of crystalline substance is to be inferred from optical and X-ray evidence respecting orientation as presented in Table L. The double refraction Δ of the filaments may be considered as the sum of the birefr. of the crystalline substance (Δ_{cr}) and that of the amorphous substance (Δ_{am}):

$$\Delta = x\ \Delta_{cr} + (1-x)\ \Delta_{am} \qquad (11.17)$$

where x is the fraction of crystalline substance. If we describe the biref. in ideal orientation (Part II Chap. IV § 6.5) as Δ^*, we may also write it thus:

$$f_o\ \Delta^* = x f_x\ \Delta^*_{cr} + (1-x) f_{am}\ \Delta^*_{am} \qquad (11.18)$$

Here f_x and f_{am} represent the orientation factors of the crystalline and amorphous substances respectively, which will not be the same as a rule. The value to be inserted for Δ^* will likewise be different for each component. It follows from formula (11.18) that:

$$\frac{f_o}{f_x} = x\ \frac{\Delta^*_{cr}}{\Delta^*} + (1-x)\ \frac{f_{am}}{f_x}\ \frac{\Delta^*_{am}}{\Delta^*} \qquad (11.19)$$

[11] Rec. trav. chim. 63, (1944) 12; *Contribution to the Physics of Cellulose fibres*, Amsterdam, New York 1946, p. 182.

As the last term of the second member is always positive, it follows that:

$$\frac{f_o}{f_x} > x\frac{\Delta^*_{cr}}{\Delta^*} \qquad (11.20)$$

It is evident from Table L that f_o diminishes more rapidly than f_x with decreasing orientation; hence, towards the isotropic state the quantity f_{am}/f_x acquires a small value. If we now calculate the f_o/f_x ratio (see last column of Table L) as a function of the degree of extension and extrapolate to the isotropic state, we find the upper limit of x to be

$$x_{max} = \lim_{(f=o)} \frac{f_o}{f_x}\frac{\Delta^*}{\Delta^*_{cr}} + \delta \qquad (11.21)$$

where δ is a very small number and Δ^*/Δ^*_{cr} a figure not far from 1. This extrapolation has been carried out in Fig. 203 with v_3 as the measure of elongation. It shows that x_{max} must be somewhere between 0.4 and 0.5. We cannot tell how much lower than this the actual value of x is, because we do not exactly know Δ^*/Δ^*_{cr} nor δ. The result is, however, compatible with other estimations which have produced values of x about 0.40 for regenerated cellulose. (Part II Chap. VII).

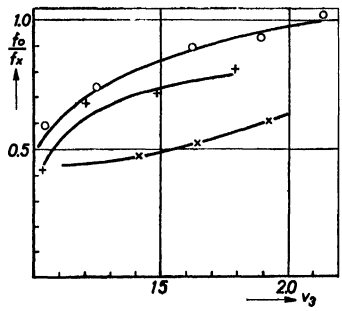


Fig. 203. The f_o/f_x ratio plotted against v_3. According to formula (11.21), extrapolation to $v_3 = 1$ produces 0.4 — 0.5 for x_{max}

§ 5. CONCLUDING REMARKS

If we consider the resultant of the theoretical views expounding the mechanism of deformation which we have dealt with in this Chapter, we shall have to admit that, despite some progress and fresh insight, we are still far from having a wholly satisfying interpretation of the experimental evidence. First and foremost, we lack a theory as to the movement of the crystalline substance and, as far as the amorphous substance is concerned, the results are still in many respects somewhat uncertain.

It can, however, hardly be doubted that fundamentally the picture of the deformation of a molecular network, as presented, reflects the truth. Thus in this mechanism of deformation the centre of gravity is the *amorphous* component of the fibres and here some substantial progress has been made.

With the help of *Kuhn* and *Grün's* theory, extended to swollen objects (p. 463), we are able to account quantitatively and fairly satisfactorily for the effect of the degree of swelling in the isotropic state and for the shrinkage occurring while the fibre is drying. This also throws fresh light on the significance of the various degrees of elongation. It also enables us to understand to some extent the general character of the orientation curves. We shall see in the next Chapter that the same theory helps us to account for the

influence of the degree of swelling of the primary gel upon the course of the orientation in filaments spun from viscoses differently compounded.

The theory was, however, propounded for long chains, whereas the parts of the chains between the junction points in cellulose are without doubt relatively short. For this reason alone it is evident that many details must necessarily be at variance.

The theory of the short chains (§ 3) attempts a better adaptation. Though the experimental data are somewhat differently interpreted, a physically similar picture is the starting point. It will be seen in Chapter XIII that this theory also helps to explain the connection between tensile stress and anisotropy. (This is where *Kuhn* and *Grün's* extended theory fails us entirely).

Discrepancies, especially at the higher degrees of elongation, do occur between fact and theory, but this is scarcely surprising when we recall that our unit of structure in these theories is *Kuhn's* statistical chain element. It is assumed that at maximum extension the vectors of these chain elements are fully orientated in the direction of the fibre axis. But in reality this will not be the end of extensibility, for the statistically kinked chain elements, themselves, can still be stretched. No theory so far takes into account this deformation of the chain elements themselves, which nevertheless undoubtedly plays some part even in moderate elongations.

Then, the theory is based on the proposition of a uniform network structure in which all the chains between the junction points are of equal length. In reality the network structure is likely to be made up of elements of unequal length.

These are merely examples to illustrate possible reasons for quantitative discrepancies.

CHAPTER XII

HOW THE MANUFACTURING CONDITIONS OF THE PRIMARY GEL AFFECT ORIENTATION

§ 1. INTRODUCTORY REMARKS

The effect of the conditions of manufacture upon the *degree of swelling of the primary gel* was dealt with in Chapter VIII. There we found that, with no change in the concentration of the coagulating bath, the alkali content and the xanthate ratio (ripeness) of the viscose made little difference, if any, whereas the cellulose concentration and the degree of polymerization of the cellulose had a perceptible effect. We shall now consider the influence of these factors upon the *deformation* of the gels. Within the limits defined in Chap. VIII, § 1.4, the alkali content of the viscose has proved to be of no account in this respect as well[1]. We shall discuss the effect of the other factors with reference to experiments made with filaments spun from viscoses composed as already described in Chap. VIII, for which see Tables XLII and XLIII (pages 428 and 429) as also Table XLIII (p. 429). The numbers of the viscoses introduced there will be cited for reference.

§ 2. EFFECT OF THE CELLULOSE CONCENTRATION AND THE DEGREE OF POLYMERIZATION OF THE CELLULOSE

2.1. *The General Effect of the Degree of Swelling of the Primary Gel*

Table XLIII (p. 428) demonstrates how the degree of swelling $(q_1)_X$ of the primary xanthate gel varies with the cellulose concentration and with the average degree of polymerization *(DP)*. This primary degree of swelling appears to be closely related to the properties of the network gel frame, for the orientation is decidedly governed by it.

It was pointed out repeatedly in the two preceding Chapters that when isotropic filaments of varying degrees of swelling q_1 — all spun from the same primary gel — were elongated, it was found that the higher q_1 is, the more rapidly does orientation take place.

The effect of the *primary* degree of swelling $(q_1)_X$ is exactly the reverse, when orientation is *quicker* according as $(q_1)_X$ is *lower*. Provided the xanthate ratio in the primary gel be constant, it seems to be immaterial

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[1] This holds for model filaments spun in ammonium sulphate and does not of course, imply that the alkali content does not affect the technical spinning process.

whether a given $(q_1)_X$ be obtained by varying the cellulose concentration or the *DP*, as will be illustrated in the next Section. It is the same with isotropic re-swollen filaments (*R* filaments), the degree of swelling of which is known always to be approximately the same, no matter what the degree of swelling of the primary gel from which they are spun. *The gel again distinctly "remembers" the state in which it was immediately after gelatination.*

The theory of a molecular network kinked at random, which was propounded in the preceding Chapter, gives mathematical expression to this faculty of remembering by the factor $q_0^{\frac{2}{3}}$, which appears in all deformation formulas and to which attention was drawn on p. 463 (cf. equations (11.2) to (11.9)). We are going to show in the present Chapter that this factor actually does enable us to describe with fair accuracy the observed influence of the degree of swelling of the primary gel.

Our yardstick for the orientation will again be the optical orientation factor and the anisotropy of swelling.

2.2. *Birefringence*

The birefringence of elongated *X*, *F* and *R* filaments was measured in the dry state for all the viscoses from No. 1 to No. 9 of Table XLIII [1a]. The curves representing the optical orientation factor as a function of the degree of elongation are similar for every viscose composition to that shown in Fig. 194, only the slopes being different. This is illustrated by Fig. 204, where the birefringence $n_{/\!/} - n_\perp$ (in the dry state) of a given degree of extension v_t is plotted against the primary degree of swelling $(q_1)_X$ [2]. Apart from some minor variations, with $v_t = 2.4$, the birefr. is higher according as $(q_1)_X$ is lower [3]. The quantitative relationships will be dealt with in Section 2.4.

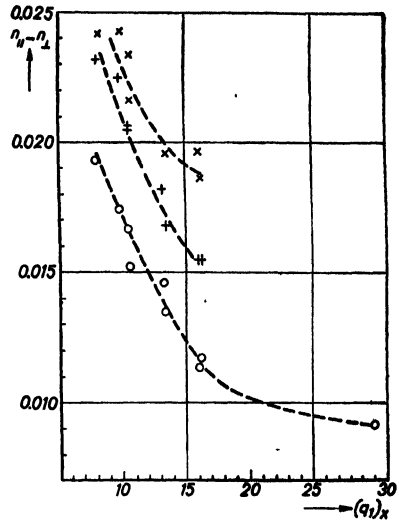


Fig. 204.
Birefringence $n_{/\!/} - n_\perp$ at degree of elongation $vt = 2.40$ for X (o), F (+) and R (x) filaments spun from the nine viscoses of Table XLIII as a function of the primary degree of swelling $(q_1)_X$ of the xanthate.

2.3. *Anisotropy of Swelling*

A picture (which we do not reproduce here) entirely similar to Fig. 204 results from consideration of the anisotropy of swelling Q_{II} of the same

[1a] *P. H. Hermans* and *D. Vermaas;* Trans. Faraday Soc., 42B, (1946) 155. General Discussion on Swelling and Shrinking, held in 1946.
[2] Much the same is found on considering $n_{/\!/} - n_\perp$ for a given v_a or v_s. Thus the phenomenon does not depend upon the choice of degree of extension.
[3] Cf. *P. H. Hermans;* Kolloid Z. 98, (1942) 69.

objects[4]. The constants of direction of the curves which correspond to formula (10.3) on p. 461 are given below in Table LIV.

2.4. *Quantitative Relations*

It was stated in Section 2.1 that the factor $q_0^{-\frac{2}{3}}$ appears in all equations for the anisotropy of the network of kinked molecules subjected to affine deformation (Chap. XI § 2.2), where q_0 stands for the primary degree of swelling and is, therefore, identical to $(q_1)x$ It will at once be recognized that the facts presented in the preceding Sections are qualitatively in accord with this. It now appears that the slope constants c_0 of the optical f_0 — v_t curves actually are, according to formula (11.9) (p. 466), almost exactly in inverse ratio to $(q_1)_x^{\frac{2}{3}}$, as should be the case if they merely stood for the orientation of the amorphous components and the theory held good. This is shown by Table LIII.

TABLE LIII

Constants of Slope c_0 of the f_0 — v_t curves for X, F and R Filaments Spun from Nine Different Viscoses; also their Values Multiplied by $(q_1)_x^{\frac{2}{3}}$

Viscose No	$(q_1)_X$	$(c_0)_X$	$(c_0)_F$	$(c_0)_R$
1	29.0	0.16[5]	0.14	0.21
3	16.1	0.21	0.26[5]	—
2	16.0	0.21	0.27	—
6	13.4	0.23	0.28	0.32[5]
5	13.1	0.24	0.30	0.34
4	10.5	0.26	0.33[5]	0.40
8	10.5	0.28	0.33[5]	0.36
7	9.7[5]	0.29	0.36	0.38[5]
9	8.1	0.33	0.38	0.41[5]

Viscose No	$(q_1)_X$	$(c_0)_X \cdot (q_1)_X^{\frac{2}{3}}$	$(c_0)_F \cdot (q_1)_X^{\frac{2}{3}}$	$(c_0)_R \cdot (q_1)_X^{\frac{2}{3}}$
1	29.0	(1.5)	(1.3)	(2.0)
3	16.1	1.34	1.71	—
2	16.0	1.31	1.72	—
6	13.4	1.32	1.58	1.85
5	13.1	1.35	1.69	1.90
4	10.5	1.34	1.61	1.94
8	10.5	1.23	1.62	1.71
7	9.7[5]	1.33	1.65	1.83
9	8.1	1.32	1.53	1.67
	Mean value*)	1.32	1.64	1.82

* Owing to the poor extensibility of the filaments from viscose No 1, the c values for viscose No 1 are not very exact and the bracketed figures have not been included in the averaging.

[4] For the meaning of Q_{II}, see Chapter X, § 4.

It will be observed that multiplication of the constants of direction by $(q_1)_x^{\frac{1}{3}}$ produces an almost constant number.

The data referring to the anisotropy of swelling, though less accurate, exhibit the same regularity. This may best be demonstrated by starting from the linear relations shown in Fig. 196 for viscose No. 5 (where $Q_{||}^{\frac{1}{3}} - 1$) is plotted against v_t). It was already stated there (p. 461) that there is always an approximately consistent relationship between the constants of direction c_O and c_Q (cf. equation 10.4). Table LIV reaffirms this on the basis of more extensive material from nine viscoses.

