present in both cases, the latter having deposited in glistening prisms melting at 229–230°. From tolylimido-methylester we obtained almost a complete conversion into the polymerized tolylnitrile. This compound (cyantoline)[5] which is recorded in the literature as crystallizing in needles, had deposited in the form of transparent tabular crystals which melted at the correct temperature, 277°, without further purification. Needles were also observed suspended in the remaining oil but the quantity was too small for ascertaining their melting point.

At what time the decomposition of these esters became apparent we have no reliable data, but it is evident from our observations that imido esters of the type examined are not organic combinations which can be preserved for long periods. It is also an extremely interesting fact that polymerization of the nitrile took place in the case of each imido ester, while the pure nitrile remained unchanged during this same period. These results are in accord with the assumption that dissociation of the imido ester leads to the formation of a labile nitrile containing free or residual valences, which rearranges to the stable nitrile and also polymerizes to cyclic derivatives.

NEW HAVEN, CONNECTICUT

THE STRUCTURE OF ELASTIC GELS[1]

BY ROBERT HERMAN BOGUE[2]

Introduction

The structure of gels is a problem which has occupied the attention of physical chemists since the inception of colloid chemistry, and even before Graham had introduced the distinction between colloid and crystalloid.

Frankenheim[3] in 1835 and von Nägeli[4] in 1858 concluded that jellies were 2-phased and that the solid phase was crystalline. This view has been supported by von Weimarn[5] and Levites,[6] and is at present championed by Bradford.[7]

[5] *Ber.*, **33**, 1055 (1900).

[1] Presented before the Pittsburgh Section of the American Chemical Society, March 18, 1922.

[2] Industrial Fellow of the Mellon Institute of Industrial Research of Pittsburgh, and Research Chemist for Armour and Company, of Chicago.

[3] Frankenheim, "Die Lehre von der Kohäsion," Breslau, **1835**.

[4] von Nägeli, "Pflanzenphysiologischen Untersuchungen," Zürich, **1858**.

[5] von Weimarn, *Kolloid-Z.*, **2**, 76, 230, 275, 301, 326 (1908).

[6] Levites, *ibid.*, **2**, 161, 208, 237 (1908).

[7] Bradford, The "Physics and Chemistry of Colloids, and Their Bearing on Industrial Questions." Report of a General Discussion held jointly by the Faraday and Physical Societies of London, October 25, 1920. H. M. Stationery Office, London, **1921**, p. 44.

Bütschli[8] introduced the idea that there were definite pores in a jelly, and van Bemmelen[9] extended this conception to the postulation of a "cell-like structure of definite form—hanging together at certain points, forming a network." This idea of a network structure in gels has been adhered to by many investigators, but from somewhat variant points of view. Hardy[10] concludes from a microscopical study that the solid phase consists of a solid solution of water in gelatin, and the liquid phase a solution of gelatin in water, and that gelation consists in the separation of the sol into a solid open framework with an interstitial fluid phase. This idea is accepted by Freundlich[11] and Anderson,[12] and in essential respects by Miss Lloyd[13] and Fischer.[14] Wo. Ostwald[15] injected the conception of a 2-phase liquid-liquid system, and Bancroft[16] has adhered to this idea.

Procter[17] has discarded the 2-phase theory of gel structure and postulated the existence of a solid solution of the exterior liquid in the colloid in which both constituents are within the range of the molecular attractions of the mass. This theory was the result of his findings that in a gelatin:acid:water system equilibrium resulted from the combination of the gelatin and acid to form easily dissociated salts, and that the osmotic pressure of these salts and the Donnan equilibrium determined the volume of a swollen jelly. Loeb[18] has carried the idea of Procter to a further explanation of colloidal behavior as described later.

These three schools of thought upon colloid structure represent the present status of the problem. For purposes of classification, although not strictly correct, they may be referred to as the crystalline theory, the colloid theory, and the molecular theory, respectively.

The concept of a crystalline structure in gels has been studied by Scherrer[19] who has made many examinations of gels by means of the Röntgen photograph. He found that certain rigid gels as silicic and stannic acids exhibited well-marked crystalline interference figures in addition to the characteristics of amorphous substances, but in the gel of gelatin the crystalline interference figures were entirely lacking. These different types of gels possess other characteristic dissimilarities. The gel of silicic acid, for example, develops on drying pores that are filled with air, and which may be filled by imbibition with a liquid other than the original solvent.[20] The elastic gels such as gelatin do not develop such pores, and the dried gel will not imbibe a foreign liquid, as, for example, benzene. Harrison[21] has even succeeded in obtaining spherical coagulation-forms of starch which strongly resemble the so-called spherites that were obtained by Bradford from gelatin, but these are not regarded as crystalline.

