of inactivation was less at the latter distance. This greater efficiency is possibly due to the fact that the light is more nearly a point source at 38.1 cm. than at 19.05 cm., causing the radiation from all parts of the radiator to be more effectively utilized. The further the source from the object, the less is the angle of incidence. As the angle of incidence becomes more acute the radiations become more effective. Therefore, the energy multiplied by the time required to destroy enzyme activity does not necessarily give a constant when intensity is varied by changing the distance between the source and the object as was done in this investigation.

The efficiency of a particular source in destroying enzyme activity is related to the type of radiations emitted. Published data[10] on the ultraviolet absorption spectrum of papain show a peak of absorption occurs at about 2750 Å. A relatively small amount of absorption occurs in the vicinity of 2500 Å. and practically no absorption above 2900 Å. Below 2500 Å. there is an increasing amount of absorption to 2400 Å. as far into the ultraviolet as has been investigated.

Since only light that is absorbed is capable of photochemical action, it follows that light having radiations at 2750 Å. should be the most effective in the destruction of the activity of papain.

Light which consisted chiefly of radiations above 2900 Å. (the filtered Uviarc) proved to be much less effective in the destruction of papain activity than the radiations distributed over the whole ultraviolet range. This is also true for radiations largely at 2537 Å. (the Sterilamp). These observations are in agreement with the conclusions reached from the absorption spectrum.

Summary

1. Quantitative data have been obtained for the photochemical inactivation of trypsin and papain solutions using various ultraviolet light sources.

2. The energy required to inactivate a papain solution is dependent on the wave length and the intensity of the ultraviolet light and the angle at which it strikes the solution.

CHICAGO, ILLINOIS RECEIVED APRIL 13, 1944

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[10] H. H. Darby, *J. Biol. Chem.*, **139**, 721 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY MEDICAL SCHOOL]

Elasticity of Keratin Fibers

BY HENRY B. BULL AND MARTIN GUTMANN

Some protein fibers are relatively non-elastic. Silk, for example, is such a fiber and X-ray diffraction studies indicate this fiber to be extensively crystallized with the extended peptide chains lying parallel to each other. On the other hand, there are several protein fibers which under the proper condition show long range elasticity. Notable among these elastic fibers are hair and wool. The elasticity of such fibers can only be understood by considering them as co-polymers of a great many polymerizing units. The presence of these diverse amino acid residues or polymerizing units in the fiber prevents the close fitting of the straightened peptide chains and leads to a great deal of kinking in the fiber; the stretching of such a fiber involves the unkinking of the peptide chains.

We wish to describe in this paper some experiments on the stretching of human hair and to report some conclusions which we have drawn from these experiments regarding the elastic deformation of hair.

Experimental.—Human hair was used in all of our experiments. A homogeneous lot of long natural hairs was obtained from a commercial dealer. The hair was exhaustively extracted with alcohol, with ether and finally washed with water and electrodialyzed. It was dried and stored in a desiccator over calcium chloride.

The tension apparatus used to stretch the hair was designed to apply a load at a uniform rate of increase or of decrease of load. The rate of application and of release of the load was set at 0.470 g. per minute. The adjustment of the length of the stretch of the hair to the load was entirely automatic and very nearly instantaneous. The hair was bathed in water while in the apparatus and the tube containing the hair under examination was surrounded by a water jacket through which water at any desired temperature could be circulated. The temperature selected for our experiments was 25°. It is not our purpose to describe our tension apparatus in detail at this time.

Results.—Figure 1 shows a typical stress-strain curve of a human hair both for extension and for contraction.

It was first pointed out by Speakman[1] that the stress-strain curves for successive extensions of a single fiber were very nearly identical under the same conditions of temperature, moisture, *p*H and rate of loading provided the extension did not exceed about 20% of the original fiber length. From our experience we can add that the agreement between successive 20% extensions improves with each successive extension. We are also able to conclude that not only is the stress-strain curve for 20% extension very nearly reproducible but likewise the stress-strain curve for

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[1] Speakman, *Proc. Roy. Soc.* (London), **B103**, 377 (1928).

contraction shows a high degree of reproducibility.