TABLE LIV

Slope Constants of the Curves for the Anisotropy of Swelling and their Relation to those of the Optical Curves

Viscose No	$(c_Q)_X$	$(c_Q)_F$	$(c_Q)_X \quad (c_o)_X$	$(c_Q)_F \quad (c_o)_F$
1	0.30	0.40	(1.8)	(2.9)
3	0.43	0.54	2.0	2.0
2	0.44	0.54	2.1	2.0
6	0.54	0.60	2.3	2.1
5	0.49	0.59	2.0	2.0
4	0.58	0.64	2.0	1.9
8	0.67	0.78	2.4	2.3
7	0.64	0.78	2.2	2.2
9	0.73	0.79	2.2	2.1
		Mean value	2.15	2.08

The approximately consistent proportion between c_O and c_Q signifies that c_Q stands in the same relation to $(q_1)_X$ as does c_O

Hence, it is seen that the comparability of cellulose gels, in their behaviour, with a molecular network originates in the fact that the product of the slope constant of the anisotropy curves with $(q_1)_x^{\frac{1}{3}}$ produces a constant. This cannot, however, be regarded as a quantitative corroboration of the theory, since the results are not accurate enough to justify that inference. A power somewhat different from $\frac{1}{3}$ would yield the same result. Nor is quantitative agreement to be expected, since the theory considers long chains, whereas we have to do with short chains. *The general trend of the phenomena is, however, in excellent conformity with the molecular network picture.*

§ 3. EFFECT OF THE XANTHATE RATIO

We saw on page 431 (Table XLIV) that the xanthate ratio of the cellulose has no perceptible effect upon the degree of swelling of the primary gel. Nevertheless, the slope of the orientation curves depends upon the former.

This is demonstrated by Table LV, which gives the slope constants $(c_0)_X$ and $(c_0)_F$ for the X and F filaments of three viscoses of diminishing XR, also the values of their products with $q_0^{\frac{2}{3}}$. It also shows what values are obtained by extrapolation to $XR = 1$ (i.e. for a theoretical primary gel produced from pure cellulose).

TABLE LV

Slope Constants of the $f_0 - v_t$ Curves for Viscoses of the same Primary Degree of Swelling $(q_1)_X$ but of Different Xanthate Ratios XR, as also their Products with $(q_1)_x^{\frac{2}{3}}$

XR	$(q_1)_X$	$(c_0)_X$	$(c_0)_F$	$(c_0)_X \cdot (q_1)_X^{\frac{2}{3}}$	$(c_0)_F \cdot (q_1)_X^{\frac{2}{3}}$
51	9.8	0.31	0.37	1.43	1.70
36	10.1	0.30	0.37	1.47	1.74
12	9.9	0.26	0.25	1.20	1.15
0 (extrapol.)	(10)	0.24	0.24[5]	1.09	1.14

It will be seen that the riper the viscose from which the filaments are spun, the more slowly is orientation accomplished. It looks as though, below $XR = 30$, the slope constants $(c_0)_X$ and $(c_0)_F$ begin to approach each other until, at $XR = 0$, they are equal.

It is difficult to say what this diminishing of the slope constants as the ripeness of the viscose increases signifies. When the xanthate decomposes, the chemical nature of the chains undergoes some change. As a result, the quantities $(\alpha_1 - \alpha_2)$, A and N in formula (11.12) may change, which is tantamount to a change in the "rigidity" of the chains (the number of monomeric residues per statistical chain element). This, in turn, means a change in their degree of coiling. At present, however, we have no means of analysing the phenomenon more precisely.

CHAPTER XIII

MECHANICAL PROPERTIES OF MODEL FILAMENTS

§ 1. INTRODUCTORY REMARKS

The general mechanical properties of cellulose fibres were discussed at length in Part II, Chap. VI. The reader is referred in particular to § 3 and § 4 of that Chapter in connection with what now follows.

When taking stress-strain diagrams it is evident that increased orientation is always involved and that this will depend upon the degree of swelling at which elongation takes place. The conditions are easiest to follow in the elongation of isotropic model filaments, and here there are two questions which interest us primarily, *viz.*,

a) What is the relation between tensile stress and orientation?

b) How can the highest breaking strengths be attained?

It is only into the theoretical aspects of the former question that we may hope to gain some insight. Breaking strength, as we saw in the Sections referred to, is governed by factors so complicated in their physics that the second point will have to be dealt with almost entirely on an empirical basis and will in any event be very intractable to quantitative handling.

Seeing that the amorphous components of the fibre are quantitatively predominant and that they are responsible for the coherence of the fibre, we may well expect the mechanical properties to depend primarily on what goes on in the amorphous substance.

§ 2. STRESS-STRAIN DIAGRAMS OF ISOTROPIC FILAMENTS

2.1. *Experimental Evidence*

The general type of the stress-strain curves of isotropic *X*, *F*, *R* and *D* filaments produced from the same primary gel was shown in Fig. 108 (p. 287) where v_2 was used as the measure of elongation (for which see p. 389). The curious crossing of the curves need cause no surprise if it be borne in mind that v_2 is not the rational degree of elongation for these objects. If the tensile stress is plotted against v_a or v_t the curves no longer cross, but lie in the order of the degrees of swelling[1]. Fig. 205 illustrates the latter case. The

[1] *P. H. Hermans;* Kolloid-Z. 89 (1939) 344.

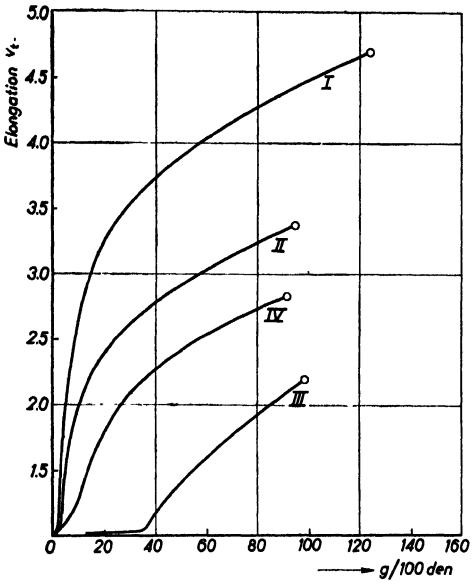


Fig. 205. Stress-strain curves of isotropic model filaments with v_t as the standard of elongation (cf. Fig. 108). I. Xanthate filaments. II. Fresh cellulose filaments. III. Air-dry filaments. IV. Re-swollen filaments (stress referred to the yarn number at the time). o = breaking point.

picture remains substantially the same, if the composition of the viscose from which the filaments are spun is varied.

If we consider that, with a given v_t the orientation of the amorphous substance is virtually the same for all the filaments (and also that the orientation of the whole fibre substance will then vary little from it), we shall see that the tensile stress for a given orientation is greater according as the degree of swelling is lower.

It should be remembered, however, that orientation only begins behind the yield point of the curves. For proper comparison the curves should be adjusted so that all have their yield points in the origin of the system of coordinates [2].

If this is done, the rule just mentioned remains valid. We shall be discussing the theoretical meaning of the tensile stress at the yield point in Chapter XV.

2.2. *Theoretical Aspects*

In working out their theories respecting the deformation of rubber-like substances (see Chap. VII, § 3.3. γ, p. 420), *Kuhn* and *Grün* and also *J. J. Hermans* calculated the stress needed to elongate the object. They then found that stress and birefringence, and therefore also stress and orientation factor, are always proportional, meaning the stress referred to the cross-section in hand at the time.

Although these theories are based on the mechanism peculiar to the elasticity of rubber, it will be interesting, for reasons previously discussed (Chap. XI, § 2.1, p. 462 and in the light of present experience) to see whether they can be made to apply to our objects. (Cf. Chap. XV). A tentative enquiry shows at once that not even approximate proportionality exists between the tension and orientation factor in swollen cellulose filaments. As Table LVI shows, the K/f_{am} ratio rises sharply with increasing extension [3]. The tension increases

[2] This means to say that the yield value is always subtracted from the measured tensile stresses.

[3] The Table was computed as follows: the degree of elongation is v_2, i.e., the condition before elastic recovery (see p. 389); v_a was calculated from the change in volume, using equation (9.4) on p. 448, and the corresponding value of f_{am} derived from f_o (according to Chap. XI, § 4). The tension values were corrected for the tension in the yield point.

far more rapidly than the orientation factor. So here the theory pertaining to rubber-like elastic bodies (number of chain elements N per chain is large) fails us utterly.

TABLE LVI

Relation between Tension K in g/100 denier (referred to actual Cross-Section) and Orientation Factor f_{am} for X and F Filaments of Viscose No. 5

X Filaments				F Filaments			
v_2	K	fam	K/fam	v_2	K	fam	K/fam
1.15	0.90	0.14[5]	6.2	1.20	1.35	0.15[5]	9.0
1.25	1.65	0.23[5]	7.0	1.40	5.20	0.30	12.4
1.40	4.3	0.37	11.5	1.50	8.5	0.37	23
1.60	10.9	0.54	20.2	1.70	20.6	0.52	43
1.80	22.6	0.69	33	2.00	59.2	0.73	81
2.10	53	0.86[5]	61	—	—	—	—

J. J. Hermans' theory for small values of N (see Chap. XI, § 3, page 469) is a different matter. That theory postulates *no* proportionality between tensile stress and birefringence. Let the force be P and the original cross-section of the filament σ_0; the theory then produces the expression:

$$\frac{P}{\sigma_0} = G_0 \, k'l \, \frac{\bar{x}_0}{A} \, \lambda \qquad (13.1)$$

where G_0 is the number of coils and $\bar{x}_0$ their average length in the direction of elongation in the isotropic state. Therefore the tensile stress (referred to the original cross-section) is proportional to the parameter λ. This in turn is dependent upon the degree of elongation and upon N according to Fig. 199. Calculating f_{am} as dependent upon λ, we find that for $N < 3$ the orientation factor is almost a universal function of λ (Fig. 206). The curves for $N > 1$ are slightly S-shaped. If we now plot the K values of Table LVI (now as referred to *original* cross-section) against f_{am}, we shall find matters as represented by Fig. 207. As $N \sim 1$ for X filaments, the shape

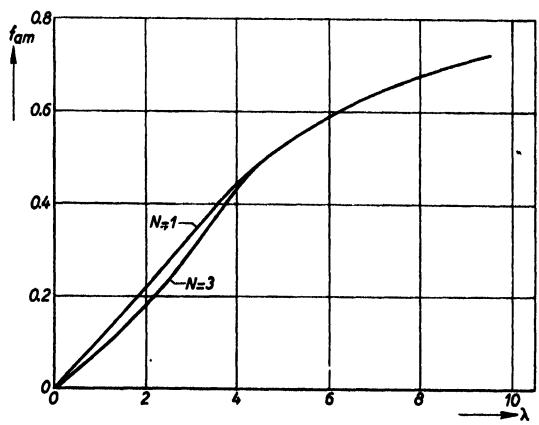


Fig. 206. Short chain theory. The orientation factor as a function of parameter λ for $N = 1$ and $N = 3$.

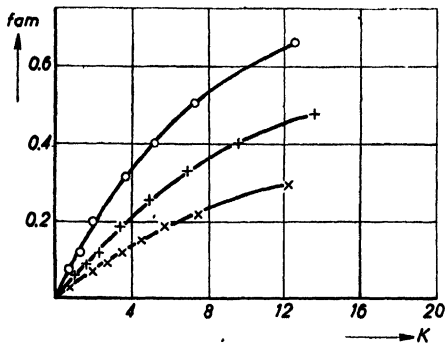


Fig. 207. Experimentally determined orientated factor fam of the amornhous substance plotted against the observed tensile stress K in g per 100 denier of the isotropic filament. (o X filaments; + F filaments; × R filaments).

of the curves fits in well with the theory; accordingly, we get a slightly S-shaped curve for R filaments (in which $N = 2$, approximately, according to p. 472).

Comparing the conditions with different degrees of swelling q, but with the same number of coils per cm³ dry substance, as must be the case for X, F and R filaments, then in (13.1) $\overline{x_0}$ must be proportional to $q_1^{\frac{1}{3}}$ and G_0 in inverse ratio to q_1. Then for a given value of λ, the quantities P/σ_0 will be related as $q_1^{-\frac{2}{3}}$ and λ must therefore be a universal function of $Pq_1^{\frac{2}{3}}/\sigma_0$ and f_{am} will then also be a universal function of this quantity in accordance with Fig. 206 (except for a minor deviation below $f_{am} = 0.50$). This theorem is proved in Fig. 208. The curves for X, F and R filaments ($N \sim 1$) now wholly coincide (cf. Addendum on p. 494)

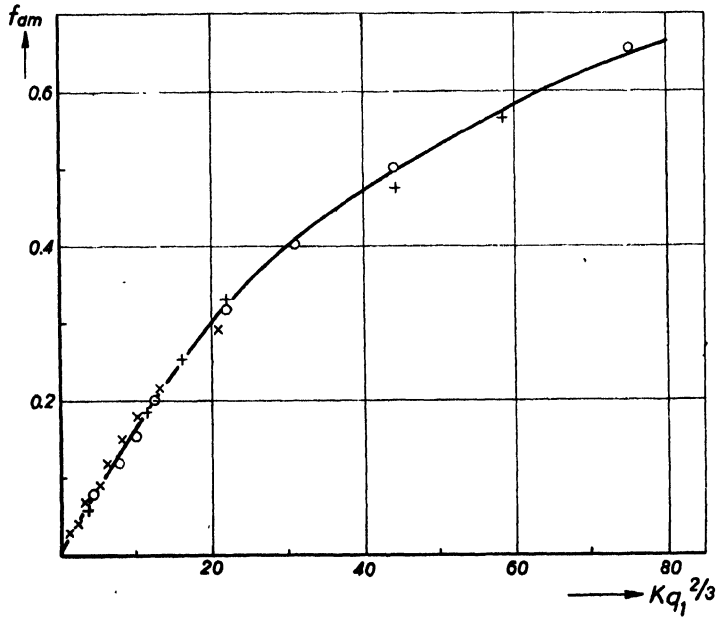


Fig. 208. Orientation factor fam plotted against $Kq_1^{\frac{2}{3}}$ (The curves now coincide).

This result is a splendid vindication of the theory respecting short chains. Applied to vulcanized rubber, it has been found to account for the stress-

strain diagrams very accurately[4]. It produced $N = 30$ and $N = 17$, respectively, for two objects vulcanized in different degrees, (*viz.*, 90 and 240 minutes). The number of monomeric residues per chain element was also computed at 6.5 and 5.0 respectively, values which correlate well with those derived after *W. Kuhn* from viscosity measurements[5].