[8] Bütschli, "Untersuchungen über Structuren," Leipzig, **1898**.

[9] von Bemmelen, *Z. anorg. Chem.*, **18**, 14 (1898).

[10] Hardy, *Proc. Roy. Soc.*, **66**, 95 (1900).

[11] Freundlich, "Kapillarchemie," Akademische Verlagsgesellschaft m. b. H., Leipzig, **1909**.

[12] Anderson, *Z. physik Chem.*, **88**, 191 (1914).

[13] Lloyd, *Biochem. J.*, **14**, 147 (1920).

[14] Fischer, "Soaps and Proteins," John Wiley and Sons, New York, **1921**.

[15] Wo. Ostwald, *Arch. ges. Physiol.* (Pflüger's), **109**, 277 (1905); **111**, 581 (1906).

[16] Bancroft, "Applied Colloid Chemistry," McGraw-Hill Co., New York, **1921**, pp. 239, 242.

[17] Procter, *J. Chem. Soc.*, **105**, 313 (1914).

[18] Loeb, *J. Gen. Physiol.*, **3**, 827 (1921); **4**, 73, 97, 351 (1921–22).

[19] Scherrer, *Machr. Ges. Wiss. Göttingen*, **1918**, p. 96.

[20] Hatschek, Ref. 7, p. 59.

[21] Harrison, *J. Soc. Dyers Colourists*, **32**, 32 (1916).

It seems probable from the differentiation found between silicic acid and gelatin gels that, as Hatschek has observed, there are many kinds of structure in gels. In the present paper we shall concern ourselves only with the elastic gels. The theory of Procter, while explaining adequately the swelling phenomena of gelatin, does not account for other colloidal behavior, such as viscosity fluctuations with time, syneresis, or the process of gelation itself.

The net structure hypothesis meets with a number of objections. Not least in importance is the failure of its proponents to account for the existence of such a structure. In the sol form, they say, the structure does not exist; in the gel form it does exist. What has brought about the change and why was it produced? The sudden appearance of structure must be accounted for.

Again, it is affirmed by this theory that the jelly consists of a sponge-like or honeycomb structure consisting of gelatin as a continuous solid or semi-solid phase, and water (containing inorganic ions and some gelatin molecules in solution) as the dispersed phase. If this were true it should not be difficult to extract the water by moderate pressures, but this cannot be done. Reinke[22] has pointed out that at a pressure of 41 atmospheres the gel of *Laminaria* increases in volume by the absorption of water 16%, and at 1 atmosphere 330%. Posnjak[23] has shown that at 377 cm. of mercury gelatin gel increases in volume nearly 100%, while at 38 cm. the increase is over 250%. Quincke[24] and Hatschek[25] have shown that a volume contraction accompanies the swelling of gelatin to the extent of nearly 2%, and Widemann and Ludeking[21] have reported that 5.7 gram calories of heat were liberated by the swelling of 1 g. of gelatin. These facts are not explained by the assumption that gelatin swells, like a sponge, by the imbibition of water into the porous structure of the gel.

It should also be urged that diffusion and conductivity take place primarily through the continuous phase and not the dispersed phase of a gel, and if the development of the structure in the gel necessitates the assumption of a reversal of phase, as assumed by Fischer[14] and others, it is difficult to understand the nearly identical degrees of diffusion and of conductivity exhibited by the sol and the gel forms, as pointed out by Graham[27] and by Arrhenius,[28] respectively.

In 1920 the writer[29] outlined his views upon the structure of gelatin-water systems. There has since that time been so much work of a more or less confirmatory character that it seems desirable to restate the theory and to add thereto further postulations based upon recent work.

Gelatin sols appear to consist of slightly hydrated molecules united into short threads[30] resembling streptococci. These threads are probably very short, but should be capable of exhibiting mechanical elasticity roughly

[22] Referred to by Hatschek, "Introduction to the Physics and Chemistry of Colloids," J. and A. Churchill, London, 1913, p. 56.

[23] Posnjak, *Kolloidchem. Beihefte*, **3**, 417 (1912).

[24] Quincke, *Arch. ges. Physiol.* (Pflüger's), **3**, 332 (1870).

[25] Ref. 22, p. 55.

[26] Widemann and Ludeking, *Ann. Physik*, N. F., **25**, 145 (1885).

[27] Graham, *Phil. Trans. Roy. Soc.*, **1864**.

[28] S. Arrhenius. See Ref. 44.

[29] Bogue, *Chem. Met. Eng.*, **23**, 61 (1920).

[30] J. Loeb has found that the assumption of a few united molecules accounts for the differences in the osmotic pressures of calcium and sodium gelatinates. [*J. Gen. Physiol.*, **1**, 496 (1919).]

proportional to their length. Procter[31] thinks that at 70°, the solution probably becomes nearly molecular.

