

Summary

1. Carey Lea's experiments indicated that iodine was strongly adsorbed from solution by silver iodide.

2. Dry, thoroughly washed silver iodide precipitated from M solutions of silver nitrate and potassium iodide was added to alcoholic and potassium iodide water solutions of iodine with no decolorization. Varying lengths of time of agitation and various conditions were tried with no appreciable adsorption.

3. Likewise, moist silver iodide precipitated from M and from $0.1 M$ solutions and washed with ammonium hydroxide and nitric acid by decantation was added to similar solutions with negative results.

4. Decolorization was obtained with unwashed silver iodide precipitated both from M and from $0.1 M$ solutions, using an excess of silver nitrate. The decolorization was due to a chemical reaction between the iodine in solution and the silver nitrate occluded in the silver iodide and adsorbed upon its surface.

5. Unwashed silver iodide precipitated from dilute solutions of silver nitrate and potassium iodide decolorized the iodine solutions most easily, due to the greater adsorption of silver nitrate by the silver iodide and the larger quantity of solution held because of the increased porosity.

6. A sherry-wine red solution of iodine contains about 0.008 millimol per cc. From the above experimental work it may be concluded that there is no adsorption of iodine from solution by silver iodide above a maximum limit of 0.02 millimol per gram of silver iodide. Hence, if Carey Lea worked with 25 cc. of sherry-wine colored iodine solution containing 0.2 millimol he must have added well over 10 g. of silver iodide to obtain anywhere near complete decolorization.

7. The above results point to the probability that Carey Lea was dealing with a chemical rather than an adsorption phenomenon.

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FURTHER STUDIES OF THE PHYSICAL CHARACTERISTICS OF GELATIN SOLUTIONS

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In a previous article¹ an investigation of the viscosity of solutions of various gelatins at 25° was reported.

The present paper covers an investigation of the following properties of gelatin solutions: (1) density~temperature 0-60°; (2) density~concentration at 40°; (3) transition point of gel-to-sol; (4) viscosity~

¹ Davis, Oakes and Brown, *THIS JOURNAL*, **43**, 1526 (1921).

concentration at 40°; (5) viscosity~temperature; (6) viscosity~hydrogen-ion concentration at 40°.

The methods of determining densities, viscosities, and hydrogen-ion concentrations were the same as described in the previous article except that in this work all values for hydrogen-ion concentration were determined both by indicators and by the hydrogen electrode. This was done because in certain ranges of hydrogen-ion concentration, notably around P_H 4 to P_H 5 and above P_H 9, the indicators are unreliable. Both methods were used because it was desired to determine the accuracy of the indicators. Outside the ranges above noted we found little difficulty in checking the hydrogen electrode within $P_H \pm 0.1^\circ$. Variations of as much as ± 0.3 or ± 0.4 in the value P_H may be experienced with gelatin solutions at P_H 4 to P_H 5 and above P_H 9. Solutions were made up according to weight per cent. concentration, and only hydrochloric acid and sodium hydroxide were used to alter the values of hydrogen-ion concentration.

Throughout the entire course of this work one sample of hide gelatin was used. This gelatin will be known as 3B and is of as high a grade as we have been able to find. The following table shows its characteristics.

TABLE I
PROPERTIES OF GELATIN 3B

P_H	Moisture %	Ash %	Jell strength at 21° Original $P_H = 4.9$	Absolute viscosity in c. p. of 1% sol. $P_H 3.5$ at 25°	
				Age Hr. min.	Viscosity
4.9	9.03	0.51	1025	1 20	3.08
				1 30	3.15
				2 0	3.37
				4 15	4.46

It will be noted that while Loeb² uses so called iso-electric gelatin which is practically ash free, the gelatin employed by the present authors contains about 0.5% of ash. Owing to the fact that in washing out the salts the more soluble (more hydrolyzed) portions of the gelatin are also washed away and the composition of the gelatin changed, and since the effects of various salts have been investigated by Loeb and found to be small in comparison with the quantities here determined we considered it best to use the gelatin as indicated.