It can furthermore be shown that the shape of the stress-strain curves for *X* and *F* filaments also agrees satisfactorily with the theory. This is to be inferred from the fact that the K/λ ratio is constant in a wide range of elongation, as may be seen in Table LVII. In *R* filaments, however, there continues to be a systematic deviation.

TABLE LVII

Proof of the constant Proportion, required by the Theory, between Tension K, as referred to the original Cross-Section, and λ

	v =	1.20	1.40	1.60	1.80	2.0
X. Filaments ($N = 1$)	λ =	1.3	2.7	4.9	10.0	
	K =	1.65	3.6	7.3	12.6	
	K/λ =	1.3	1.3	1.5	1.3	
F. Filaments ($N = 1.15$)	λ =	1.0	2.2	4.0	7.0	12
	K =	2.3	4.9	9.6	18.0	30.6
	K/λ =	2.3	2.2	2.4	2.6	2.5
R. Filaments ($N = 2.2$)	λ =	0.6	1.0	1.5	2.1	
	K =	1.23	2.6	4.4	7.5	
	ν/λ =		2.6	2.9	3.5	

§ 3. BREAKING STRENGTH OF ISOTROPIC FILAMENTS

The breaking point is given by the moment at which the filament breaks in the elongation test. For a given isotropic filament the breaking strength will be all the greater as the degree of extension is greater at the breaking point, because the stress increases steadily with the degree of extension. The orientation at the breaking point is then likewise higher. Since the orientation increases almost linearly with v_t [5a], the latter will be the most convenient relative measure for the orientation if we wish to enquire at what degree of orientation the breaking point is going to be.

Looking at Fig. 205, we see that, in the case of isotropic filaments originating from the same primary gel, the v_t value, and, therefore, the orientation at breaking point, falls as the initial degree of swelling decreases. The most pronounced difference is between *X* and *F* filaments, while it is relatively small between *F* and *R* filaments. Highly swollen xanthate filaments also possess the greatest breaking strength. Thus, if the aim is to obtain filaments

[4] It is known that these diagrams also tend to be S-shaped if the stress is referred to the original cross-section.

[5] *J. J. Hermans;* J. Polymer Sci. 1 (1946) 233.

[5a] Cf. p. 459.

of the best possible orientation, it is necessary to perform „stretching" in the xanthate state, a fact which has long been known in practice.

It is well worth noting that, by so simple an experiment as the elongation of an isotropic *X* filament, breaking strengths are attained in the swollen state which are considerably greater than those reached about fifteen years ago in technical viscose spinning, or, indeed, ever thought to be possible. If experiments of the kind had been known before, the problem of enhancing the strength of the filaments would even then have been regarded very differently.

Fig. 205 also shows that, to obtain a certain v_t (and thus a given orientation), the higher the degree of swelling, the less force need be brought to bear. (It must be borne in mind that the tension is here expressed in g/100 denier and is referred to the existing dry substance; were it to be referred to the cross-section of the swollen filament, the difference would be greater still.) The internal readjustments which take place in the process of orientation set up a resistance which is in equilibrium with the stress. The slighter this resistance, the further can the molecular net be stretched and orientated before break occurs. We have already considered what the mechanism of break may be (Part II, Chap. VI, § 3).

As we shall see directly, the breaking points of filaments of the same degree of swelling, but produced by different methods of manufacture, are liable to be very different despite the same resistance — hence same course of the stress-strain curves. Here we have to assume differences in the degree of molecular entanglement (see p. 420 ff); with this, breaking as a process, is likewise intimately connected (p. 278).

A comparison of the breaking strengths of isotropic filaments spun by different methods provides interesting data. We shall take those objects which were produced from viscoses whose cellulose concentration and average degree of polymerization *(DP)* were varied (Table XLIII, page 429)[6]. The extensions at break of these objects have already been recorded in Table XLV (page 435). Table LVIII, which now follows, shows their breaking strengths.

TABLE LVIII

Breaking Strength of isotropic Filaments Spun from the Nine Viscoses of Table XLV (g/100 Denier).

Viscose No	*X*	*F*	*R*	*D*
1	29	14	12	32*
2	130	62	44	51*
3	57	41	36	44*
4	188	94	107	101
5	101	75	98	90
6	61	38	53	50*
7	134	99	98	111
8	90	82	65	81
9	95	77	78	100

[6] The effect of varied alkali concentration and different xanthate ratios is comparatively slight and is therefore less interesting.

In Fig. 209 the breaking strengths of the *X* filaments of Table LVIII have been plotted against the degree of swelling $(q_1)_X$ of the primary isotropic gel. It will be observed that they do not, like the orientation, represent a continuous function of $(q_1)_X$ but fall into groups of constant *DP*. These are connected by lines in the Figure. The encircled numbers stand for the cellulose concentration. Following the lines, we see that at a given degree of polymerization the breaking strength increases with increasing cellulose concentration. The influence of increasing the *DP* while keeping the cellulose concentration the same (when $(q_1)_X$ scarcely changes) is considerable. This will be evident when looking, from below upwards, for the rings encircling identical numbers. Viscose No 4 (with 6% cellulose and 390 *DP*) exhibits the best breaking strength.

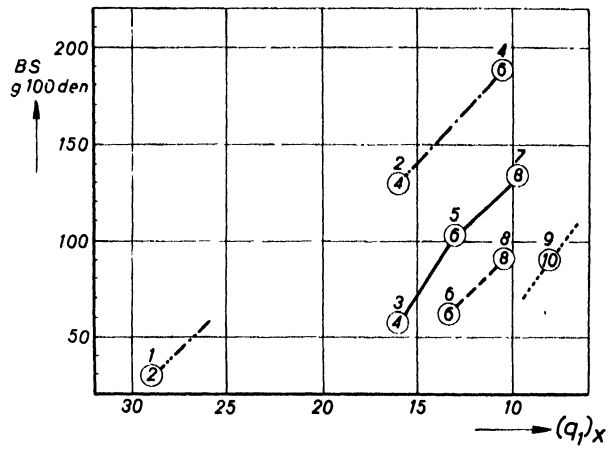


Fig. 209. Breaking strength (BS) of isotropic xanthate filaments in g/100 den., plotted against the primary degree of swelling $(q_1)_X$ for the nine viscoses of Table XLIII. Encircled numbers: Cellulose content of the viscose; numbers beside circle: number of the viscose. The lines refer to equal degrees of polymerization, viz., —.— DP 650; — . — DP 400; — — DP 280; — — — DP 200; ..... DP 180.

The picture is similar when the breaking strengths of *F*, *W* and *D* filaments are plotted against $(q_1)_X$ but in this case viscose No 7 produces somewhat better breaking strengths than No. 4.

We find, moreover, that the breaking strength of the *D* filaments spun from viscoses 1, 2, 3 and 6, marked with an asterisk in Table LVIII, is particularly low (between 32 and 51 g/100 denier). It is these viscoses which also show particularly low extension at break (Table XLV, page 435), this being between 20 and 30 per cent., whereas it ranges from 80 to 120 per cent. with other viscoses. These are the viscoses of low cellulose content (2—4%) or medium cellulose content (6%) combined with low *DP*. They also have the highest primary degree of swelling and the chains, therefore, are the most convoluted in the dry state. Probably the pronounced molecular entanglement in the D state is in this case responsible for poor extensibility. There is no sign of particularly poor extensibility in the corresponding re-swollen *(R)* filaments. Apparently swelling breaks down the internal resistance to elongation caused by excessive molecular entanglement.

Interesting results are obtained by plotting the breaking strengths and

extensions at break of the air-dry isotropic *D* filaments of the various viscoses against each other (Fig. 210). The points then come, with but little scattering, upon one curve, which has the shape of the stress-strain diagram of an isotropic D filament. This means that *the S-S curves of the isotropic D filaments are virtually the same for all viscoses, only the end point being different.*

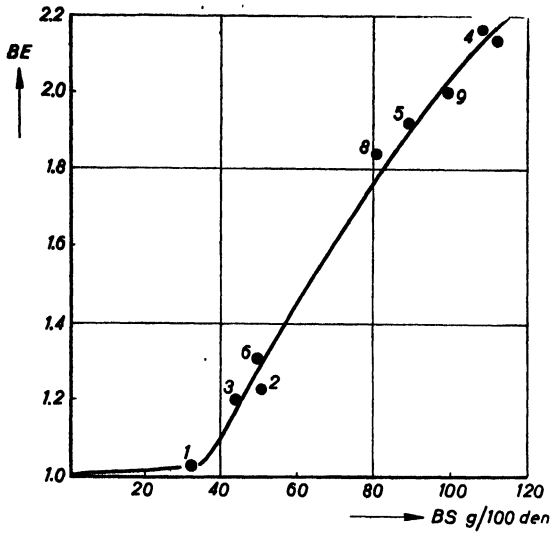


Fig. 210. Extensions at break (BE) at 65% rel. hum. of isotropic filaments spun from various viscoses, plotted against their breaking strength (BS). (The numbers are those of the viscoses in Table XLIII).

The curves do not coincide for the other states of swelling. There is no perceptible simple relationship between $(q_1)_X$ and the shape of these curves. Thus the influence of the conditions of manufacture makes itself felt before all in the swollen objects. It is cancelled out, so far as the slope of the S-S curve is concerned, in the dry state, when only the lengths of the curves are different.

This is undoubtedly owing to the large number of secondary junction points in the *D* state, as the result of which all dry gels come to be virtually in the same condition.

§ 4. BREAKING STRENGTH AND EXTENSION AT BREAK OF FILAMENTS PREVIOUSLY STRETCHED IN THE XANTHATE STATE AFTER DECOMPOSITION TO CELLULOSE AND DRYING

Isotropic filaments which have attained a certain orientation in the *X* state and have then been decomposed and dried, may be considered as models of technical rayon filaments. Their orientation advances when they are tested on the dynamometer for their mechanical properties, but this continued orientation takes place in a different (lower) state of swelling as compared to that in which primary orientation occurs. The case is a far more complicated one, it seems.

The general picture resulting from an analysis of the S-S curves of filaments previously stretched to different lengths has already been reproduced in Fig. 105 (page 285). We must briefly mention here something which is not manifested in that picture, but which has been observed recurrently in other sets of experiments.

In Fig. 105 the breaking strength of the pre-orientated filaments increases steadily in step with the preliminary elongation in the *X* state. But, if

preliminary extension is pushed to the extreme, one often finds that the strength begins to diminish again. In practice this is known as "over-stretching". It looks as though something happens besides further increase in orientation shortly before the breaking point of the xanthate filament is reached, and that this something is in the nature of an inner deterioration of the structure. Indeed, it is not difficult to realize that, if an irregularly constructed molecular network is being progressively tightened, there will come a point at which certain molecular chains are so strained that further extension will of necessity cause a rent; thus "micro-tears", weakening the subsequently decomposed and dried filament, will take place before the macroscopic break.

It would take us too far afield to represent the stress-strain curves of the filaments, pre-stretched in the X state, of the nine viscoses of Table XI,III [7]. We shall only show the maximum breaking strengths attained with each viscose. In Fig. 211 these are represented (as a function of the primary degree of swelling) in the same way as the strengths of the xanthate filaments in Fig. 209. Besides the values at 65% rel. hum. we have given the values in the wet (i.e., re-swollen) state. (The low values for viscose No 1 have been omitted.) The picture, it will be noticed, is entirely similar to Fig. 209, the only exception being the breaking strength in the wet state of viscose No 4 [8]. These "rayon models", then, display the same dependence upon the composition of the viscose as xanthate filaments. It is worth noting that viscose 4, which proved to be the strongest, was also found to be the most extensible in the X state.

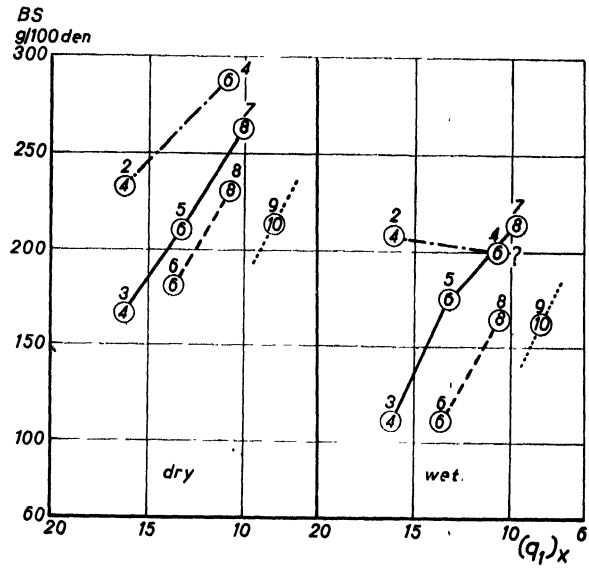


Fig. 211. Maximum breaking strength of filaments preliminarily stretched in the xanthate state and then decomposed and dried in the dry and wet states, plotted against the primary degree of swelling $(q_1)_X$. (For the meaning of the numbers see Fig. 209).

Model filaments provide us with a somewhat better opportunity of studying the conditions than do those spun in practical experiments. We shall try to

[7] There are, on an average, six different preliminary elongations to each viscose. Seeing that the filaments were, moreover, measured in the wet and in the dry state, it is a matter of 108 curves.

[8] This may be mere coincidence. Lack of material limited the test to one single filament. The other points are always average values of several experiments.

find out what the "actual stretch" is at the moment when the filaments of Fig. 211 break, taking the isotropic state as zero. Actual stretch consists of two parts, viz., the stretch accomplished in the preliminary elongation in the *X* state, and that added during the elongation test upon the dry filament in the elongator. If one of these components is to be added to the other, it is necessary to have a common measure for them. This is afforded by the v_t degree of elongation, which refers to the dry state. The product of the v_t of the preliminary stretch and the extension at break then gives us the total extension at the breaking point as referred to the isotropic state.