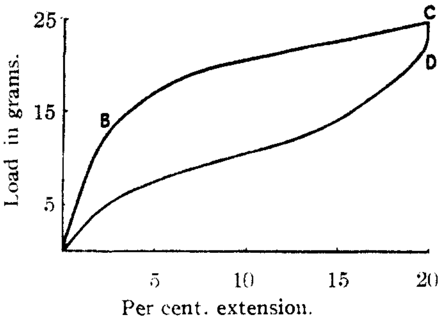

Fig. 1.—Stress-strain curve for a human hair: Upper curve is for extension, while lower curve is for contraction.

The area under the stress–strain curve when multiplied by the acceleration of gravity is evidently equal to the work of extension or of contraction depending upon which curve is considered. The work of extension or of contraction offers a convenient basis for comparison of stress-strain curves. For example, the data plotted in Fig. 1 are for the second extension of this particular hair and based upon 100 centimeters of fiber, 3.80 × 10^5 ergs of work were required for extension to 20% while 2.13 × 10^5 ergs of work were gained back when the hair contracted. The third extension of this hair required 3.79 × 10^5 ergs and 2.11 × 10^5 ergs were returned upon contraction. The work of extension was thus 99.66% of the second extension and the work of contraction was 99.35% of the second contraction. This satisfactory reproducibility of the work of extension and of contraction under the same conditions is very valuable in the study of the influence of various physical and chemical agents on the elasticity of hair.

In order to determine as closely as possible the extension which leads to irreparable damage to the hair, a fiber was stretched 15% of its length. After a rest period in a relaxed condition, it was reëxtended at 5% intervals up to 40% stretch with relaxed recovery periods of several hours between each successive extension. The area under the initial 15% stretch curve was assigned the value of 100 and the area under the curve up to 15% stretch for the 20% extension was then compared with the original 15% extension. This type of comparison was made between the area under the stress–strain curves up to 15% stretch at 5% intervals through the 40% extension. These comparative results are shown in Fig. 2. Apparently, no permanent damage is done to the hair up to about 18% extension. Beyond this extension however, the work of successive extensions becomes less and a permanent deformation of the hair results. The extension to 40% of the original length of the hair resulted in a 1.5% elongation of the hair in its relaxed state. The intermediate extensions gave values between zero and 1.5% elongation; the permanent elongation increased with increasing stretch.

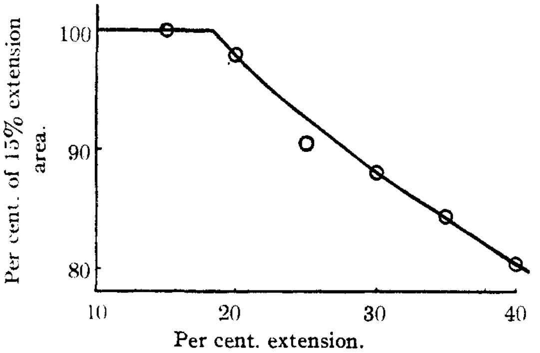

Fig. 2.—Showing the 15% work of extension as a function of the stretch.

As we have seen, the extension and the contraction curves form well defined and characteristic loops. The process of extension and contraction is, however, an irreversible one. In order to explore this question in somewhat more detail, the following experiment was performed: A reproducible extension–contraction loop up to 20% extension was established. The hair was then extended to 7% of its original length and the load released at the standard rate. This was repeated at 13.5% extension. The hair was then extended to 20% of its original length and allowed to contract to 11.5% of its length and reëxtended. This process was repeated at 5% extension. These results are plotted in Fig. 3.