A lengthening of these threads seems to take place as the temperature falls, and at the same time the water-absorbing power of the gelatin increases.[32] This accounts for the rapid increase in viscosity with drop in temperature. At temperatures above 40° the change in length of thread or water absorption, per unit change in temperature, is small, but at 30°–20° the change is very great. A solid jelly will result only when the relative volume occupied by the swollen molecular threads has become so great that freedom of motion is lost, and the adjacent heavily swollen aggregates cohere. The rigidity seems to depend on the relative amount of free solvent in the interstices of these aggregates, and on the amount of solvent that has been taken up by the gelatin in a hydrated or imbibed condition. The resiliency or elasticity is probably dependent upon the length and number of the catenary threads. A solution, or change from the gel to the sol form, may result only through the reversal of these processes; that is, a release of a part of the water retained by the heavily swollen molecules, and a partial disintegration of the long enmeshed fibrils of the gel. Any tendency on the part of the fibrils towards an orientation would imply an attractive force between them which would result in a shrinkage. This becomes manifest in syneresis. That some such orienting force does exist is indicated by the lenticular form of bubbles that are generated within gels. The degree of swelling that may be produced in cold water or electrolyte solutions is determined by osmotic forces, as described by Procter, and may be controlled by observing the principal of the Donnan equilibrium as shown by Procter and by Loeb.

The writer[33] has shown that the gel consistency is proportional to the undegraded protein present in a gelatin or glue. It follows, therefore, that the unhydrolyzed gelatin possesses a much greater water-absorbing capacity than the proteoses or peptones. It was also pointed out that the viscosity varied apparently with the size of the colloid aggregate in the solution. The present theory demands that viscosity vary with the degree of water absorption (measured by the rigidity of the gel) and with the size (length) and number of the colloid fibrils (measured by the elasticity of the gel[34]), and also, of course, with the concentration of the solute. The "melting point" was shown[35] to be determined by the protein content and was found to give a "grading" lying between that resulting from measurements of gel strength, and of viscosity at high temperatures (60°). Since it has been indicated in a previous paper[36] that "melting point" is in reality

[31] Procter, Ref. 7, p. 41.

[32] Whether or not this is real hydration is undetermined. McBain and Salmon [*J. Chem. Soc.*, **119**, 1374 (1921)] have reported an increase in hydration of soap upon a lowering of the temperature. Jones [*Z. physik. Chem.*, **74**, 325 (1910)] has shown that the hydration of molecules and ions increases with a fall in temperature.

[33] Ref. 29, p. 105.

[34] See apparatus of Sheppard, *J. Ind. Eng. Chem.*, **12**, 1007 (1920).

[35] Ref. 29, p. 64.

[36] Bogue, THIS JOURNAL, **44**, 1313 (1922).

only a transitional period between the sol and gel forms, and in this paper that the transition involves only a change in the water-absorbing capacity and the length and number of the colloid molecule-threads, it follows if the above is true that any measure of "melting point" will indicate a resultant between the effects of hydration or water absorption and of length or number of threads, or, differently expressed, a resultant between gel strength and viscosity at high temperatures, which is exactly in conformity with the data reported in an early paper.

Fischer[37] is of the opinion that "the phenomena of hydration (swelling) and of 'solution' while frequently associated are essentially different. Hydration is to be regarded as a change through which the protein enters into physico-chemical combination with its solvent (water); 'solution,' as an increase in the degree of dispersion of the colloid." This is in satisfactory agreement with the ideas expressed above, for although we do not consider that a true solution may exist at low temperatures on account of the heavy hydration or water absorption, yet the change in a jelly upon conversion to a liquid seems to involve a disintegration of the colloid aggregates (increase in degree of dispersion) as well as a lessening in the degree of hydration or water absorption.

The recent work of McBain and his collaborators[38] on the structure of the sol, gel, and curd of soaps is of especial interest, and is in agreement with the theory outlined. They report that in soaps "the colloidal particles in the sol and gel are the same, but whereas in the former they are independent, in a fully formed gel they stick together probably to form a filamentous structure." They further add that "the sol and gel differ only through the mechanical rigidity and elasticity of the gel form." That is precisely what would follow in gelatin sol and gel from the postulations made above, and is a further indication of the gradual nature of the changes which obtain in the sol-gel equilibrium as urged in the previous paper. They state as their belief that a filamentous structure is the general characteristic of soap gels as distinguished from sols. They regard these filaments, however, as normally amicroscopic in size, while in the curds a probably crystalline formation is produced. In gelatin systems the curd or crystalline condition is not known. Harrison[39] reports that he has obtained ultramicroscopic photographs of gelatin and cellulose gels which showed them to consist apparently of "minute portions joined together in a somewhat irregular manner."