In Fig. 212 the breaking strengths of the filaments preliminarily stretched (in the *X* state) to different lengths are plotted against this " total v_t " for the nine viscoses of Table XLIII. The starting point of every curve is the breaking point of the isotropic (hence not previously stretched) filament (marked with an "i" in the Figure). It will be seen that at first the curves gradually rise, almost linearly. Then, above a certain total v_t they often

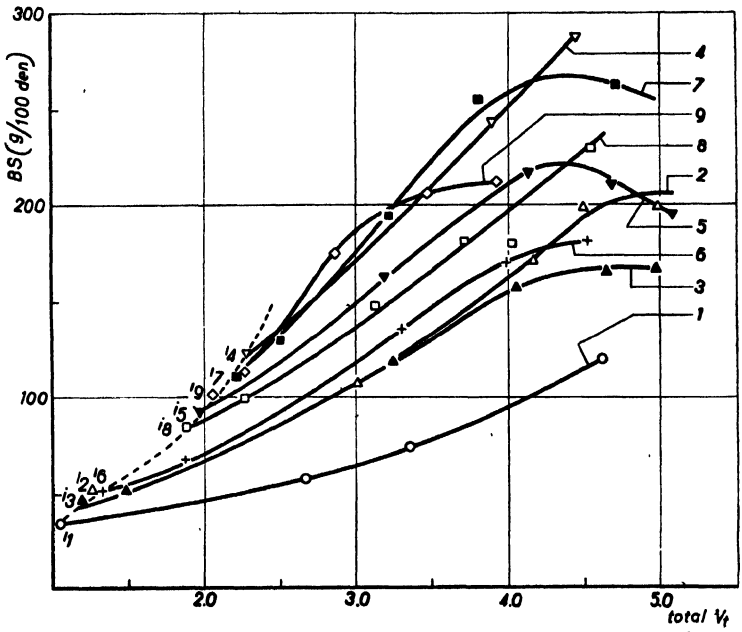


Fig. 212. Breaking strengths of filaments pre-stretched in the xanthate state to different lengths, plotted against their total vt at the breaking point. (Viscose numbers in Table XLIII, p. 429). Broken curve: Breaking points of the isotropic filaments (for which compare Fig. 210).

suddenly deflect. (Occasionally they pass through a maximum; see for this page 489). The broken curve on which the isotropic filaments (i) lie is, of course, identical to that in Fig. 210.

The maximum attainable strength obviously depends upon two conditions, viz.,

1) The steepness of the curve's ascent.

2) The distance to which it rises with the original slope before bending and breaking off.

On closer examination we now find that, broadly speaking, the steepness of the curve increases as the primary degree of swelling decreases. The deflection of the curves is a secondary effect, associated mainly with the degree of polymerization, since it is most in evidence in the case of viscoses of low *DP*. Compare, for instance, 3 (*DP* 270) with 2 (*DP* 390), or 6 (*DP* 200) with 5 (*DP* 270) and 4 (*DP* 390).

We see that the ideal case would be that of a filament the primary degree of swelling in the *X* state of which is = 1. Its curve would run alongside the i curve and, moreover, in this dry state it would be in the highest degree extensible. Naturally, no such low primary degree of swelling is realizable in practice, for the spinning substance has to remain fluid.

Summarizing the facts discussed in this and the preceding Sections, it would seem that the following rules apply to all varieties of filaments:

1) At a given *DP* the breaking strength is the greater according as the cellulose concentration in the solution from which the gel is produced is higher.

2) The higher the cellulose concentration in the solution, the lower may be the minimum DP necessary to attain a given breaking strength.

3) At a given cellulose concentration, the higher the *DP*, the greater is the breaking strength.

It is clear from these facts that no such simple relationship between *DP* and tensile strength can exist as was recently suggested by *A. M. Sookne* and *M. Harris* and discussed by *P. J. Flory*[10]. The latter deduced from the measurements of the former that there would be a linear relation between *BS* and the reciprocal of the *DP*.

Analyzing the results obtained with model filaments, we see that the only unequivocal relationship between *BS* and $1/DP$ is in filaments produced from a solution of the same cellulose concentration. This relationship, however, does not seem to be a linear one in our case.

§ 5. BREAKING STRENGTH AND BIREFRINGENCE

Determining the breaking strength and the birefringence of a number of rayons chosen at random, the investigator will perceive no clearly defined relationship between these two quantities. The same applies to the model filaments, pre-stretched in different degrees, spun from the nine viscoses discussed above. Although the points for filaments spun from the same viscose lie on smooth curves when the *BS* is plotted against the birefringence (see Fig. 213), each viscose produces a different curve. The curves, moreover,

[9] *A. M. Sookne* and *M. Harris*; Ind. Eng. Chem. 37 (1945) 478.
[10] *P. J. Flory*; J. Amer. Chem. Soc. 67 (1945) 2048.

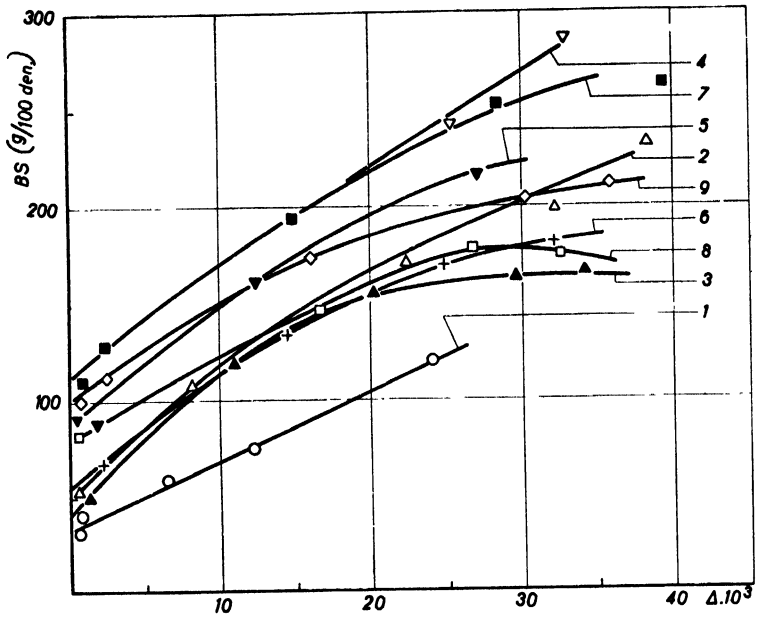


Fig. 213. Breaking strength of the filaments preliminarily stretched in varying degrees, plotted against their birefringence $\wedge$ (numbers are the viscose numbers).

intermingle in a manner difficult to unravel. Indeed, the two quantities compared here are not cognate. The birefringence had been determined in the pre-orientated filament *prior to* the determination of its breaking strength.

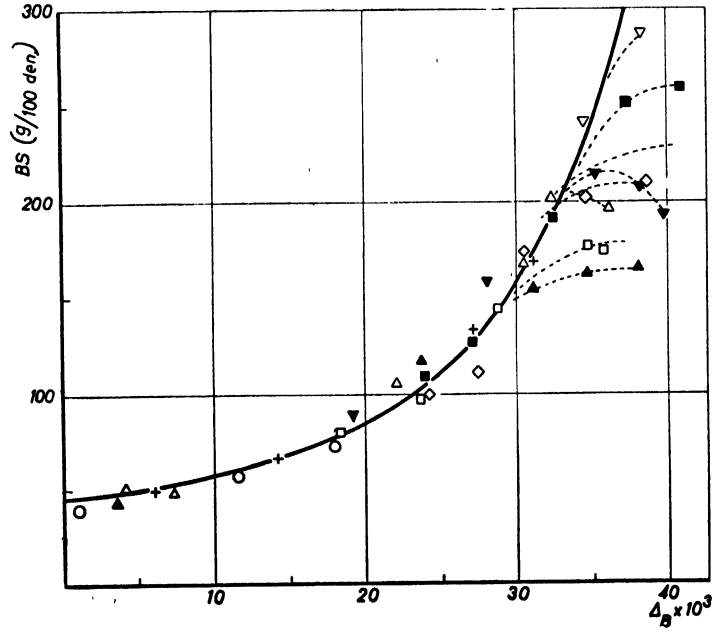


Fig. 214. The same breaking strengths of the filaments of Fig. 212, plotted against the birefringence $\triangle^B$ at breaking point.

In the later determination the filament is further extended on the elongator until it breaks, and this operation entails further orientation.

Comparison, on the other hand, of the *BS* with the birefringence of the filament at *the breaking point* is rewarded by an interesting result, which is shown in Fig. 214. We then see that *the breaking strength of a filament is governed within fairly narrow limits by its birefringence, i.e., by its average angle of orientation at breaking point,* by whatever process it may have been spun. This holds good so long as the breaking strength is not unduly high. As the Figure shows, there is very wide scattering with the higher values, owing to the deflection of the curves. This is merely another instance of what we saw in Fig. 212; viz., though the v_t increases further and the birefringence rises, there is no further increase in the *BS* (internal rent; cf. page 489).

If we express the birefringence Δ in the optical orientation factor f_o we find that the equation

$$BS\ (1 - f) = C \qquad (13.2)$$

is approximately fulfilled. The fully drawn curve in Fig. 214 was calculated in accordance with this equation for $C = 45$ (which is the yield value for dry filaments)[11]. The equation can also be written as follows (see eq. 5.2 page 255):

$$BS = \frac{2}{3} \cdot \frac{C}{\sin^2 \alpha_m} \cdot \qquad (13.3)$$

where α_m is the average angle of orientation.

Thus the breaking strength is inversely proportional to the sine of the average angle of orientation at breaking point squared. On the most elementary theoretical suppositions, this is precisely the obvious equation, provided the process of breaking be initiated by subjugation of the lateral cohesive forces between the chains[12].

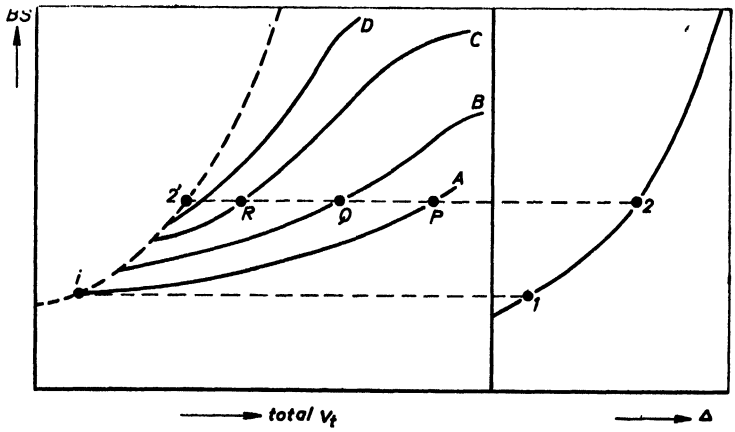


Fig. 215. Figures 212 and 214 juxtaposed (in diagram).

[11] For air-dry filaments f is calculated from $f = \Delta/0.043$.

[12] *P. H. Hermans;* Kolloid-Z. 88 (1939) 89, 344; Proc. Acad. Sci., A'dam, 42 (1939) 798.

To make all this clearer, we shall once more represent the facts, somewhat idealized, in diagram, thereby aiming, not so much to express them in exact terms, as to bring out the essentials graphically in clear relief. In Fig. 215, figures 212 and 214 are placed side by side diagrammatically. The broken curve to the left is the "ideal" stress-strain curve (which all the air-dry isotropic filaments follow). The right-hand part of the figure shows how the birefringence rises along this curve. Any isotropic filament chosen at random follows the broken curve when being elongated, but only for a limited distance until the filament breaks. In the case of viscose A this already takes place at point i. The average orientation which may thereby be attained can be seen on the birefringence curve to the right, at point 1.

To avoid this premature cessation of the process of orientation, the best course is to elongate the filament to the utmost in the xanthate state, decompose and dry it and then determine its breaking strength. It will then be located, say, at point P of curve A. The correlative orientation then reached is read to the right at point 2. It corresponds to point 2' of the "ideal" broken line to the left. If one had elongated the dry, instead of the *X* filament, it would already have broken at i. Thus the stretch i — 2' on the ideal curve has been bridged by the circuitous route of the xanthate gel. This has necessitated a far higher total vt than would be required for stretching in the dry state.

With viscoses B and C the same orientation would have been reached at points Q and R (that is to say with less total vt). Nevertheless, continued elongation would have taken one even further and would have conquered longer distance on the ideal curve.

This is a diagrammatic empirical picture of the processes in technical spinning.

ADDENDUM TO § 2.2 (p. 48.)

The experimental force-strain curves are different from the theoretical curves in that they exhibit a yield value. In order to compare the observed curves with the theoretical ones we have simply subtracted the yield value of the force (a very small quantity in the case of highly swollen filaments) from the observed force values on the force-strain curve. The stress values listed in Tables LVI and LVII were thus corrected.

The physical meaning of this correction is, that we attribute the yield value to a mechanism which has no direct bearing on the general form of the curves (cf. the considerations on the yield value given on p. 297 ff. and p. 499).

CHAPTER XIV

DEFORMATION OF NITRATED MODEL FILAMENTS

On the properties of nitrated model filaments we have for reference investigations published by *D. Vermaas*[1], which we shall discuss briefly here. The subjects of his research were filaments obtained by the nitration of isotropic cellulose filaments. They contained 13.1 per cent. of nitrogen (trinitro-cellulose theoretically 14.1% N, dinitrocellulose 11.1% N) and were deformed both in the dry state and swollen in ethyl alcohol and in mixtures of this and acetone. The analogy to the deformation of the cellulose filaments from which they were produced was striking.

The two categories of filaments were about equally extensible. The anisotropy of swelling and orientation, assessed by the X-ray diagram, increased more rapidly with elongation, according as the degree of swelling was higher. When plotted against v_t instead of against v, the curves of the filaments for the anisotropy of swelling coincided. The v_t curves were the same as those produced by the original cellulose filaments. Nor did the mechanical properties of the filaments suggest anything new.

The impression received from these investigations is that the properties of the gel frame subjected to deformation are modified little or not at all by nitration. One is again reminded of the predominating influence of the primary gel. It is significant that this should continue to be noticeable even after so radical a change as this in the chemical character of the molecules. The optical properties of the swollen filaments are also dealt with at length. Owing to the birefringence of adsorption, these are more complicated in nitrocellulose than in cellulose filaments. But we shall not enter in this matter here.

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[1] *D. Vermaas;* Diss. Utrecht 1941; cf. *H. R. Kruyt, D. Vermaas* and *P. H. Hermans;* Kolloid.Z. 99 (1942) 245, 251; 100 (1942) 111.