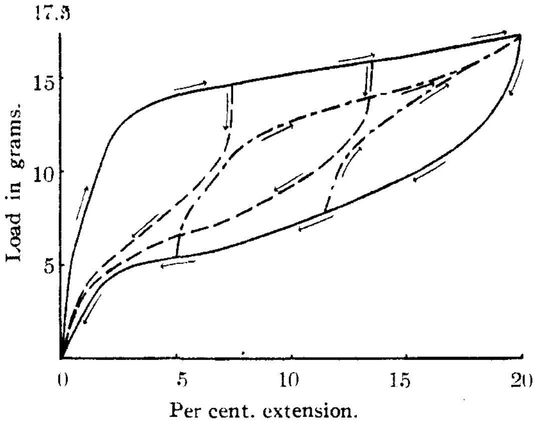

Fig. 3. -Intermediate extension–contraction loops within a 20% extension–contraction loop.

It is evident from Fig. 3 that over a wide range of the extension and contraction of hair, both the extension and the contraction are irreversible. There are two regions, however, in which we have reversible extensions and contractions. From 0 to B and from C to D the contraction follows through the same curve as does the extension (see Fig. 1).

It becomes apparent to anyone who studies the extension and the contraction of hair that the rate of application or of the release of the load is very important in determining the deformation of a hair under a given load. At certain extensions the influence of the rate of loading is more conspicuous than at other extensions. From 0 to B (Fig. 1) which is the so-called Hooke's law region, the fiber quickly comes to a definite extension under the application of a given load and there is no further extension. Beyond point B, however, the extension observed under a given load depends very largely on the rate of application of this load and an equilibrium extension is never attained in any finite time. The rate of release of the load is also, in general, important. From C to D (Fig. 1) the fiber contracts to a definite length rather quickly as the load is released but from D to 0 the length of the fiber is a function of the rate of release of the load.

We have attempted to establish as closely as possible the "equilibrium" loads at which the fiber neither contracts nor extends for a series of extensions and contractions. To do this we applied the load at 0.470 g. per minute to a selected extension. We then released the load and observed the load at which the fiber begins to contract. We immediately started the addition of the load and noted the load at which the fiber begins to extend again. Evidently the "equilibrium" load at which the fiber will neither extend nor contract must lie between these two loads and it is possible by this method to make a rather close estimate of the "equilibrium" loads throughout the extension and contraction regions of the reproducible extension–contraction loop. In Fig. 4 are shown "equilibrium" loads determined in this manner for a hair. Also shown is the extension–contraction loop up to 20% extension for this same hair at the standard rate of application of the load.

The work of extension of the hair shown in Fig. 4 at 0.470 g. per minute was 4.13 × 10^5 ergs while the work of extension at "equilibrium" loads was 3.47 × 10^5 ergs. This means that 16% of the extension at 0.470 g. per minute was due to frictional losses. Correspondingly, 10.5% of the energy gained from contraction at "equilibrium" loads was loss through internal friction of the hair when the hair was unloaded at 0.470 g. per minute. The difference between the energy of extension at "equilibrium" loads and that of contraction at "equilibrium" loads must represent heat energy which is evolved in the extension–contraction loop and has nothing to do with internal frictional losses since the extension of a hair at "equilibrium" loads should be independent of friction of any kind. The evolution of this heat, which amounts in the above case (Fig. 4) to 26.9% of the total "equilibrium" energy of extension, results from the essentially irreversible character of the extension–contraction process. Presently we shall attempt to interpret this heat loss in terms of the mechanism of the extension process.

It appeared profitable to study the influence of temperature on the extensibility of hair. It is important, however, that the temperature not be raised so high as to lead to a permanent damage to the hair structure. We extended a hair at 25° and established a reproducible stress–strain curve. We then reduced the temperature to 15° and measured the work of extension and of contraction. Assigning a value of 100 for the work performed or gained at 15°, the relative values at 25° are shown in Table I.

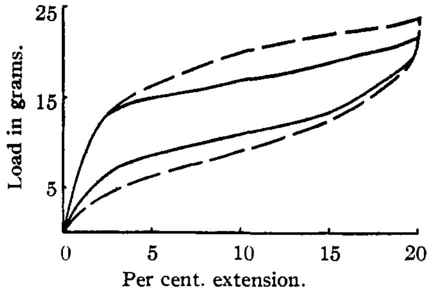

Fig. 4.—Stress–strain curves for human hair. The broken lines are for the standard rate of application and release of the load, while the unbroken lines represent the deformation at "equilibrium" loads.