Variation of Density with Temperature

One per cent. solutions of 3B gelatin at P_H 8.0 were investigated over a range of from 0° to 60°. As stated in a previous contribution¹ the density of gelatin solutions is affected but little by changes in hydrogen-ion concentration and the character of the gelatin has practically no effect upon

² Loeb, *J. Gen. Physiol.*, 1918-21.

the density. In Fig. 1 the density results have been plotted along with the densities of pure water over the same range. From this figure it is seen that the density changes of 1% gelatin solutions parallel those of pure

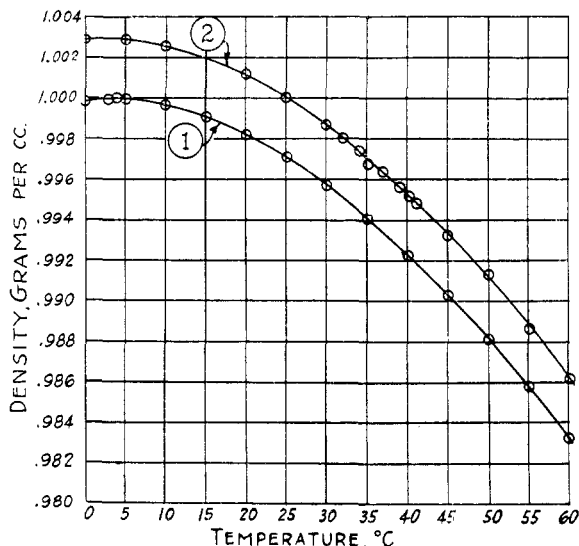


Fig. 1.—Variation of density with temperature, 1=water, 2=1% solutions of 3B gelatin, $P_H=8.0$.

water over the range 0–60°, and may be represented by the formula $D_g = D_w + 0.00290$ where D_g is the density of 1% gelatin solution and D_w is the density of pure water at the same temperature.

Variation of Density with Concentration at 40°

The densities of 1, 5 and 10% concentrations of 3B gelatin at P_H 8.0 were determined at 40° and were found to be 0.9954, 1.0067, and 1.0210, respectively.

These results, plotted in Fig. 2, show that the density is a straight line function of the concentration and may be represented according to the formula, $D_g = D_w + X \times 0.00290$, where D_g is the density of gelatin solution, D_w the density of water and X the percentage of gelatin. Since the constant at 40° is the same as at all other temperatures between 0° and 60° this is a perfectly general formula for the density of gelatin solutions at any temperature between 0° and 60°. Concentrations of this gelatin greater than 10% could not be used at 40°, and at 25°, 1% solutions jellied in 3 hours.

Transition Point of Gelatin

The fact that gelatin solutions increase in viscosity with aging of solution at 35° while at 40° the viscosity is constant indicated a method of

locating the transition point rather accurately. C. R. Smith,³ in an article "The Mutarotation of Gelatin and its Significance in Gelation" has pointed out the probability of the existence of two forms of gelatin. Smith was led to his belief by polariscopic investigations while our viscosity determinations led us to the same conclusions. Smith did not attempt to locate definitely this transition point: Sol form A \rightleftharpoons Gel form B, but placed it somewhere between 33° and 35°. In order to study the behavior of the two forms at 35°, two 1% solutions of 3B Gelatin of P_H 4.9 and 7.8, respectively were prepared and each was divided into two parts, "A" and "B." A samples were placed immediately in the thermostat at 35°, while the B samples were placed in the ice-chest for 1 hour and then removed and placed in the thermostat along with the A samples. Both samples of B had formed a solid jelly when they were removed from the ice-chest. The viscosity results obtained on these 4 samples are plotted in Fig. 3. The viscosities of both solutions at P_H