CHAPTER XV

THE MECHANICAL PROPERTIES OF CELLULOSE COMPARED WITH THOSE OF RUBBER-LIKE SUBSTANCES

§ 1. INTRODUCTORY REMARKS

According to the theories put forward in the preceding Chapters, the amorphous components of cellulose are primarily responsible for its mechanical properties. The proposition that the structure of these amorphous components is intrinsically a molecular network of coiled, or kinked, chains has proved to be a pregnant one. The same idea was enlisted to explain the deformation of rubber-like substances. Surely then, this conception must supply the key to the deformation of all so-called linear polymers? The distinctive differentiations would, it must be supposed, reside in the length and rigidity of the convoluted chain sections between the junction points and in the degree of intermolecular cohesion.

Weak cohesion, as in the hydrocarbon rubber, involves the theoretically simpler cases, there being none of those intermolecular interactions of an energy character which it is always so difficult to formulate quantitatively. Cellulose, with its powerful intermolecular cohesion, stands for the other extreme and formidable obstacles undoubtedly stand in the way of its quantitative theoretical treatment. The problem is eased somewhat when more dilute systems, i.e., swollen gels, are made the subject of study and in the foregoing we have availed ourselves liberally of that opportunity.

In this Chapter some general qualitative points will now be examined finally.

§ 2. THE ELASTIC AND VISCOUS ELEMENTS

At this juncture we can pick up the threads as we left them in Part II (Chap. VI § 4.4), where we discussed the mechanical deformation models comprising springs and devices for the representation of frictional resistances. We may think of those springs as molecular. On being stretched, a convoluted molecule freely embedded in a solvent takes up a position which, statistically, is fairly improbable; its entropy is reduced. As a result, it develops an elastic force and we might call it an "entropic spring". We know that within a wide span of elongation the elasticity of slightly vulcanized rubber may be considered as pure entropy elasticity. The same factor will undoubtedly come into operation in cellulose, but in this case there will, in addition, be energy factors of elasticity, especially in undilute systems. The latter may be due to

hampered freedom of rotation of the chain sections, distortion of valence angles, or other deformations of the molecules which enhance the potential energy.

The greater the internal friction of the system, the more likely is it that the entropic spring will also have the character of an energetic spring; and the less dilute the system is and the greater the intermolecular cohesion, so much the greater will the internal friction be. Rubber is the example of a substance in which the molecular springs retain their entropic character in the solid, unswollen substance. They will not do so in cellulose.

The "dashpots" in the deformation models represent the frictional resistances which the molecules experience during the internal readjustments of their positions necessitated by the deformation. They stand for the times of relaxation of the material.

We have seen that the mechanical behaviour of cellulose fibres can be satisfactorily described with reference to the relatively simple mechanical model of Fig. 117 (page 297), which contains a "free" spring and two spring-dashpot combinations behind it. We had there, however, to introduce certain assumptions regarding obstruction of spring A_2 (about which see below). The model contains no dashpots without parallel springs and therefore depicts no macroflow, only microflow (p. 299). It will be obvious that this fits well into the picture of a molecular network having fixed, unalterable junction points between the chains.

§ 3. DEFORMATION OF RUBBER-LIKE SUBSTANCES

When a thread of rubber is elongated quickly, the originally coiled molecules in it stretch. When the thread is released, it springs back, or "recovers". It is possible to prove by the thermal effects that this elasticity is purely entropic in character (for example, the power of recovery is enhanced by increased temperature).

As the molecules in rubber are able to glide past each other with ease, there is little frictional resistance. That is why macroflow takes place in unvulcanized rubber (especially at raised temperature) when it is stretched slowly or for a long time. With prolonged elongation the molecules, by gliding past each other, are able to revert to their "innate", most probable convoluted position. Then, upon release, there is no recovery, or at all events recovery is not complete. This means that there is permanent extension without a corresponding straightening-out of the molecules and, consequently, *without a corresponding permanent anisotropy* of the system.

The molecules in vulcanized rubber are interlocked by chemical bridges at various points; so there can be no macroflow. Elongation of the system then causes a certain amount of straightening out and thus a certain anisotropy of the system.

There is something else which prevents molecular gliding in rubber stretched to the higher degrees; it is the *crystallization* which can be shown by X-ray

to take place here and there in the system. Crystallization releases heat and forces of attraction come into operation in the crystallized areas. Under normal conditions, however, these are not powerful enough to prevent recovery. When the applied tension is removed, the system recovers, destroying the crystallized agglomerations. The increased entropy defeats the work of crystallization.

There is no recovery, however, if the balance between the two factors is altered by sufficiently cooling the stretched crystallized filament; it is then crystallization which predominates. This obstruction to recovery can be removed by the re-application of heat. The same effect can be obtained by swelling.

A more permanent fixation of the stretched state can be brought about with rubber if the stretched filament is effectively vulcanized in the cold. In this way *W. Busse*[1] was able to produce filaments from rubber the breaking strength of which was 180 g/100 denier. (In the unvulcanized state the breaking strength was only 0.01 of this amount). It will be evident that the structure of these objects is comparable with that of rayon. Like the latter, they have little extensibility and their recovery is imperfect. By increasing the energetic intermolecular interlocking we can transform rubber to a condition resembling that of cellulose.

Let us now ask ourselves what happens when we cool rubber in its unextended — i.e., isotropic — state. Though crystallization takes place, the crystallites are not orientated as they are in elongated rubber.

If any orientation is to take place at all, the molecular cohesive bonds must first of all be torn apart in deformation. Since this demands a certain amount of force, a yield point will occur.

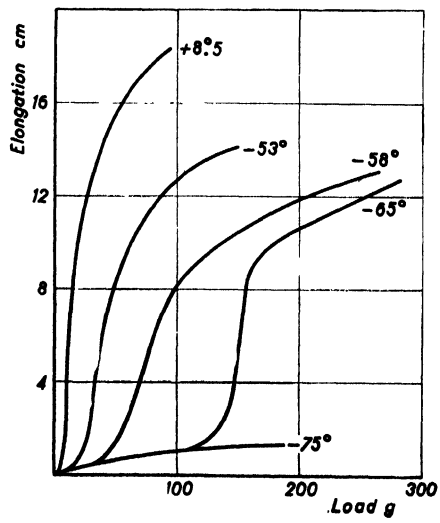


Fig. 216. Stress-strain diagram of a vulcanized isotropic rubber object at different temperatures. (Cf. Fig. 205 for isotropic cellulose filaments at different degrees of swelling).

Fig. 216 shows the stress-strain curves of a rubber object at decreasing temperatures according to *T. Fujiwara* and *T. Tanaka*[2]. There is a striking analogy here to the S-S curves of isotropic cellulose filaments at decreasing degrees of swelling (cf. Fig. 205, p. 482).

[1] *W. Busse*, J. Phys. Chem. 36 (1932) 2862; Rubber Chem. and Techn. 7, (1934) 503.
[2] *T. Fujiwara* and *T. Tanaka*, Rubber Chem. and Techn. 7, (1934) 610; also cf. *M. Leblanc* and *M. Kröger*, Kolloid.Z. 37, (1925) 205.

Those substances, Balata and Gutta Percha, so closely allied to rubber, supply, perhaps, an even better example. They are hydrocarbons, whose temperature of crystallization lies higher than that of rubber; indeed, they crystallize at room temperature. When an isotropic balata is elongated at room temperature, there is at first a yield point. (Fig. 217). The springs have to be pulled apart to some extent before they can come into action. At higher degrees of elongation there is fresh crystallization, this time orientated. That is why the recovery of this substance is limited: the springs are again partially blocked in their stretched state. Further recovery supervenes when the material is heated (removal of the obstruction). At higher temperatures gutta percha behaves like rubber: the yield point disappears and recovery is complete.

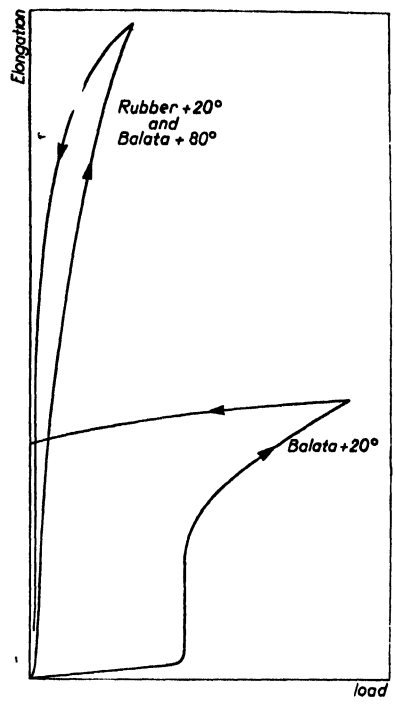


Fig. 217. Stress-strain diagrams on the strain and release of a sample of Balata at 20° and at 80°. In the latter case the object behaves like rubber at ordinary temperature.

§ 4. THE PHENOMENA OF BLOCKING WITH INCREASED MOLECULAR COHESION

Enhanced interaction of energy between the molecular chains, then, confronts us with two new phenomena, *viz.*,

1) Recovery is blocked. New junction points are formed between the chains in the new alignment created by the deformation, and these *partially* arrest recovery. Heating or swelling breaks down this blockage.

2) There is a yield point at the commencement of deformation. Before the molecules can change their positions (that is to say, before microflow can begin), existing junction points have to be torn asunder. This, too, is a species of blockage, but *it is already there in the isotropic initial state.*

Thus there are two kinds of blocking. One already exists *without* previous deformation (in rubber-like substances as the result of low temperature; in cellulose owing to a low degree of swelling).

The other form of blocking is associated with the deformation. It leaves anisotropy in its train and a "recollection" of the preceding deformation; its removal initiates recovery.

Pre-orientated, blocked objects likewise exhibit a yield point, of course, but this is to be attributed to a superposition of *both* forms of blocking. Hence the yield value will increase in proportion as pre-orientation is more advanced. From the molecular-mechanical aspect, the two forms of blocking are essentially the same phenomenon; and they are overcome by the same means (raising the temperature and swelling). It is only in the second case that recovery then takes place. In the former case we are not aware of the disencumbrance until we subject the object to deformation (lowered yield value).

In terms of the mechanical models (Part II, Chap. VI, § 4.4, p. 294 ff.) we might speak of the blocking of the dashpots, instead of that of the springs; indeed, the former might be preferable. In Fig. 115 B this means congelation of the friction fluid. (p. 296).

That the yield value increases in sympathy with the extent of pre-orientation is clearly demonstrated by the S-S diagrams of calendered balata foil with the direction of extension parallel or perpendicular to the direction of calendering. Similar diagrams can be made of cellophane foil.

§ 5. THE DEFORMATION OF CELLULOSE

Cellulose is an extreme example of a substance of great intermolecular cohesion. We now know, therefore, how it may be expected to behave. In a compact state it will behave like rubber cooled to a very low temperature — say that of liquid air — which by then has become a hard, glassy, non-extensible mass. The characteristic behaviour of rubber-like substances at ordinary temperature is governed by mere *occasional* cohesion of the molecular chains, i.e., here and there (scattered junction points). This conditions the net-like character of the structure. At very low temperature the molecules cohere firmly everywhere and then the substance is like amorphous glass.

When bone dry, cellulose really is a brittle, non-extensible glass. It can be pulverized in a mortar[3]. It is entirely thanks to their great affinity to water that cellulose filaments are extensible under more normal conditions. Owing to the formation of the cellulose hydrates and further absorption of water, the cohesive forces in the amorphous regions are so weakened as to create a situation in which regions of very strong junction points (e.g. in the crystalline regions) alternate with areas of far weaker cohesion; and it is then that the structure of the cellulose acquires its net-like character. This becomes more pronounced in proportion as the system is more dilute, i.e., swollen.

It was shown in the preceding Chapters that the cellulose gels obtained from cellulose solutions by gelatination resemble, in their behaviour, nets made up of convoluted chains and that the primary junction points, which we have conceived to be crystallites, have a decisive part to play, as indeed, the whole

[3] *P. H. Hermans*, Cellulosechemie, 18, (1940) 97. (Cf. Fig. 51 on p. 177).

structure of the primary network. It retains its original character even in other states of swelling. In the already very compact air-dry state, when there is only little water, it has partly lost this character and the new, secondary junction points, which are added during the process of shrinking, are by this time anything but negligible factors.

If not stretched excessively, primary xanthate gels still possess considerable elasticity, as do also highly swollen cellulose filaments [4]. But recovery is never complete, because fresh points of contact are formed during deformation (new secondary junction points between the chains), which block recovery at the time. The greater the degree of elongation, the more pronounced will this phenomenon be. If the filament is allowed to swell, however, there will be some further recovery (swelling retraction).

The secondary junction points may be far weaker than the primary and need not be thought to involve an increase in the amount of crystallized substance. (Nor is there any in a noticeable degree, as *Kratky* pointed out). They consist merely of new points of contact between the chains of varying attractive energy. In the deformed gel there will be a whole spectrum of such junction points. The extent of swelling retraction depends upon how far in the spectrum the swelling agent used succeeds in dissolving the secondary junction points. A strong swelling agent brings about greater retraction than a weaker one, but we have seen before that this always involves a *true reversal of the deformation.* Quantities, such as the volume and the orientation of the gel, change in exact proportion to the effected retraction. (see p. 443).

Secondary junction points will likewise be added whenever shrinkage takes place; the spectrum is widened. Deformation at a low degree of swelling will produce a spectrum showing a larger number of energetic junction points than deformation at a higher degree of swelling.

It is well to bear in mind that swelling retraction of a cellulose filament only takes place when swelling proceeds beyond the point at which deformation took place. The spectrum of secondary junction points formed at a given degree of swelling by deformation can, of course, only be destroyed — and that partly — by stronger swelling agents.

It is thanks to this fact that we are able to retain in the dry filament the orientation brought about during the spinning of rayon by deformation at high degrees of swelling, and that it is maintained even when the filament is swollen in water up to about $q = 2$. If we steep rayon filaments in stronger swelling agents, however, such as strong sodium hydroxide, they will "recover", at any rate partly.