TABLE I

WORK TERMS AT 25° IN % OF THOSE AT 15°

Equilibrium contraction	109.4
Internal friction of contraction	93.8
Irreversible work	87.3
Equilibrium extension	102.5
Internal friction of extension	94.7

Possibly a more illuminating experiment to illustrate the influence of temperature on the elastic properties of hair was performed in the following manner. A hair was stretched 2% of its original length at 25° and the "equilibrium" load determined. The temperature was then lowered to 12° and the "equilibrium" load at this temperature was measured. The temperature was then returned to 25° and the "equilibrium" load redetermined. This type of experiment was done at 12% extension on the extension limb of the 20% reproducible loop as well as at 12% extension on the contraction limb. Load was then applied to obtain a 35% extension and the "equilibrium" loads as a function of the temperature evaluated at this extension. These results are shown in Table II.

TABLE II

"EQUILIBRIUM" LOADS AS A FUNCTION OF TEMPERATURE AT VARIOUS EXTENSIONS

%. extension	Absolute load in grams at 25°	—Weight change in grams per degree— Increasing temperatures	Decreasing temperatures	Average wt. change per degree
2	7.75	−0.0324	−0.0121	−0.0222
12	11.58	− .0081	+ .0101	+ .0010
12	8.62	+ .0092	+ .0054	+ .0073
35	18.67	− .0037	+ .0120	+ .0042

In Table II the negative sign indicates that the load is antibatic to the temperature while a positive sign indicates that the two functions are symbatic.

Discussion.—Astbury[2] from X-ray diffraction studies has suggested that when keratin is stretched, a change from what he calls α-keratin to β-keratin is involved. The α-keratin is characterized by a repeating distance of 5.15 Å. along the fiber axis. The order of crystallinity of α-keratin is, however, quite low. A curious feature of the α- to β-keratin is that the β-keratin which is characterized by a 3.32 Å. spacing along the fiber axis, begins to appear only after the fiber has been extended in excess of about 20%.[3] In short, the extent of stretch which leads to a permanent deformation of the fiber coincides with the beginning of the production of β-keratin.

Astbury[2] has proposed various structures for α-keratin. It is not our purpose to enter into an extended discussion of this phase of the problem. Neurath[4] has shown that the first α-keratin structure advanced by Astbury and which involved the closure of a six-membered ring by a lactam–lactim or by a keto–enol shift does not provide sufficient space for the side chain residues. Astbury[5] has withdrawn these proposed structures for α-keratin and in their place has put forward a new structure which involves the coalescence of side chain residues above the peptide chain and below the chain in groups of three. The coalescence in groups of three is extended throughout the chain and gives rise to a definite type of folding of the chain. Astbury's newer structure for α-keratin provides for an extension of slightly over 100% in the conversion of α to β-keratin.

While it is indeed possible to extend a hair or a wool fiber 100% of its length, the extension has to be done in boiling water or in alkali and no doubt involves a rupture of the disulfide cross-links between the peptide chains with extensive slipping of the chains past one another. Actually, when a fiber is extended to 70% of its length in water the X-ray diffraction pictures show the transformation of α to β-keratin to be substantially complete at this extension.[3] Since this transformation of α to β-keratin does not start until the fiber has been extended to about 20% of its length, the transformation of α to β-keratin is essentially complete in the range of stretch from 20% to 70% of the original length. With a fiber which is 100 centimeters in length this corresponds to a stretch of 120 to 170 centimeters. In short, the transformation involves an elongation of about 40% of the stretched α-keratin structure. This is much smaller elongation than is required by Astbury's newer structure for α-keratin and the conclusion is drawn that Astbury's structure is too condensed and is not the principal structure of α-keratin.