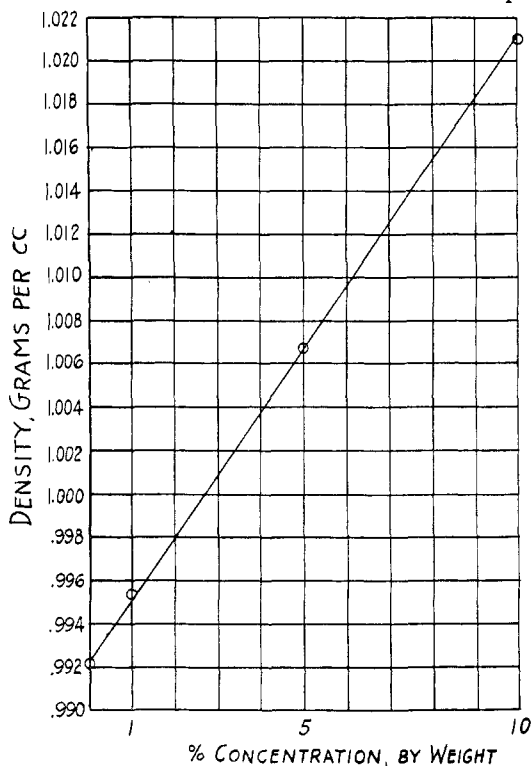


Fig. 2.—Variation of density with concentration; solutions of 3B gelatin at 40°, $P_H = 8.0$.

4.9 remained constant, Sample B giving a higher viscosity than A due to the portion of gelatin which had gone over into the gel form. Since the viscosity at P_H 4.9 changes rather slowly with age it was expected that near the transition point the change might be too slow to manifest itself in a short time. The fact that Sample B did not change in viscosity shows that while the gradient is not great enough to cause gel to form in A, neither is it great enough to cause more to form in B, or if 35° is above the transition point to destroy the gel already formed. In other words the change at this hydrogen-ion concentration is too slow to measure. Of the two samples at P_H 7.8, B kept increasing in viscosity, showing that in the hour during which it was in the ice-chest

³ Smith, THIS JOURNAL, 41, 135 (1919).

not all of it had reverted to the gel form and this change continued to take place at 35°. The transition point must then be above 35°. The A sample of this set behaved exactly like a solution in a state of suspended transformation in that the viscosity remained constant for nearly 4 hours and then increased at about the same rate as did that of the B sample. It is evident from this, then, that the transition point is above 35° and that alkali catalyzes the transition. Since it was found that at 40° the solutions did not increase in viscosity this work was repeated at 40° in exactly the same way except that 2 samples of B were investigated. Sample

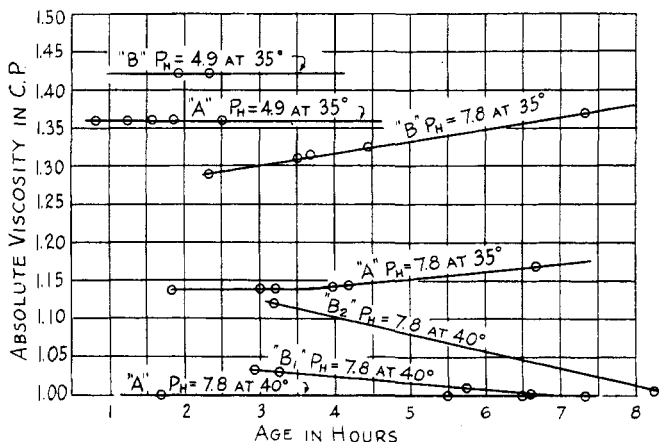


Fig. 3.—Variation of viscosity with age; 1% solutions of 3B gelatin, P_H 4.9 and 7.8 at 35° and 40°.

B_1 was left in the ice-chest for 1 hour and B_2 was left 2 hours. Both B_1 and B_2 were solid jellies when removed from the ice-chest. The results plotted in Fig. 3 show that while the viscosity of Sample A remained constant, those of B_1 and B_2 decreased continually and uniformly until the viscosity was the same as that of the A sample. This then definitely establishes the transition point as between the limits of 35° and 40°. It is also interesting to note that it requires only a small amount of the gel form B to transform the solution into a solid jelly.

In order to locate the transition point definitely a 4% solution of 3B gelatin was made up to P_H 8.0. This increased concentration was chosen in order to bring out smaller changes than a 1% solution would show. This sample was divided into 3 parts. B_1 and B_2 were put in the ice-chest for 1 and 2 hours respectively, when they were removed and placed in the thermostat at the temperature indicated in Table II. The viscosity is given in seconds rather than in absolute units since it is only the point at which the viscosity just ceases to change with age that we are trying to locate. A was not cooled below 38°.