Shrinkage, itself, likewise widens the junction point spectrum. Shrinking starts a blocking and it is for this reason that a dry isotropic filament exhibits a quite considerable yield value. The mechanism of deformation (when the

[4] In rapid elongation to over 30 per cent and release, a filament of this kind recovers to an extension of only 3 per cent.

primary network changes shape) cannot get into its stride, as it were, until some of the junction points have been loosened.

The properties of system 2 of Fig. 117, discussed on page 297, will now be understood. The preliminary elongation of spring A_2 represents the preliminary extension of the network in the xanthate state which had taken place earlier. It also corresponds to the anisotropy of the filament.

It will now also be evident why the yield value drops so much when the filaments are moistened: part of the junction point spectrum is destroyed by swelling. We now also know why it is that filaments elongated in the dry state retract so remarkably when wetted (Fig. 109, p. 288).

Qualitatively, the mechanism of the deformation of cellulose would now seem to have been fairly satisfactorily explained. The quantitative aspect of the problem is, however, incomparably more difficult, and the less swollen the objects studied are, the more implacable does the problem become.

CHAPTER XVI

SOME GENERAL REMARKS ON THE PRECEDING CHAPTERS. UNSOLVED PROBLEMS

§ 1. CRITICISM OF THE PICTURED STRUCTURE AS SET FORTH IN THE FOREGOING

The investigations covering the deformation of cellulose gels which we have been discussing leave little doubt that the hypothesis endowing them with a structural network of molecular threads accounts for much of their experimental behaviour; but as soon as we commit ourselves to generalizations, we are confronted with many difficulties and fresh problems.

We have seen that the number of *Kuhn's* statistical chain elements between two junction points in the primary gels must be of the order of 1. This means, however, that the chains are very short and comprise only relatively few monomeric glucose residues. It is therefore necessary to discard the original notion that the crystalline regions represent the junction points of the network. It looks more as if the amorphous components themselves contain the network structure, with the crystalline regions embedded in them, in the form of well-ordered islands, somewhat as represented diagrammatically in Fig. 218. The same principle is, of course, applicable to a "low-distance order" (see Figs. 156 and 157, p. 407 and 408).

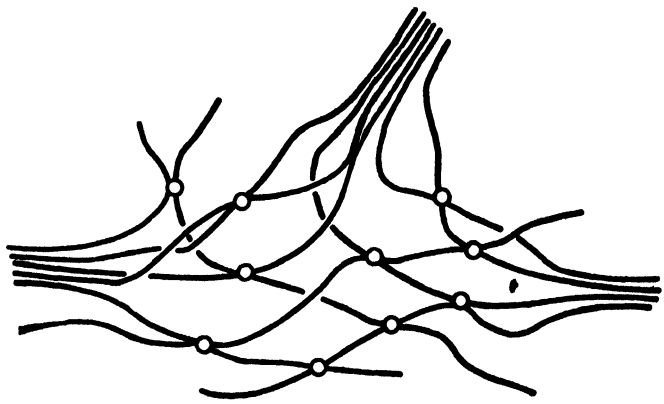


Fig. 218. Diagram showing the network structure in cellulose gels. (The thick points stand for "junction points").

Looking more closely at structures like these, however, one will soon realize that the deformation must necessarily be a more complicated process than it

is shown to be in Figure 161 page 410 in diagram, where only a deformation of the meshes of the net is accounted for. The fact becomes patent when it is remembered that the crystallites have also to be orientated; there must inevitably be some internal rearrangement as well, in the sense suggested on page 407. It is no easy matter to picture this to oneself more graphically. And, of course, new questions thrust themselves forward, such as, for example, how can any correlation be found with the theoretical propositions which are based merely upon the deformation of the meshes of the net? It will also be difficult to reconcile considerations relating to short chains with earlier theories respecting the primary and secondary junction points.

Without assuming the dislodgement of many junction points and the formation of new ones in other places, it is barely possible to visualize the orientation of structures of the kind we have been studying. One is tempted to ask whether the stated fact that the threads of the net consist of only one chain element ought not rather to be accepted in a statistical sense. If so, junction points would be constantly dissolving and as many new ones forming during the deformation. Even then it would have to be explained why theoretical assumptions, which take no account of reciprocal actions of energy, have nevertheless led to acceptable results.

A parallel question is whether the involutions of the structure, assumed for very good reasons to take place when isotropic primary gels shrink, really can be represented as so simple a process as that illustrated graphically in Figs. 161, page 410. We ought, possibly, to think rather that in shrinkage all the radii of curvature recognizable in Figs. 156 and 157 become smaller. Then, perhaps, the apparent increase in the number of chain sections per chain discussed in Chapter XI, § 6.3 should be interpreted differently from what it is there.

These few hints should be sufficient to show that we are still far from having explained to our full satisfaction the processes of deformation to which we have been devoting our attention. The theoretical results so far obtained are to be regarded merely as side-lights, each, maybe, illuminating some aspect of the problem. Or they might be considered as parts of a jig-saw puzzle which it is the task of future research to fit into their proper places.

§ 2. MECHANISMS OF DEFORMATION OF A DIFFERENT NATURE

In this book we have been concerned, to the exclusion of almost everything else, with the deformation of gels as implicated in the ordinary process of viscose spinning, our justification being that this is the best tested case on record. But it involves a one-sidedness which it would be wrong to overlook. There are other methods of manufacturing artificial cellulose fibres, and these probably entail deformation processes of a fundamentally different character.

To take an example: viscose made by the *Lilienfeld* process is spun in baths

of strong sulphuric acid and the resulting filaments have different properties. The scientific principles underlying this interesting process are still uninvestigated, but it is known that, freshly coagulated, the filaments are far more extensible than ordinary xanthate filaments. This points to a totally different mechanism of deformation, as, indeed, was to be inferred from X-ray analysis (Part II, Chap. VI § 3.4, page 279). This marked extensibility would seem to imply that our network theory cannot be appealed to in this case and that the fundamental principle is totally different.

It is practical experience that acetate cellulose filaments preliminarily swollen in certain solvent mixtures (such as mixtures of water and dioxane) are exceedingly extensible and, moreover, after being freed from solvents, very strong.

In these instances the cohesion between the molecules is greatly weakened in deformation by exceptional states of swelling and one is inclined to think of chains gliding past each other, rather than of the deformation of a net. Probably, too, pure macroflow (see page 299) is set up by the deformation. It is a strange fact, however, that neither every swelling agent, nor a given degree of swelling is itself capable of creating this state of high extensibility, which is produced only under very special, usually narrowly confined conditions, the exact nature of which is unknown.

Here, maybe, lies potentially a field for the improved manufacture of artificial filaments from cellulose. Already special grades of thread are being produced on a technical scale along these lines.

CHAPTER XVII

THE LONGITUDINAL SHRINKAGE OF RAYON

§ 1. INTRODUCTORY REMARKS

Both the manufacturers and the consumers of rayon yarn are frequently faced with the problem of shrinkage, which sometimes leads to trouble. Though much has been published on the subject, these phenomena of shrinkage have never been co-ordinated and viewed from one particular angle. Since the work done on model filaments affords some insight into this matter as well, it seemed appropriate that a chapter should be devoted to it.

In what follows, shrinking will be understood to mean the reduction in length (expressed as a percentage) which a filament undergoes when, starting from a condition of relative humidity and temperature, it is allowed to swell and then return to its initial state (if necessary, preceded by one or more states of different rel. hum. or temperature). For our fundamental state we shall take the standard atmosphere and room temperature, and our swelling agent will be water.

We shall see that two effects, differing in principle, are liable to bear upon these phenomena of shrinking, which we shall denote as retraction shrinkage and hysteresis shrinkage.

In essence, retraction shrinkage is identical to the swelling retraction dealt with in Chap. VIII § 5 (p. 443), or to the *drying retraction* discussed in Chap. IX § 5 (p. 450). In both cases the active cause is a partial decline of inner stresses set up during the manufacture of the filament.

The cause of hysteresis shrinkage is the hysteresis in the sorption of water vapour (Part II, Chap. II) and the hysteresis of the changes in dimension during the absorption or emission of water vapour.

§ 2. RETRACTION SHRINKAGE

It is a generally known fact that filaments which cannot freely shrink while they are drying will do so after being swollen with water and conditioned to 65% rel. hum. The stress while drying is equivalent to elongation at a degree of swelling intermediate between that of the wet and that of the conditioned filament. Then, upon subsequent swelling to a higher degree of swelling in water, swelling retraction takes place.

If a rayon filament, dried under stress, is passed once through the cycle: 65% rel. hum. — water — 65% rel. hum., shrinkage ceases and the length of

the filament remains constant upon repetition of the cycle. This does not hold for the far thicker model filaments, which shrink a little less each time the cycle is repeated until, asymptotically, they approach a final value. Even if these thicker objects are dried without tension, stresses are set up in the gel which do not disappear until it is re-swollen to a higher degree of swelling than that at which the stresses were initiated. The same applies to isotropic filaments which have never previously been under tension. The changes in length of an isotropic filament after repeated cycles are shown in Fig. 219.

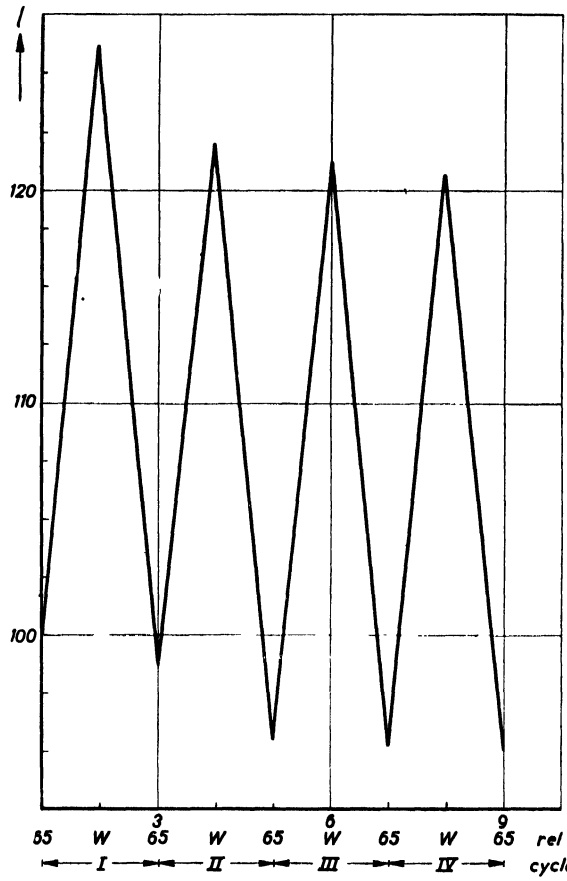


Fig. 219. Retraction shrinkage of an isotropic model filament upon repeated swelling in water (w) and drying to 65% rel. hum.

After the first cycle the shrinkage is 2.5%, after the second, 1.2% and not until the fourth has been passed does its length remain constant. The total retraction shrinkage amounted to about 5 per cent.

If filaments like these are allowed to swell in boiling water or in vapour of 100° and are then conditioned, they undergo the same total shrinkage of 5% and do not change noticeably on going through further cycles. They then exhibit a lower degree of swelling (for which cf. page 442). The degree of swelling of rayon filaments cannot so easily be lowered in this way; for that

they have to go through longer steaming. The temperature of the water, however, does affect the extent of retraction shrinkage. After being swollen in water of 20° and 90°, a rayon filament dried under tension shrank by 2.2% and 3.2% respectively. The filament treated with water of 20° suffers further shrinkage of 1.2% in a second cycle with water of 90°.

Retraction shrinkage is induced, not only by drying under tension, but by every elongation at degrees of swelling of the filament below that in water. These elongations take place when rayon is subjected to excessive stress on the loom or in other manipulations, and when the fabric is wetted subsequently, it will be found to shrink. This is responsible for many flaws, such as "shining picks".

§ 3. HYSTERESIS SHRINKAGE

Fig. 220 illustrates the general type of hysteresis shrinkage. In it are depicted experiments with a rayon filament redeemed from retraction shrinkage. After its first treatment with water (condition 2), the filament was placed in air of 65% rel. hum. (3), then in air of 1.5% rel. hum. (4) and once again in air of 65% rel. hum. (5), after which in water (6), and so on (cycles I to III in Fig. 220). It will be seen that the filament is longer at 65% rel. hum. when it emerges from water than when it comes out of the dry air of 1.5% rel. hum. From condition 5 to condition 7 the treatment with water lengthens the

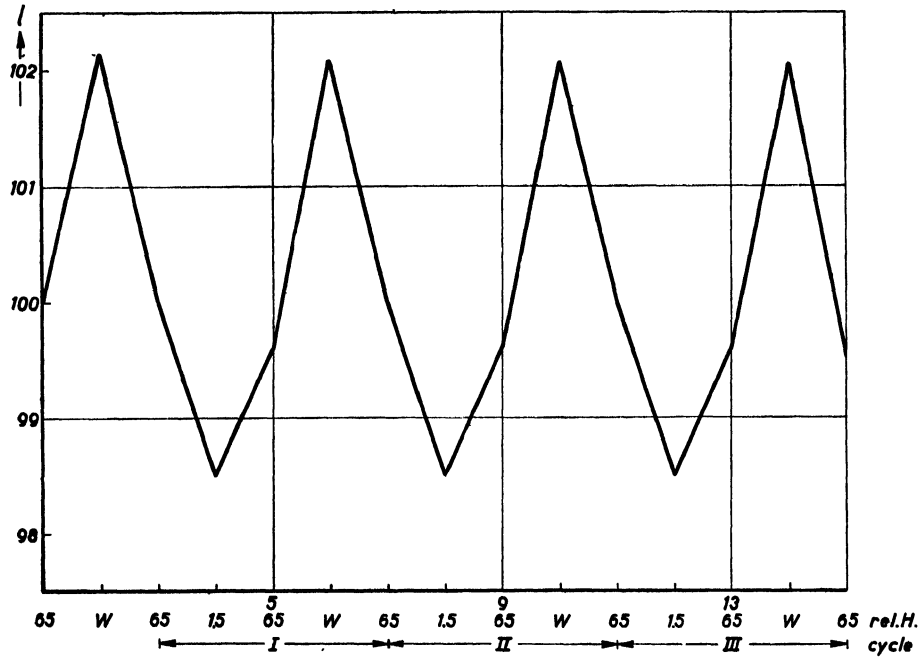


Fig. 220. Hysteresis shrinkage of a rayon filament.

filament by about 0.5% ("negative shrinkage"). Thus the ordinary cycle of 65% rel. hum. — water — 65% rel. hum. may cause the filament to lengthen

if it has previously been drier than 65% rel. hum. The phenomenon may superpose a retraction shrinkage.