Barratt[40] has accepted the fibrillar structure theory as representing most adequately the properties of elastic gels, and reports that ultramicroscopic examination, when it reveals any structure at all, shows the gel to consist "not of liquid droplets enclosed by (solid) septa, as the honeycomb theory requires, but of a mass of intersecting fibrils, which run perfectly straight, and are united at their points of intersection." He concludes that "the real structure of these gels is a fibrillary network, at first amicroscopic and later becoming ultramicroscopic."

A gradual and regular change in properties accompanying the transformation of the sol to the gel or the gel to the sol also supports the theory of structure that has been set forth. This gradual and regular change is indicated by the viscosity-plasticity studies described in a preceding paper;[36] by the finding of Walpole[41] that the refractive index of a gelatin-water system is a linear function of the concentration, and when plotted against the temperature no break occurs in the region of gelation; by the conclusion

[37] Fischer and Coffman, This Journal, **40**, 304 (1918). Fischer, "Soaps and Proteins," John Wiley and Sons, New York, **1921**, p. 219.

[38] Laing and McBain, J. Chem. Soc., **117**, 1506 (1920). Drake, McBain and Salmon, Proc. Roy. Soc. London, **98A**, 395 (1921).

[39] Harrison, Ref. 7, p. 57.

[40] Barratt, Biochem. J., **14**, 189 (1920). Ref. 7, p. 49.

[41] Walpole, Kolloid-Z., **13**, 241 (1913).

of McBain[42] that the sol and gel forms of soap differ only in the formation of a filamentous structure which accounts for the different properties of the latter; by the reports of C. R. Smith[43] that mutarotation exists between the temperatures 15° and 32°; by the demonstration of Arrhenius[44] that the conductivity of salt: gelatin: water systems was the same in the sol and the gel conditions; and by the findings of Thomas Graham[27] that the rate of diffusion in dilute gels was approximately the same as in pure aqueous solutions.

It is also of interest to note that dibenzoyl-*l*-cystine which has recently been described by Gortner,[45] and which is capable of forming an elastic gel at concentrations as low as 0.2%, was also shown by an ultramicroscopic examination to have, in the gel condition, a fibrillar structure.

Specific Influence of Electrolytes

The specific effects of electrolytes upon the sol and gel forms of gelatin were studied in a special series of experiments. The influence of hydrogen-
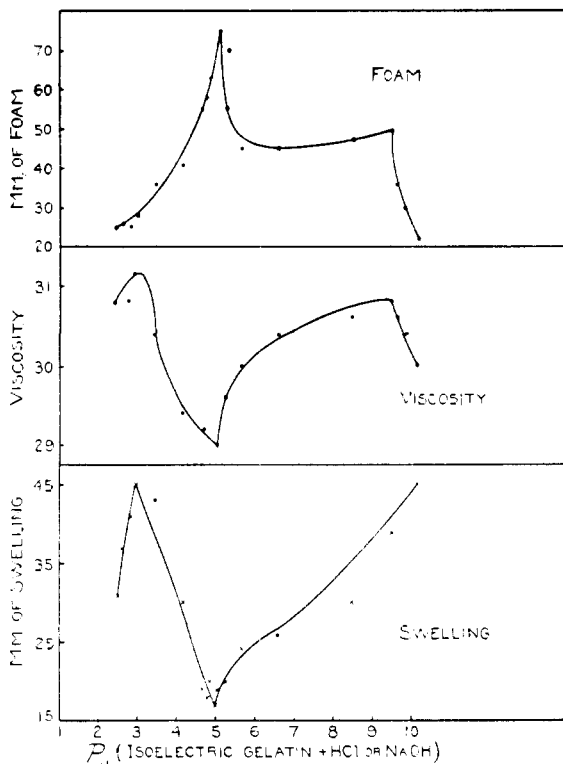

Fig. 1.—Influence of hydrogen-ion concentration on the swelling, viscosity and foam of gelatin.

[42] Laing and McBain, Ref. 38.

[43] Smith, This Journal, **41**, 146 (1919); Ref. 53.

[44] S. Arrhenius, *Ofvers. Stockh. Akad.*, **1885**, No. 6, p. 121.

[45] Gortner, This Journal, **43**, 2199 (1921).

ion concentration on the swelling, viscosity, jelly consistency, foam, turbidity and alcohol number was investigated.

The technique of the procedure was adopted from the method reported by Loeb,[48] and is described in detail elsewhere.[46]

An example of the data of these experiments is shown graphically in Figs. 1 and 2.