In any discussion of the structure of α-keratin or of any other type of protein it must be realized that we are not dealing with a single isolated molecular chain but with chains surrounded on all sides by other chains; there is no doubt extensive interaction between these chains. Also keratin possesses a wide variety of massive polar and non-polar side chains. Indeed, it is primarily to these groups that keratin owes its elasticity. The presence of these diverse groups prevents the peptide chains from crystallizing in a regular structure such as is the case with silk. A great many different types of folds in the peptide chains of α-keratin are to be expected and probably no single type of fold of the peptide chain will satisfy the α-keratin structure; there is a great deal of randomness in the α-keratin fibers as the X-ray diffraction studies show.

It is possible to account quite simply for the observed 5.15 Å. axial spacing of the α-keratin by assuming a close packing of the amino acid residues along the peptide chain in the direction of the chain. That is, there has been a collapse of the chain so that while alternate residues extend above and below the chain, as in β-keratin, the residues touch each other in a direction corresponding to their shortest cross sectional axis. Likewise those below the chain now lie up against each other in the direction of their shortest dimension. The cross sections of the amino acid residues are not symmetrical; even the hydrocarbon chains have anisotropic cross sections when in an extended condition. Beyond the β-carbon atom of the residues, free rotation is present so that the residues can adjust themselves according to the stress applied to the chain. In β-keratin the peptide chains are not fully extended as is shown by the fact that the calculated identity distance[6] for an extended peptide chain is 7.2 Å. while the measured identity distance is 6.7 Å.; α-keratin represents a further departure from the idealized stretched peptide chain and is qualitatively the same structure as β-keratin.

The residues of a protein such as those of keratin must differ appreciably in their cross sectional dimensions and it is, therefore, curious that a definite axial spacing of 5.15 Å. is observed. While this spacing is not very sharp in the case of wool and hair keratin, feather keratin exhibits a considerable degree of sharpness. The uniformity of the axial spacing probably arises from the influence of the neighboring peptide chains, that is, it is necessary that the distance between successive residues in any given chain be uniform in order that interaction between the polar residues in neighboring parallel chains can occur to the greatest extent. This is only possible with a uniform residue spacing along the chain otherwise the polar residues would frequently be out of

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[2] Astbury, *Trans. Faraday Soc.*, **34**, 377 (1938).

[3] Astbury and Woods, *Trans. Roy. Soc.* (London), **A232**, 333 (1933).

[4] Neurath, *J. Phys. Chem.*, **44**, 296 (1940).

[5] Astbury, *Nature*, **147**, 1 (1941).

[6] Corey, *Chem. Revs.*, **26**, 227 (1940).

"phase" with the polar residues from a neighboring chain. Probably more important still, the sulfur atoms from neighboring peptide chains must react to form disulfide linkages. This condition likewise imposes a necessary uniformity on residue spacing.

Such a structure as pictured above would have a marked tendency to form layers of parallel peptide chains as Huggins[7] has suggested.

The pulling apart of two residues to the open spacing of the β-keratin represents an extension of about 30% (5.15 Å. to 2 × 3.32 Å.). While this extension is not sufficient to account entirely for the observed extension of 40%, it is of the right order of magnitude. The discrepancy can be accounted for in two ways. It is possible that the α-keratin structure does not consist exclusively of successive alternate residues in close packing but may at intervals along the chain involve a coalescence of residues of groups of three as pictured by Astbury. On the other hand, it is improbable that the straightening of the α-keratin is complete at 20% stretch and some stretching of the α-keratin continues to occur as the β-keratin is produced.

The general outline of the sequence of events in the stretching of hair from 20% elongation up to 70% is reasonably well understood and involves as we have discussed above the transformation of α to β-keratin. The question arises, however, as to what is happening prior to this transformation, *i. e.*, from zero to 20% elongation. We should like to outline a theory of this initial extension which does not involve the α to β-transformation.