The explanation of hysteresis shrinkage would seem obvious. In Fig. 220 the filament contains more water in conditions 3, 7, 11, etc., owing to hysteresis of sorption, than in conditions 5, 9, 13, etc. We know by Fig. 59 that at a given regain, the degree of swelling — and, therefore, also the length and the diameter of the filament — will acquire a fixed value, whether the filament be conditioned by sorption or by desorption.

All the same, calculations made with reference to model filaments, on which we shall not dwell here, show that hysteresis shrinkage is approximately three times greater than that which can be computed from the difference in degree of swelling. Thus there is, in addition, an hysteresis in the dimensional changes of the filament, which is also manifested in anomalous values for the anisotropy of swelling at low regains. *Speaking generally, at below 65% rel. hum. the changes in length become relatively too large and those in diameter too small.* Hence hysteresis shrinkage is likewise closely associated with the so-called "Trockenstarre" of the gel (Cf. Part III, Chap. VIII § 4.1).

What we call "negative shrinkage", then, depends upon the conditions of drying, as is demonstrated clearly by the experiment represented by Fig. 221, when the filament was dried in conditions 5, 8, 12, 16 in ever drier air at 20°.

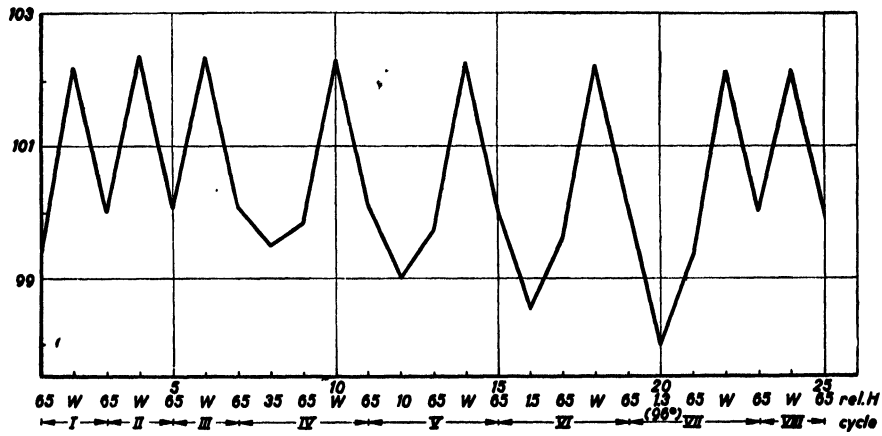


Fig. 221. Hysteresis shrinkage of a rayon filament as a function of the drying conditions.

The negative shrinkage from 9 to 11, 13 to 15, etc. becomes progressively greater. That the drying temperature also plays its part is clear from the last cycle, where the filament was dried in condition 20 at 96° and 1.3% rel. hum. We cannot fail to notice that the filament shrinks almost as much in the drying process from 18 to 19 as from 19 to 20, although the regain diminishes in the former case by about 80% and only by roughly 15% in the latter. This means that the differential anisotropy of swelling of the filament (see p. 395)

diminishes while it is drying. We were able to estimate the relative changes in diameter and length of rayon filaments according to their regain by a series of volumetric analyses which will not be reproduced here, but the result is shown in Fig. 222.

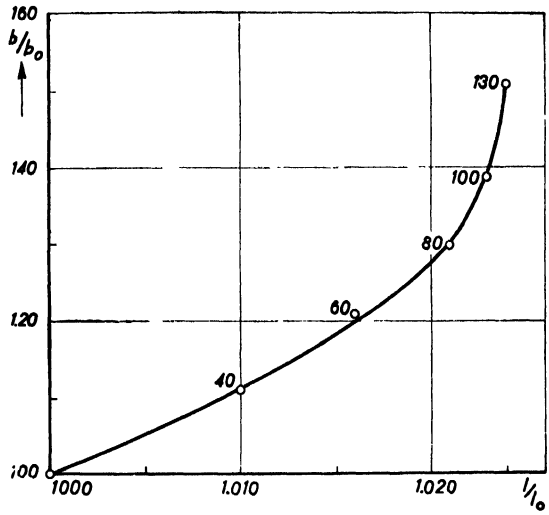


Fig. 222. Relative changes in dimension of a rayon filament, depending upon the regain; l and b = length and diameter; l_o and b_o = length and diameter with 20% water. The numbers are the water content in per cent.

In practice it will as a rule be necessary to allow for a super-position of hysteresis and retraction shrinkages. By employing suitable tests, the nature of which follows from the foregoing, they can usually be determined individually.

CHAPTER XVIII

TECHNICAL QUALITY AS RELATED TO THE STRUCTURE OF NATURAL AND REGENERATED FIBRES

§ 1. INTRODUCTORY REMARKS

The question as to what conditions determine the practical value of a fibre as a textile raw material is not an easy one to answer; indeed, at the moment it cannot be satisfactorily answered at all. Moreover, to discuss it we should have to encroach upon purely technological ground and thus wander beyond the confines of our province.

Nevertheless, even fundamental research has shown a growing tendency, especially in recent times, to grapple with this matter, as also with the problem of the connection between valuable technological properties and fibre structure. This is the natural result of the enormous development of the artificial fibre industry, which set up as its aim to provide the best possible fibres for an almost unlimited number of purposes. Whereas manufacturers were content to regard an enquiry into this cause and effect in natural fibrous materials as more or less academic, they were very much concerned to know what prospects there were of improving the properties of regenerated fibres by manufacturing tactics, or of producing new types of high-grade artificial fibres.

At the same time, it was becoming an ever more urgent necessity to devise methods by which the practical value of a fibre could be tested in the laboratory, or to translate the signification of existing methods of test into terms expressing practical value.

A short review of the present position may fittingly serve as the subject of the concluding chapter of this book, confining ourselves to some general points of view related to our material. This field of enquiry, however, is still in the early stages of development and is for the most part mainly speculative in character.

We shall draw largely on a paper published recently by *E. Franz, F. H. Müller* and *E. Schiebold* [1], with whose views the author substantially agrees.

§ 2. TECHNICAL QUALIFICATIONS OF GOOD FIBRES

2.1. Strength

It has long been recognized that, although tensile strength is an admirable and appreciated quality, it is by no means always essential to the practical

[1] *E. Franz, F. H. Müller* and *E. Schiebold* Kolloid-Z. 108 (1944) 233.

value of a fibrous material. It has been found, with cellulose regenerated fibres especially, that increased strength by no means necessarily implies an improvement (see Part II, Chap. VI § 3 and § 6). As a rule, practical needs are met by other properties.

2.2. Extensibility or Elasticity.

A textile fibre must be extensible to some extent, but the exact requirements have never been precisely formulated. They may also depend upon the particular application of the yarn in question. Extensibility is required to be neither excessive nor inadequate and should, if possible, be elastic in character. At present, however, nothing is to be made of these summary stipulations. Very little progress has yet been made in regulating these properties of cellulose regenerated fibres to suit a given demand.

2.3. Bending Resistance.

Fibres must not be hard and brittle, otherwise they are inconvenient to handle and produce too hard a fabric; in other words, they should be flexible. Under the strain of bending to which they are actually subjected, they should not far exceed the limits of pure elasticity. The fibre should, moreover, be able to withstand repeated flexions. As the bending radius concerned is fairly small, and there will therefore be considerable extensions and compressions, this is a requirement often not easy to fulfil, the less so the thicker the fibre is. The minimum requirements for periodic strain have not yet been gone into. Nor is there as yet any unanimity of opinion as to what structural principle would best equip a fibre to withstand this ordeal.

2.4 Fatigue Test

The use of rayon in cord for the motor tyre industry, which has come very much into favour of late years, led to the introduction of the fatigue test[2]. On an appliance specially constructed for the purpose, the threads are exposed to rapid alternations of tension and release, the time which elapses till they break under this strain being recorded. It is still not clear what relevance this test has to the structure of the thread, but there seems to be some connection between the thickness of the skin of rayon (see Part II Chap. 1, § 2) and the fatigue test, in the sense that thicker skins produce better results. It has also been found that the kind of cellulose used as raw material for the manufacture of viscose has something to do with it (linters produce better results than wood cellulose), though it is by no means certain whether it is the average degree of polymerization or the chain length distribution which is the determinative factor.

2.5. Resistance to Wear and Tear

Here again it is difficult to formulate the demands. Fibres have been rubbed and chafed in order to discover how this maltreatment affects them and

[2] Cf. e.g., *R. C. Waller* and *W. E. Rosevaere;* J. Applied Phys. 17, (1946) 482.

there has often been found to be some fibrillar splitting (see Part II, Chap. I, § 2). Obviously, fibres should be endowed with the necessary properties to offer at least minimum resistance to such treatment.

2.6. The Effect of Moisture upon the Mechanical properties

Contact with water should not unduly modify the mechanical properties of the fibres mentioned. Artificial cellulose fibres are among those whose tensile strength suffers considerably upon wetting and this seems to be inherent to their structure. Numerous attempts have been made to improve upon this undesired property by aftertreatments which aim at reducing swelling, e.g., by crosslinking agents or impregnation with resins. The succes has thus far remained very limited and treatments of this kind often impart other undesirable properties to the fibre. It would seem that a skilful improvement of the intrinsic structure of the fiber is possible in principle and would be more promising (cf. Part II, Chap. VI § 3.3).

2.7. Sorption of Water (Swelling)

For hygienic reasons fibres should be capable of absorbing moisture with evolution of heat. Then, in the positive heat change accompanying abundant perspiration, the clothing shields the body from sudden, excessive cooling. The same effects would result from emerging, in winter, from a heated room, where the air is dry, into the colder outdoor air of higher relative humidity[3]. Investigations respecting the heat-insulating properties of clothing materials in the Finsen Laboratory (Denmark) have produced some further surprising results[4]. Woollen and silk fabrics were found to insulate heat far more effectively when damp than when dry. This property was lacking in vegetable and synthetic fibrous materials, from which facts it is plain that there are still many operative factors which we do not yet understand.

2.8 Resistance to Thermal and Chemical Effects

The fibres have to meet the customary demands in respect of washing, drying and ironing. And their stability upon exposure to light and perspiration has also to be taken into account.

§ 3. LABORATORY TESTS

Strenuous efforts have been made, especially in latter years, to enlarge the stock of tests designed to assess the practical utility of a fibrous material. This field of enquiry, which is only at its beginnings, bristles with difficulties. Practical wear and washing tests have been carried through again and again under carefully controlled conditions, but even so experience has shown it

[3] Cf. *A. B. D. Cassie* and *S. Baxter*, J. Text, Inst., 34, (1943) T 41; 37, (1946) T 39.
[4] See Zellwolle und Kunstseide 2, (1944) 160.

to be exceedingly difficult to make any conclusive pronouncements. We cannot enter further into the matter here and must refer the reader to the literature [5].

§ 4. GOOD FIBRE PROPERTIES AND STRUCTURE

So far as our present knowledge goes, we know that good fibres can be built up only from substances containing chain molecules [6]. Moreover, the molecular chains must be selectively orientated in the fibre axis. In the isotropic state, organic glasses, such as polystyrene and polyamides, are unusable, brittle fibres, which do not acquire good properties until they have been elongated. The same applies to cellulose fibres. They should contain only a moderate number of chemical cross links. If, for example, fairly large amounts of multivalent compounds are added during the condensation of dicarboxylic acids and diamines, very brittle fibres will result. If too many oxymethylene bridges are built into the cellulose fibre, it will be spoiled, for, though they reduce its swelling capacity, it has to forfeit too much of its bending strength.

This does not imply that all long-chain substances are suitable fibre producers. There is insufficient cohesion between the chains of rubber-like substances. Many other linear polymers, like polystyrene, are unsuitable because they soften at too low a temperature and then become like rubber. If heated to a high temperature in their orientated state, they would show signs of retraction and, therefore, pronounced contraction.

There only remain, then, the polymeric chains possessing powerful intermolecular cohesion; these are, for instance, cellulose, polyamides and certain proteins. They are, moreover, usually able to acquire the crypto-crystalline state, i.e., to form crystalline regions. In these the cohesion between the molecules is particularly firm and lasting and the intermediate amorphous components of the fibre may be regarded as the carriers of the required flexibility and elastoplasticity. At very low temperatures, even these

[5] *M. H. Houston* and *H. Fletcher*, Trans. Kansas Acad. Sci. 43, (1940) 309.
H. Bohringer; Die Kunstseide 23, (1941) 194; Melliands Textilber. 22, (1941) 358, 409; 24, (1943) 347; Klepzigs Textil Ztg. 44, (1941) 1204.
R. Stoll and *F. Ball*, Melliands Textilber., 21, (1941) 270; 22, (1941) 125; 23, (1942) 221, 317, 373; 24, (1943) 211; 25, (1944) 344, 364, 385 (1944).
E. Wagner, Melliands Textilber., 22, (1941) 633; 23, (1942) 395; 24, (1943) 129; 25, (1944) 378, 396; 27, (1946) 84; 28, (1947) 30, 65, 103.
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H. Biczyko; Zellwolle, Kunstseide, Seide 47, (1942) 334.
E. Franz; Die Chemie 56, (1943) 113, 132.
Added in Proofs: Recently a review of Textile Testing in Germany by *H. F. Schiefer, L. Fourt* and *R. T. Kropf* has appeared in Textile Res. J. 18, (1948) 18.