It will be observed that on the acid side the maximum viscosity and swelling occur at a Sörensen value (P_H) of 3.0–3.5, while the maximum jelly consistency is at a P_H of 4.0–4.5. All of the properties except turbidity and foam appear to have their minimum values, and these two properties their maximum values, at or near the iso-electric point, P_H
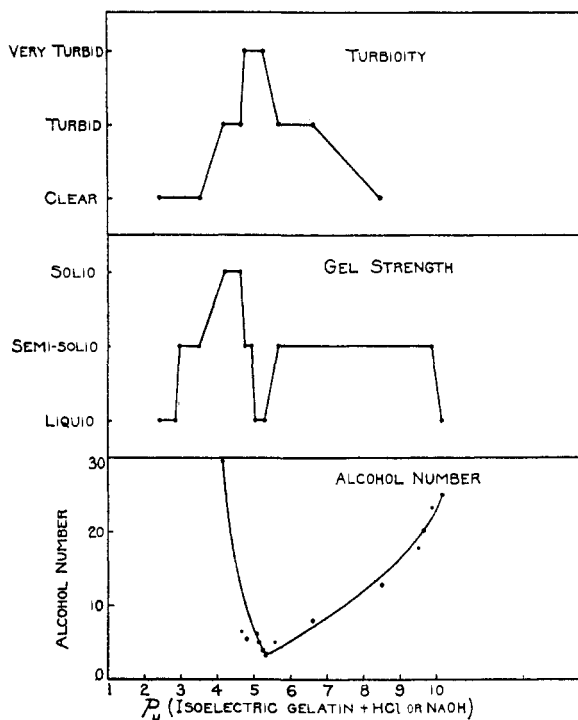

Fig. 2.—Influence of hydrogen-ion concentration on the alcohol number, gel strength and turbidity of gelatin.

4.7–5.0. If acid is present in excess of the optimum specified, the properties again decline. On the alkaline side the properties rise with increasing alkali concentration, but only at very high values of hydrogen-ion concentration do they approach those reached on the acid side.[47]

[48] See Bogue, "The Chemistry and Technology of Gelatin and Glue," McGraw-Hill Co., New York, 1922.

[47] Bogue, *J. Ind. Eng. Chem.*, **14**, 32 (1922); see experiments on the alkaline side.

These results are in very good agreement with those published by Loeb.[48]

Similar experiments were performed with sulfuric, phosphoric and lactic acids, with the intent of noting whether all acid ions behaved similarly, or in what respects they differed. The data are given in Fig. 3. They show that phosphoric and lactic acids behave quite similarly to hydrochloric acid, while the swelling and viscosity of the gelatin is much lower in the case of sulfuric acid.

The most probable significance of such behavior has been shown by Loeb, from a study of the relations between the osmotic pressure and con-
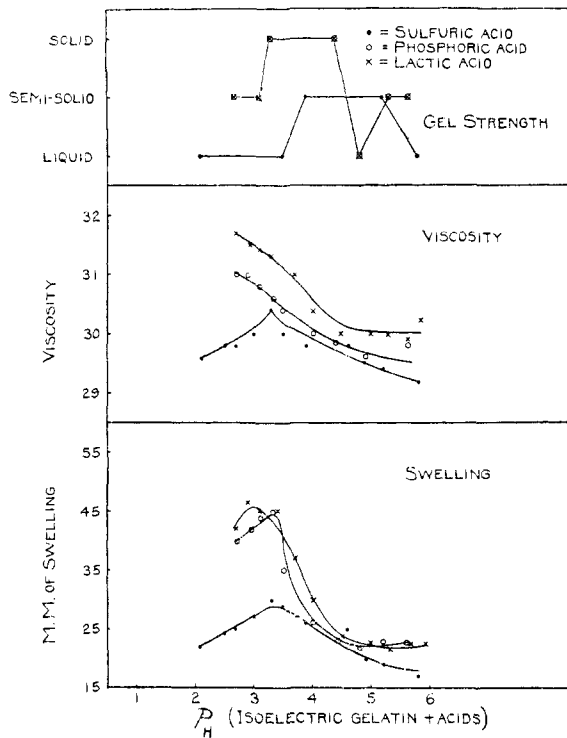

Fig. 3.—Effect of sulfuric, phosphoric and lactic acids on the
gel strength, viscosity and swelling of gelatin.

ductivity of such solutions, to lie in a difference in the electrical charge upon the ions in question. All monobasic acids react with gelatin resulting in the formation of a gelatin salt in which the gelatin is positively charged, and all mono-acid bases react with gelatin resulting in the formation of a metal gelatinate in which the gelatin ion is negatively charged.