The hair fiber exists in nature as a gel with strong as well as weak cross-links between peptide chains. Some of these cross-links are covalent chemical bonds such as disulfide bonds (about every eight amino acid residue of keratin in cystine). Many of the other bonds, however, are much weaker, consisting of hydrogen bonds and salt linkages. No doubt there is also considerable van der Waals interaction between the non-polar residues. This extensive interaction between the neighboring peptide chains leads to extensive kinking of the α-keratin fiber. Such kinks are no doubt long range and have a great deal of randomness in their occurrence.

At small stresses the fiber extends as a gel without rupture of any cross-links between peptide chains. This type of extension which is strictly reversible, embraces the Hooke's law region which extends from 0 to B (Fig. 1). As the fiber is extended beyond point B secondary valence bonds between the peptide chains are disrupted. In colloid parlance the hair gel has become a viscous sol. As long as a sufficient stress is employed to produce stretching the gel continues to be converted into a sol. The moment the load on the hair is decreased the hair resets to a gel. This behavior is strongly reminiscent of a thixotropic gel–sol transformation.

As the extended fiber is unloaded, the gelled fiber contracts reversibly until sufficient internal stress in the hair is built up to rupture the newly formed secondary cross links between the peptide chains. From this point on the hair contracts under its own internal stress as a viscous sol until finally all of the external load has been removed and the sol sets to the initial configuration the hair had before extension providing the stretch has not exceeded about 20%.

Let us return to a discussion of the energy changes involved in hair stretching. In this discussion we shall confine ourselves to the reproducible stretch region which as we have seen extends up to about a 20% stretch and involves essentially a straightening of the α-keratin structure. As we have concluded from the results shown in Figs. 1, 3 and 4 the extension and contraction of hair while reproducible up to about 20%, stretch is essentially an irreversible process in which heat is lost to the surroundings. We can account for this heat loss in the following way: At point B (Fig. 1) the gelled hair begins to be transformed into a viscous sol. This transformation involves the rupture of secondary valence bonds between segments of the peptide chains. This requires energy which is supplied by the external load falling through a distance under the influence of gravity. These bonds do not have the opportunity of reforming until the external stress is decreased. When the release of the external load is started the bonds then reform between new groups which have been brought into neighboring positions by the shifting of the peptide chains incidental to the stretch which the fiber has undergone. The forming of these new bonds converts the sol to a gel. A portion of the energy stored in these bonds by the stretch is then released in the form of heat. As the fiber is progressively unloaded the internal stress becomes larger until it is sufficient to begin the rupture of the secondary bonds. The fiber gel is transformed into a sol and the energy required is supplied by the elastic structures of the hair. When the hair is returned to its original length, it resets to a gel and energy is released as heat. The area between the extension and contraction curves for "equilibrium" loads thus represents the heat evolved in the conversion of the sol to a gel at the end of the extension plus the heat of conversion of the sol to a gel at the end of the contraction.

No doubt the conversion of the gel to a sol is not nearly so distinct and clear cut as intimated by the above discussion. Thus from point B (Fig. 1) to the C the gel is progressively converted into a sol and at any point along the curve a certain fraction of the fiber will exist, as a gel. The same is true of the region from D to 0. However, from 0 to B and from C to D the fiber is all gel and no sol is present. It is also no doubt true that only certain portions of the fiber are capable of being converted into a sol, *i. e.*, that part of the fiber

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(7) Huggins, *Chem. Revs.*, **32**, 195 (1943).

whose peptide chains are cross linked by secondary valence bonds. There is no evidence that co-valent bonds such as the disulfide bonds can be ruptured by stretching the fiber. Indeed, if the disulfide bonds are broken by chemical agents as Harris, Mizell and Fourt[8] have shown, the work of extension of the fiber is very greatly diminished. In terms of our picture the entire gel structure of the fiber has been disrupted and the fiber begins at a very small load to be converted into a viscous sol.

Freundlich and Rawitzer[9] have studied the elastic properties of thixotropic iron oxide gels. The gel was inclosed between two vertical, concentric cylinders. The inner cylinder was suspended by a torsion wire and the outer cylinder rotated through successive small angles and the displacement of the inner cylinder noted. This displacement of the inner cylinder from its original position gave the torque exerted by the torsion wire on the gel. Freundlich and Rawitzer report that the adjustment of the inner cylinder to the torque was substantially complete in about two minutes. The results of Freundlich and Rawitzer appear to parallel, in a remarkable manner, the behavior of a hair fiber under stress. The thixotropic gel showed identically the same type of extension-contraction curve as given in Fig. 1 of this paper.