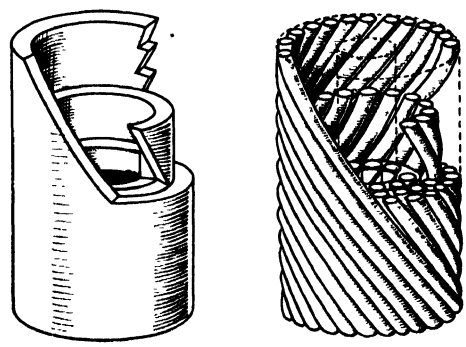
[6] Fibres spun from glass are, admittedly, used for special purposes, but they have no very outstanding properties as textile raw material. For instance, their properties endow them with relatively little powers of resistance to the stress and strain of bending

components "freeze"; thus all fibres become hard and brittle. The same thing happens in the very dry state. We have already seen how water acts as a "softener" in cellulose and promotes the "internal mobility" of the amorphous components. The same principle of structure is found in the possibly best synthetic fibres so far known, polyamide fibres [7]. At sufficiently low temperature (between -70° and -100°), well-orientated rubber fibres would also probably constitute convenient fibrous material. At any lower temperature they would again become too brittle.

Comparison of synthetic cellulose fibres with cotton fibres (those fibres pre-eminently suited to the technical needs of textile manufacture) shows that the type of structure we have just been discussing is by no means the sole decisive factor calculated to endow the fibre with the desired properties. The morphological structure is at least as important a factor. In this respect Nature provides us with an example which, admittedly, it is very difficult to copy.

Maybe the ribbon shape of the cotton fibre in itself constitutes a favourable moment under the strain of bending. There are various ways of producing this shape in artificial fibres, either by spinning through slitted nozzle orifices, or by spinning "hollow fibres", tubular systems which are afterwards flattened while drying and then become tapes or ribbons with a lumen.

The special morphological micro-structure found in cotton fibres, however, is a far more important matter. It represents a "super-structure" which it is impossible to obtain in synthetic fibres, in which only a statistical orientation of the molecular chains and crystallites is brought about.



a b

Fig. 223. Indication of a) the cylindrical lamellar structure of a natural cellulose fibre, and b) the location of the fibrillae in diagram.

We shall here briefly discuss the structure of cotton fibres with reference to recently published investigations by *H. Dolmetsch, E. Franz* and *E. Correns* [8] and that mentioned at the beginning of this Chapter by *Franz, Müller* and *Schiebold* [9]. Fig. 223 shows in diagram the structural principle of natural cellulose fibres, according to which the fibres consist of cylindrical telescoped lamellae, each of which, again, is composed of spirals of fibrillae. In the latter the molecular chains are orientated almost ideally and consist largely of crystallized substance. This arrangement would seem to be a very

[7] *K. Hess* and *H. Kiessig*, Z. physik. Chem. 193, (1944) 196.
[8] *H. Dolmetsch, E. Franz* and *E. Correns*, Kolloid.Z. 106, (1944) 174.
[9] *E. Franz, F. H. Müller* and *E. Schiebold*, Kolloid-Z. 108, (1944) 233; cf. *C. M. Conrad* and *E. E. Berkley*, Textile Res. 8, (1938) 341.

propitious one for good mechanical properties. The natural fibre, as related to the synthetic variety, may perhaps be likened to a plaited braid as compared to a massive thread.

When the natural fibre is flexed, the cylindrical lamellae will be able to slide over each other to a certain extent and the spirals will be able to enlarge or narrow their pitch somewhat. Irreversible deformations will be easier to avoid than in a massive structure. The demand for great breaking strength, elastic extension and high reversible flexibility is thus met and is compatible with a relatively small proportion of amorphous substance.

We do not yet know whether the fibrillae, or the lamellae, are separated by a foreign substance,, or by amorphous cellulose. In any event, the lamellae, as likewise the individual fibrillae, are parted with relative ease in the customary swelling processes. More drastic measures (swelling with degradation) will bring about, in addition, those familiar lateral cleavages which we have often had occasion to mention (Part I, Chap. I, § 1). The fibrillae then break up into fragments of a certain length (dermatosomes, according to *Wiesner,* cellulose particles, according to *W. Farr).*

Franz, Müller and *Schiebold* are inclined to associate this with pre-formed fragments. They developed an hypothesis, according to which crystallites of the same length are arranged to a regular pattern in the fibrillae, separated by intermediate amorphous regions (for which see page 168). Each fibrilla, again, is supposed to consist of pliant sections, like a string of pearls.

It will be evident that so specialized a microstructure can never be achieved in artificial fibres by the practicable technical means at our disposal. It was stated in Part II, Chap. VI, § 6 that with highly orientated model filaments spun from viscose, it is possible to heighten resistance to flexion by providing a micellar texture arranged in spirals. But even this can scarcely be realized economically in technical fibres. On the other hand, the good properties of natural silk and synthetic polyamide fibres are there to show that a complicated morphological structure is not indispensable to good fibres. The question arises, however, whether any such refinements can be dispensed with where artificial fibres from cellulose are concerned. The answer which Nature gives, when consulted, seems to be in the negative. There, too, where cellulose fibres are of simpler structure, as, for example, in ramie fibres, they are found to possess fewer favourable textile properties. As against great breaking strength, the resistance to bending is inferior.

Nevertheless, the great commercial success of artificial cellulose fibres is proof enough of their usefulness for very many purposes. Though they may be superseded by other, newer artificial fibres for some particular use or uses, they will hold their ground elsewhere, or conquer fresh territory. They are being steadily improved and it is hardly to be conceived that they will ever have to abandon the eminent position they still hold at this time.

APPENDIX

The Crystalline-Amorphous Ratio in Cellulose Fibres

Since this book went to press some fresh evidence has come to light from the examination of cellulose fibres by X-rays, the principles of which investigation were dealt with in Part II, Chap. VIII. Seeing that it is the crystallinity of cellulose upon which general interest is at present centred, the author thought it would be as well to record briefly the results of these supplementary investigations in an appendix[1].

Figure 224 reproduces in a convenient form a nomogram[2] comprising both the results reported in Part II, Chap. VIII, and the new ones.

The value of A_m is plotted on the ordinate against the value of I_{cr} on the abscissa (for the signification of these values see Part II, Chap. VIII). The average results have likewise been plotted for five native fibres and for nine rayons (borrowed from Table XXXVII, p. 314) (see crosses in heavy type). A straight line has been drawn through these two points, carrying a scale for the percentage of crystalline matter. A dotted line indicates the spread exhibited by the individual measurements, from which the two calibration points were derived.

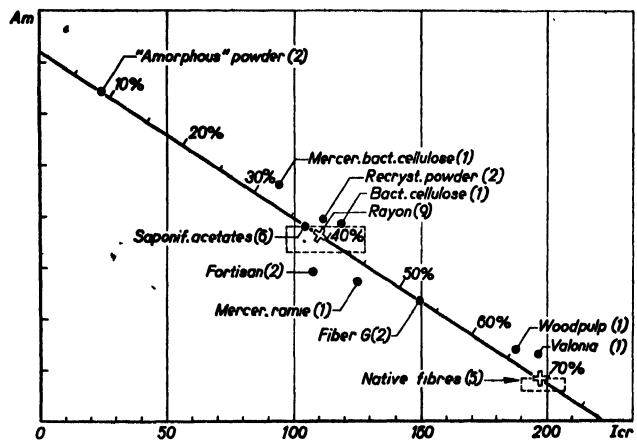


Fig. 224. Nomogram of crystallinity of various cellulose objects derived from X-ray measurements. The scale along the slanting line indicates the percentage of crystalline matter. (The number of determinations upon which the point is based is given between brackets for each object.)

If the premisses of the investigation are correct, the points for all other cellulose objects should, within the experimental error, likewise fall upon this line. It will be seen that this condition is satisfied. We shall now briefly consider the latest observations.

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[1] For fuller details see a forthcoming publication by *P. H. Hermans* and *A. Weidinger* in J. Polymer Sci. 1948.

[2] This form of representation was suggested by Prof. *W. Kast*.

The point representing an observation on the cellulose of the cell wall of the marine algae *Valonia* comes quite near to that of the native fibres. The crystallinity of this object can be classed between woodpulp and native fibres.

Fibre G (a new high-tenacity rayon produced by Du Pont)[3] is distinguishable from all other rayons hitherto examined by its unusually high percentage of crystalline matter (50 — 55 per cent.).

The average figure for the six samples of saponified acetate rayon is within the spreading area of the nine other rayons. These saponified acetates were prepared from the same sample of a commercial acetate rayon by different procedures of saponification. The products of saponification in 3 N ammonia at 100° exhibited the spectrum mainly of cellulose IV (with a little cellulose II). Saponification at lower temperature produces less and less cellulose IV. At 40° C and lower one gets cellulose II only. The percentage of crystalline matter, however, appears to be constant within experimental error, whatever the ratio of cellulose II to cellulose IV may be. Another sample of acetate rayon was "recrystallised" by heating in methanol at 100° C prior to saponification. The X-ray diagram of acetate thus treated is more sharply defined and more profusely lined than that of the original acetate. Nevertheless, after this so-called recrystallised product has been saponified at room temperature, the resulting fibre again has the same percentage of crystallinity as the other saponified products.

The "amorphous powder" (top left-hand part of Fig. 224) was obtained by dry-grinding viscose rayon[4]. The X-ray observations show that it contains less than 10 per cent. crystalline substance. The relevant point nicely fits the straight line in Fig. 224 and so does the product obtained after treating this powder with hot water, whereby a true recrystallisation takes place and the crystallinity is raised to 35—40 per cent. It could be shown that the difference between the heat of wetting of the original and that of the recrystallised powder is in quantitative conformity with these figures.

The majority of rayons having an equal percentage of crystallinity, the method for the determination of total crystallinity cannot serve to differentiate one rayon from another, although it is known that these fibres show huge variations in other physical properties. It has, however, been found that the quantitative evaluation of the X-ray pictures does provide another means of differentiation after all if note is taken of the relative intensities and of the width of the two principal interferences (the two peaks which can be seen on the photometer curves reproduced in Fig. 120 B, p. 313).

In native fibres the relation between the integrated intensity of the second peak and that of the first is always more or less constant and not far from the theoretical value which *Andress* calculated from the lattice structure. In the different rayon specimens, however, this relation is seen to vary considerably

[3] Cf. *J. V.* and *S. L. Sherman*, The New Fibers, v. Nostrand, New York 1946, page 221.
[4] *P. H. Hermans* and *A. Weidinger*, J. Amer. Chem. Soc. 68, 2547 (1946).

and, moreover, always to be substantially larger than the theoretical value following from *Andress'* calculations.

It has been pointed out (cf. Part II, Chap. V § 2.2 and Fig. 77) that the first peak corresponds to the lamellar plane of the ribbon-shaped crystallites (A_0) and the second to a plane (A_3) normal to the former. Closer examination shows that the variations are mainly due to variations in A_0, the intensity of A_3 being constant to within about 10 per cent.

The high value of the intensity ratio indicates that lateral order of the molecular chains according to the A_3 plane is favoured against that according to the A_0 plane, which is only another way of stating that the crystallites are preferentially lamelliform. Cohesive forces between the A_3 planes are very much stronger than those between the A_0 planes. This preferential arrangement in accordance with the A_3 planes may likewise prevail in the transitional areas between the crystalline and amorphous regions (see Fig. 120 C on page 316).

What the variations in the intensity ratio of the two peaks reveal is that the difference of one rayon specimen from another consists in the degree in which the Ao order is inferior to the A_3 order. *The differences between the various rayons are differences in the distribution of lateral order rather than such in the total degree of orderliness* (which is approached in the measurements of the crystallinity percentage).

The evaluation of the X-ray pictures also shows that the sharpness of the A_3 line varies little in the different rayons, whereas that of the A_0 line varies very much.

A positive correlation exists (see Fig. 225) between the ratio of the integrated intensities A_3/A_0 and the half-width of the A_0 line (which, in turn, is a measure of the sharpness of the line). A sharper line (lower half-width) means that the average thickness of the lamellae and/or the definition of lateral order in this direction is better.

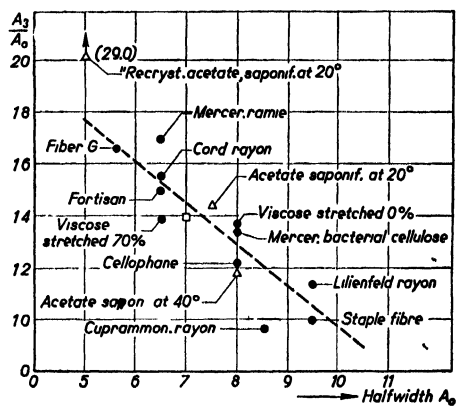


Fig. 225. Correlation between the intensity ratio A_3/A_0 and the half-width of the A_0 line for various rayons, measured in mm on the photometer curve (magnification 3.9 x; distance sample to film 40 mm).

It follows from Figure 225 that, if the average thickness and/or perfection of the lamellar order increases (A_0 line sharper), the total number of well-ordered A_0 plane contacts diminishes (integrated intensity of A_0 drops), the total mass of lattice-ordered matter remaining constant. In other words, thicker and better-formed lamellae involve a smaller total number of ordered A_0 plane contacts.

The explanation may possibly be something like this: Upon formation of the cellulose gel, the A_0 planes, whose cohesion in the lattice is weakest, will tend to be the least well ordered. The A_3 contacts enjoy preference and their number is almost constant.

If by some process of "recrystallisation" lamellar order is improving in certain nuclei, tensions will arise in the network in the immediate surroundings of the nuclei and other (possibly smaller, or imperfect) lamellae will be torn loose. Order according to the A_3 planes held together by much stronger forces is affected far less, if at all, and is approximately constant under all conditions. This suggested explanation would seem to find support in the behaviour of the saponified, preliminarily re-crystallised acetate (triangle in the left-hand top part of Fig. 225). Its A_0 line is unusually sharp and it also has very low total intensity, amounting to no more than 3 to 4 per cent. of that of the A_3 intensity. The saponified acetates not previously re-crystallised occupy, by contrast, average positions in Fig. 225.

It would seem that the "recrystallisation" of the acetate, as provoked by previous heating in methanol, involves a similar process of redistribution of lateral order, rather than an increase in the total amount of ordered substance. Provided the process of recrystallisation be interpreted strictly in that way, we may perhaps still in a sense associate various degrees of recrystallisation with the various rayon specimens investigated. It then appears that the highly orientated rayons (where some kind of improved order is most to be expected) actually come in the upper left-hand part of Fig. 225 (except Lilienfeld rayon, which seems to represent a special case).

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