TABLE II
 VISCOSITY OF 4% SOLUTIONS OF 3B GELATIN, P_H 8.0, AT TEMPERATURES NEAR THE
 TRANSITION POINT

Temp. °C.	Time	Elapsed time between runs Min.	Viscosity in seconds
Solution A			
38.0	11 : 25		312.8 ^a
38.0	11 : 45	20	313.8 ^a
38.0	12 : 05	20	315.0 ^a
Solution B ₁			
38.0	11 : 18	..	344.7 ^b
38.0	11 : 33	15	346.9 ^b
38.0	11 : 52	19	348.0 ^b
38.2	2 : 20	148	342.1 ^b
38.2	2 : 30	10	341.8 ^b
38.2	3 : 25	55	337.5 ^b
38.2	3 : 35	10	337.2 ^b
Solution B ₂			
38.1	3 : 56	..	410.7 ^a
38.1	4 : 07	11	408.4 ^a
38.1	4 : 18	11	407.7 ^a

Time for water for No. 2 viscometer (a) at 38° = 59.2 sec.

Time for water for No. 4 viscometer (b) at 38° = 59.8 sec.

It is obvious from Table II that the transition point of gelatin, Sol form A \rightleftharpoons Gel form B, lies between 38° and 38.1°. A close inspection of the results shows that the transition point is nearer 38.0° than 38.1°. By interpolation the value 38.03° is obtained. It is interesting to note that 4% solutions do not exhibit the lag in the transformation noted in the case of 1% solutions. Smith³ has also pointed out that the more concentrated solutions come to equilibrium more quickly than the more dilute solutions. It should also be noted that the more of the gel form present the more rapid the increase in viscosity below the transition point and the more rapid the decrease above this temperature.

Another factor liable to affect the determination of the transition point is hydrolysis with its consequent lowering of viscosity. At certain hydrogen-ion concentrations, namely, in very acid or very alkaline solutions, even at ordinary temperatures this factor is quite evident.

With decreasing acidity or alkalinity the temperature must be raised to induce hydrolysis. The question of hydrolysis is entirely separate from the one of transition point and is mentioned only because it is so often confused with the latter. If, at a given temperature and in the absence of the gel form, a decrease in viscosity with age is noted we are evidently dealing with hydrolysis. It is evident from the results described at 40° and at P_H 7.8 no hydrolysis is apparent and the results herein described are free from such effects.

Since gelatin above the transition point is in the soluble form it is inter-

esting to speculate on the physiological significance of this transition temperature 38.03° C. or 100.5° F.

Determination of Viscosity of Gelatin Solutions at Temperatures below the Transition Point⁴

Since it is only when gelatin solutions reach a temperature below the transition point that the viscosity begins to increase with age, we have modified the procedure for determining the viscosity of gelatin solutions as described in a previous article. This change consists in reheating the solution to 50° after filtering and then immediately placing the solution in the thermostat at the desired temperature and stirring vigorously until the temperature of the thermostat is reached. The age is then reckoned from the moment the solution registers 38.03° . This change in procedure eliminates the last obstacle to securing exact checks by different workers.

Variation of Viscosity with Concentration at 40°

As has been pointed out in a previous article¹ the viscosity-concentration formulas so far proposed do not hold for gelatin solutions at 25° . Owing to the fact that the gelation factor is different for each gelatin and at each hydrogen-ion concentration it was found quite impossible to apply any such formulas. Furthermore, gelation does not take place at a uniform rate, but the solution may exist for some time in a state of suspended transformation, thus rendering unreliable the application of a formula containing a factor covering the gelation effect. Evidences of this state of suspended transformation were apparent at the time of publication of the earlier paper but were not confirmed until the completion of that part of the present paper dealing with transition point.