Lactic acid is monobasic and reacts like hydrochloric. Phosphoric acid is tribasic, but the secondary and tertiary valence force is so slight that with

[48] Loeb, J. Gen. Physiol., 1, 39, 237, 363, 483, 559 (1918-19).

gelatin the acid acts only as monobasic, so on treating it as such and using molecular equivalent quantities it acts as does hydrochloric. Sulfuric acid is dibasic, and Loeb has shown that both valences function in reactions with gelatin.[49] The swelling, viscosity, etc., of gelatin sulfate are consequently much lower than those of the corresponding salt of a monobasic acid. Furthermore, on the acid side of the iso-electric point gelatin can combine only with anions and is uninfluenced by cations, while on the alkaline side of that point the gelatin can combine only with cations and is uninfluenced by anions.

A further very exact study was made of the effect of hydrogen-ion concentration upon viscosity, using gelatin of 3 typical kinds: iso-electric gelatin, normal gelatin which was calcium gelatinate of P_H 5.8, and gelatin chloride of P_H 3.5. The results of these experiments have been described in a previous report.[50] They show the same behavior as the experiments above described, but at varying concentrations of gelatin.

Discussion of Results.—The foregoing data are found to furnish additional evidence in favor of the theory that has been described. The swelling may be taken as a measure of the water absorption or hydration and this is found to be parallel to the viscosity. An increase in viscosity must be due to an increase in the effective volume of the gelatin in the solution. This volume is obviously at a minimum at the iso-electric point which signifies that hydration is least at that particular hydrogen-ion concentration. This may be due to the fact that at that hydrogen-ion concentration gelatin is un-ionized and ions appear to be capable of greater hydration than un-ionized molecules.[51] The viscosity of iso-electric gelatin increases upon standing, however, at a greater rate than at any other hydrogen-ion concentration, and this appears to be due to the very marked insolubility of the gelatin at that point, for the tendency of the gelatin molecules and colloid fibrils to increase in size by flocculation or polymerization is so decided at the iso-electric point that it is easily observable under the ultramicroscope. It is especially significant to observe that the jelly consistency of iso-electric gelatin (see curves) becomes very low at that point which also indicates a low degree of hydration.

The increases in viscosity observed by raising or lowering the hydrogen-ion concentration from the iso-electric point are apparently attributable to a variation in the degree of hydration or water absorption, as shown by the parallelism of the viscosity and swelling curves. The sudden

[49] The primary ionization of phosphoric acid is about fifty thousand times the secondary ionization, and this in turn about five hundred thousand times the tertiary ionization. In the case of sulfuric acid, however, the primary ionization is only about 33 times the secondary ionization. (See Stieglitz, "Qualitative Chemical Analysis," The Century Co., New York, I, p. 104.)

[50] Bogue, THIS JOURNAL, **43**, 1764 (1921).

[51] Jones, *Am. Chem. J.*, **34**, 291 (1905).

drop in both viscosity and swelling at a Sörensen value above 9 or below 3 seems to be due to a "solution" or breaking down of the colloid molecule-threads, and this disintegration is accompanied by a corresponding lessening in the ability of the smaller aggregates or molecules to take up water in hydrated or imbibed form. That this reasoning is justified is further evidenced by the known inability of the proteoses and peptones to become swollen to anything like the degree attained by the gelatin aggregate.

The depressing influence of inorganic ions on the swelling and viscosity of the gelatin is probably partly attributable to the withdrawal of water from the hydrated gelatin by these ions. And since the high viscosities are due to the heavily swollen gelatin aggregates, any decrease in the degree of such hydration or imbibition must be reflected by a drop in the viscosity of the solution. Divalent ions appear to be capable of greater hydration than monovalent ions and should therefore be expected to be capable of withdrawing larger amounts of water from the gelatin particles. From the studies of Fischer[52] it is also shown that divalent base soaps and proteinates dissolve less water than monovalent ones.

The turbidity curves indicate that the greatest opacity results from the largest aggregates of least swollen particles. This maximum of opacity occurs at the iso-electric point. Any decrease in the size of the aggregates or increase in the water absorption results in greater clarity or transparency of the solution.

The foaming qualities appear to be influenced in a manner similar to the turbidity, the maximum of foam being obtained at the iso-electric point. This is exactly what would be expected for, since the foam consists of bubbles of air retained by a continuous film, only molecules that have a strong tendency to adhere to each other would be efficacious in film formation. At the iso-electric point gelatin molecules show their maximum tendency to form large aggregates.

The alcohol number is at its minimum value near the iso-electric point, and rises rapidly to infinity on the acid side and somewhat less rapidly on the alkaline side. Since the alcohol number refers to the precipitability of gelatin by alcohol it would be expected that the larger the molecular aggregate, and the less the water content of the aggregate, the more readily would such precipitation be brought about. This is especially significant in that alcoholic precipitation of proteins probably consists essentially of a dehydration or extraction of water. Therefore, in systems that are only slightly hydrated, precipitation is readily brought about by alcohol, but in systems containing large amounts of absorbed water the dehydrating influence of added alcohol may be insufficient to effect precipitation.