An "equilibrium" stress–strain curve for hair is given in Fig. 4. The term "equilibrium" when used in this connection should be qualified; the quotation marks which have been used indicate this qualification. If a hair is placed under an "equilibrium" load as we have determined it, the hair will in time become fatigued and additional stretch will be noted. The cause of this fatigue is obscure and we are not prepared to enter into a discussion of this effect at the present time.

The influence of temperature on the work terms of extension and of contraction (see Table I) throws some light on the nature of the elastic element of keratin. The internal friction both of extension and of contraction decrease with increasing temperature. This is as it should be and tends to confirm our interpretation of these terms. The irreversible work also decreases with increasing temperature. It is believed that since the irreversible work is a reflection of the rupture and formation of polar bonds, it should decrease with increasing temperature; such bonds are weaker at higher temperatures. Both the work of contraction and of extension at "equilibrium" loads increase at the higher temperature. The interpretation of this increase is complicated by the fact that both of these work terms involve the irreversible work. The decrease in the irreversible work which is observed, would tend to increase the "equilibrium" work of contraction and to decrease the "equilibrium" work of extension. The fact that the work of contraction increases more than the work of extension with increased temperature is probably a reflection of this change in the irreversible work. It would appear, however, that since both the work of extension and of contraction increase with temperature we can conclude that the hair becomes less elastic with increasing temperature. As pointed out by Guth,[10] this type of behavior with increasing temperature is typical of rubber-like substances and arises from an increase of entropy or of randomness of the rubber chains. It is impossible with our present knowledge to make an unambiguous decision regarding the nature of elastic element of keratin, but the results in Table I would indicate that in the 20% stretch region a rubber-like type of elasticity is important.

The conclusions to be drawn from the study of the "equilibrium" loads at two temperatures and at various stretches (Table II) are in essential agreement with those derived from Table I but give a somewhat more detailed picture. It is evident that in the Hooke's law region hair stretches as a normal body, *i. e.*, the elasticity increases with increasing temperature. The results for the 12% stretch on the extension limb as well as for the 35% stretch are not unambiguous. In both cases the "equilibrium" load decreases with decreasing temperature (25 to 12°) but likewise the "equilibrium" loads decrease with increasing temperature (12 to 25°). However, the decrease of load with increasing temperature was not as large as the decrease with decreasing temperature (see last column of Table II). Strictly interpreted these results mean that at these two extensions the rubber-like elasticity is more important as the temperature is decreased while for increasing temperatures the normal body elasticity is more important. The results at 12% extension on the contraction limb are clear cut and indicate that a rubber-like elasticity is present and furthermore that it is the controlling factor on the contraction limb.

Acknowledgment.—It is a pleasure to acknowledge the financial assistance to one of us (H. B. B.) from the Abbott Research Fund of Northwestern University which permitted this research problem to be completed.

Summary

1. The stress–strain relations of human hair in pure water have been studied and reported.

2. It is concluded that while the stress–strain behavior of hair is reproducible up to about 20% stretch, the process is essentially irreversible.

3. The extent of stretch which leads to irreparable damage to the hair has been established. This begins at about 18% extension.

4. A method has been devised to determine the

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[8] Harris, Mizell and Fourt, *J. Research Natl. Bur. Standards*, **29**, 73 (1942).

[9] Freundlich and Rawitzer, *Kolloid-Beihefte*, **25**, 252 (1927). See especially thesis by Rawitzer, Berlin, 1927.

[10] Guth, "Surface Chemistry," Am. Assoc. Adv. Sci. Pub. No. **21**, 103 (1943).

"equilibrium" loads at which the hair fiber neither contracts nor extends.