[52] Ref. 14, p. 14.

Mutarotation

In order to test the theory further the data of C. R. Smith[53] on mutarotation were examined critically in their applications to the sol-gel equilibrium. The change in specific rotation, or mutarotation, of gelatin solutions of a constant concentration upon reduction of the temperature from 35° to 15° was found to drop off very markedly with a decreasing jelly consistency of the gelatin or glue employed. That is, the mutarotation was highest in a (3%) solution of a gelatin which was capable of gelling (at 15°) at a concentration of about 0.56% and very low in a (3%) solution of gelatin which would gel (at 15°) only when the concentration had been raised to 2.00% or higher. To have a more concise picture of the exact relations the data of Smith have been plotted, the ordinate representing the mutarotation (15–35°) and the abscissa the minimum amount of gelatin required to produce a standard jelly at 15°. This curve is shown in Fig. 4.
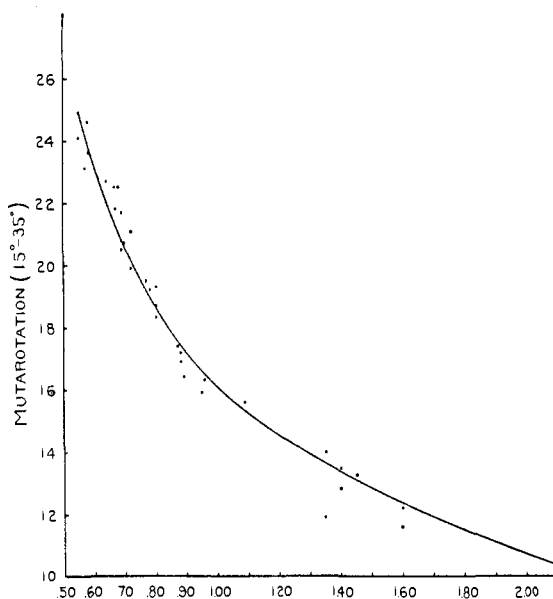

Fig. 4.—Mutarotation and jellying power.

There are many minor discrepancies observable, but these are attributable to the failure of the method employed for measuring jelly consistency[54] to distinguish between rigidity and elasticity of the gel. The general tendency of the curve is, however, incontrovertible.

[53] Smith, *J. Ind. Eng. Chem.*, **12**, 878 (1920).

[54] A standard viscosity which would permit a bubble of air to rise through a tube of the gelatin sol-gel at an arbitrarily selected rate.

Since the jellying power of a gelatin solution has been shown[33] to be proportional to the content of unhydrolyzed protein present, it follows that the mutarotation is also proportional to the protein content. We have given evidence which indicates that the proteins (of gelatin) are capable of vastly greater hydration than the proteoses and peptones. It appears, therefore, necessary to conclude that the mutarotation, or increase in specific rotation upon reduction in temperature (35° to 15°) must be dependent for its existence upon the greatly increased water absorption and aggregation or polymerization which such unhydrolyzed proteins are found to undergo upon similar reductions in temperature.

The Occlusion Theory

Loeb[18] has recently questioned the whole conception of hydration, in the sense in which the term was used by Pauli, at least in so far as it applies to solutions of the proteins (gelatin, casein and crystalline egg albumin), and finds it impossible to reconcile the results of his experiments upon the viscosity and osmotic pressure of such solutions with the early hydration theory.

To study the question Loeb performed a long series of experiments with solutions and suspensions of gelatin. He found that the influence of electrolytes on the viscosity of *suspensions* of powdered particles of gelatin in water was similar to their influence on the viscosity of *solutions* of the gelatin in water. He found it unnecessary to assume that the high viscosity of proteins is due to the existence of a different type of viscosity from that existing in crystalloids, but that such high viscosities could be accounted for quantitatively and mathematically on the assumption that the *relative volume* of the gelatin in the solution is comparatively high. And since iso-electric gelatin is not appreciably ionized, the large volume cannot be due to an hydration of gelatin *ions*. Loeb therefore postulates that the high volume of gelatin solutions is caused by the existence in the gelatin solution of "submicroscopic pieces of solid gelatin occluding water, the relative quantity of which is regulated by the Donnan equilibrium." This view was supported by experiments on solutions and suspensions of casein chloride and gelatin chloride in which it was shown that viscosity was due chiefly to the swelling of solid particles, occluding quantities of water regulated by the Donnan equilibrium, and that the breaking up of these solid particles into smaller particles, no longer capable of swelling, diminished the viscosity.

Loeb asks why such substances as amino acids and crystalline egg albumin behave so differently from gelatin. But such substances should not be expected to show variations in degree of hydration with changes in hydrogen-ion concentration of a nature parallel to those resulting from similar changes in gelatin solutions. The writer[33] has already shown

many differences in fundamental properties between true gelatin, pro-
teose and peptone. Thus the swelling, viscosity, and power of gelation
vary directly as the gelatin content (of a commercial gelatin or glue),
and probably as the size of the gelatin aggregate, and further evidence
has been given[47,50] that these variables are controlled to a large extent
by the degree of hydration or imbibition.

To understand the importance which Loeb attaches to his whole argu-
ment against the hydration theory, it is necessary to emphasize that the
term *hydration* was used in a very specific sense. By it Loeb referred
exclusively to the hydration conception postulated by Kohlrausch and
extended by Pauli.[55] According to this conception each individual
protein ion is surrounded by an enormous shell of water molecules, while
the non-ionized molecule of protein has no, or little, such a shell. If
this theory were correct, the variations in swelling, viscosity, osmotic
pressure, etc., should follow the variations in degree of ionization of the
protein; but Loeb has shown by conductivity measurements that this is
not the case.

The sense in which the term *hydration* has been used in the present
report is that adopted by Wo. Ostwald and Martin Fischer to signify
only the taking up of water by the protein ions, molecules, or particles,
and without any necessary implication upon the mechanism of such combi-
nation. Loeb has confined his argument for the most part to a considera-
tion of the intermolecular mechanism by which such combinations with
water may be most satisfactorily accounted for. The two points of view
seem to be in no way contradictory.

Summary

The several theories of gel structure have been reviewed and discussed,
and the postulations of the writer that were made in 1920 are repeated and
amplified. Many contemporary investigations have been found to
support a catenary or fibrillar structure hypothesis, and are set forth.

The premises of this theory are as follows. The sol consists of slightly
hydrated or swollen molecules united into short chains. When the
temperature falls the threads increase in length and number, and their
power of water absorption increases, resulting in an increase in viscosity.
A solid jelly results when the relative volume occupied by the swollen
molecular threads has become so great that freedom of motion is lost,
and the adjacent heavily swollen aggregates cohere. The rigidity is
dependent upon the relative amount of free solvent in the interstices of
the aggregates, and on the amount of solvent that has been taken up by
the gelatin in a hydrated or imbibed condition. The resiliency or elas-
ticity is dependent upon the length and number of the catenary threads.

[55] Personal communication from Jacques Loeb.

Solution is the reverse of gelation. Swelling is determined by osmotic forces and the Donnan equilibrium.

The influence of electrolytes, of varying hydrogen-ion concentration, and of the valence of the combining ion has been studied upon several of the characteristic properties of gelatin and found to be entirely in agreement and to give additional evidence in support of the theory presented.

Data on the mutarotation of gelatin were found to be in accord with the theory.

The occlusion theory of Loeb is reviewed and found not to be out of harmony with the present theory, but rather to explain the distribution of absorbed water and its variation with hydrogen-ion concentration mathematically in terms of the Donnan equilibrium.

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THE REACTIONS OF THE ARSINES. II. CONDENSATION OF AROMATIC PRIMARY ARSINES WITH ALDEHYDES[1]

By CHARLES SHATTUCK PALMER WITH ROGER ADAMS[2]

The arsines, in spite of their close relationship in constitution to the amines, have been investigated only to a slight extent. The known reactions of the primary arsines are limited to: (1) the ready oxidation by air or inorganic oxidizing agents to arseno compounds, arsine oxides or arsonic acids;[3] (2) the replacement of hydrogen bound to arsenic by halogens or sulfur by treatment with halogens, sulfur, or compounds which readily give up these elements;[4] (3) the formation of quaternary arsonium halides by heating with alkyl halides;[5] (4) the condensation with compounds of the type $RAsO$, $RSbO$, $RAsCl_2$, $RSbCl_2$, $SbCl_3$, $BiBr_3$, etc., to yield compounds of the type $RAs=AsR$, $RAs=SbR$, $RAs=BiBr$, etc.[6] In addition might be mentioned the fact that the arsines

[3] *Ber.*, **34**, 3597, 3599 (1901); *Am. Chem. J.*, **33**, 124, 144, 149 (1905); **40**, 105*ff* (1908).

[4] *Am. Chem. J.*, **33**, 126, 150 (1905); **40**, 105 (1908).

[5] *Ibid.*, **33**, 128, 145, 152 (1905); **40**, 112 (1908).

[6] *Ibid.*, **40**, 108 (1908); *Ber.*, **46**, 3564 (1913). Ger. pat. 254,187; 269,743; 269,744; 269,745; 270,259.