5. The influence of temperature on the elasticity of hair has been investigated. The elasticity of hair increases with increasing temperature in the Hooke's law region. The results obtained on other portions of the stress–strain curve are somewhat ambiguous except on the contraction limb of the 20% stress–strain loop. In this region the elasticity decreases with increasing temperature and accordingly indicates a rubber-like behavior.

6. It is concluded that Astbury's newer structure for α-keratin is much too condensed and the suggestion is made that the principal feature of α-keratin is the close packing of successive alternate amino acid residues along the peptide chain.

7. It is suggested that the stretching of hair from about 3 to 20% extension involves a process which resembles a thixotropic gel–sol transformation. This transformation is mainly responsible for the irreversible nature of the extension–contraction process.

CHICAGO, ILLINOIS RECEIVED APRIL 20, 1944

[CONTRIBUTION FROM THE SCHOOL OF MEDICINE, ST. LOUIS UNIVERSITY]

A Study of Some Reactions between Dry Inorganic Salts. VI. The Reciprocal System $CsCl + KBr \rightleftarrows CsBr + KCl$ below the Fusion Temperature[1]

BY J. WM. VOGT WITH LYMAN J. WOOD

It has been previously reported[1a] that when an equimolar mixture of cesium chloride and potassium bromide is heated at from 50 to 100° below the fusion temperature it is partly converted into cesium bromide and potassium chloride. If the heating is continued for a sufficient length of time an equilibrium is established which is represented by the equation

$$CsCl + KBr \rightleftarrows CsBr + KCl$$

The same equilibrium mixture is obtained if an equimolar mixture of cesium bromide and potassium chloride is heated at the same temperature. When the equilibrium mixture is quickly cooled to room temperature, it is found to consist of two binary solid solutions, one of which is made up of cesium chloride and cesium bromide and the other of which is made up of potassium chloride and potassium bromide. Preliminary results obtained for this reaction indicated that equilibrium mixtures result at various temperatures and for different starting compositions. In the work that is now being reported the range of the starting compositions has been widened, the temperature has been more carefully controlled and new techniques have been introduced that have resulted in more satisfactory analytical data.

Materials, Apparatus and Methods.—The potassium chloride and potassium bromide were Analytical Reagent quality and the cesium chloride and cesium bromide were C. P. stock supplies from the Maywood Chemical Company. The chemicals were fused and, after cooling, were ground and kept in a desiccator until needed. In general, larger amounts of the CsCl–CsBr mixtures were used than in previous work, thus minimizing the effect of the unavoidable error in weighing. Also, for the most part, the whole of any given mixture was used for any given heat treatment whereas in previous work mixtures were sometimes subdivided before heating, which would produce errors in composition in case the mixing was not thorough. A miniature mixing mill was devised for mixing samples that were to be subdivided.

The compositions of the equilibrium mixtures were determined by the method of X-ray crystal analysis, using the same X-ray diffraction equipment as previously described. Several changes in manipulation, however, were made. A bearing and pulley wheel were mounted on the cassette in such a way that the small sample tube could be rotated. This was considered to be quite important since spotted interference lines had often been obtained when photographing reaction mixtures that had not been melted.

In the earlier work with this reaction the interference pattern of the sample was photographed on one edge of the film and that of the standard was photographed on the other. Some of the starting mixture, which was not subjected to the heat treatment, was generally used as the standard. In this way differences in density between the sample and the standard were avoided but there was introduced the possibility of a greater or smaller amount of interaction between the components of the standard. It was believed at the time that the amount of such reaction was entirely negligible but it has since been found that such was not always the case. Any small amount of cesium bromide resulting from the interaction of a CsCl–KBr standard mixture could form a solid solution with the residual cesium chloride and the use of any of the interference lines of this solid solution, on the assumption that they were due to pure cesium chloride, would lead to erroneous measurements. Because of the uncertainty

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[1] Read at the Detroit Meeting of the American Chemical Society, April, 1943.

[1a] H. L. Link and Lyman J. Wood, THIS JOURNAL, **60**, 2320 (1938); **62**, 766 (1940).