In order to test the application of the various viscosity-concentration formulas to gelatin solutions in which the gelation factor was absent, the viscosities of solutions of varying concentrations of gelatin at P_H 8.0 were investigated at 40° . At this temperature the viscosity of gelatin solutions made up as previously described, and not allowed to cool

⁴ On the basis of Smith's work the question has been raised whether it would not be better to refer to a "transition region" with limits at 15° and 38° than to a "transition point" at 38° . The answer to this is not possible at the present time from the data at hand. Gelatin is made up of varying proportions of the different products of the hydrolysis of chondrin. Each of these different products of hydrolysis may have a different transition point. In such a case the product having the highest transition point will determine that of the entire sample.

On the other hand, the transition is extremely slow and requires days or weeks for completion at temperatures near the transition point. By reducing the temperature the "transition gradient" is increased and the change takes place more rapidly, reaching completion in a few hours at temperatures up to 10° . There is evidence substantiating each of these views. We are continuing the investigation along these two lines and at present are more inclined to the latter as being the true explanation.

below 40°, does not change with age. The gelation factor being eliminated it was thought a formula could be found which would apply.

The results for these solutions are given in Table III, and when plotted in Fig. 4 the logarithmic form of the graph suggested at once the application of Arrhenius' formula⁵

$$\log \frac{\eta}{\eta_0} = \theta c. \quad (1)$$

This formula, while first advanced for so called non-colloidal solutions has since been applied with success to protein solutions.⁶ As first proposed

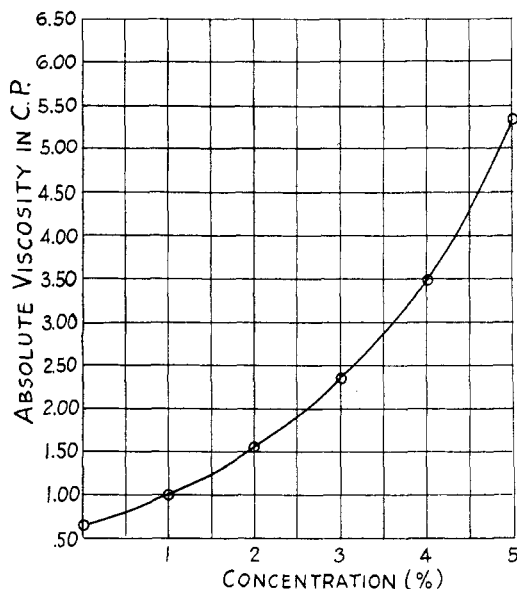


Fig. 4.—Variation of viscosity with concentration; solutions of at 3B gelatin 40°, $P_H = 8.0$.

by Arrhenius the concentration c could be expressed as volume, or weight per cent. Kendall⁷ has modified this so that c is expressed as molecular concentration which modification has been accepted by Arrhenius as giving closer agreement with experimental data. Since the molecular weight of gelatin is unknown c has been expressed in weight concentration and the formula applied to these data. The average value for θ when substituted in the original equation gives a calculated viscosity equal to the observed viscosity within the limits of accuracy of the latter, c being taken as per cent. concentration by weight.

⁵ Arrhenius, *Z. physik. Chem.*, **1**, 285 (1887).

⁶ Arrhenius, *Medd. K. Vetenskapsakad. Nobelinst.*, **3**, 13 (1916); *Biochem. J.*, **11**, 112 (1917).

⁷ Kendall, *Medd. K. Vetenskapsakad. Nobelinst.*, **2**, 25 (1913).

TABLE III
 VARIATION OF VISCOSITY WITH CONCENTRATION OF GELATIN SOLUTIONS AT 40° AND
 P_H 8.0

Concentration of gelatin %	Observed absolute viscosity C. p.	Calculated viscosity C. p.	θ
0	0.656 ³		
1	1.00	1.00	0.1831
2	1.55	1.53	0.1867
3	2.37	2.33	0.1858
4	3.47	3.55	0.1810
5	5.33	5.42	0.1818
		Ave.	0.1836

Arrhenius⁶ considers that for substances like proteins, whose molecules are extremely large compared with those of water, c may be expressed sufficiently accurately by the expression

$$c = \frac{100 p}{100 - (n + 1)p} \quad (2)$$

where p is the number of grams of solute in 100 g. of solution, and n is the hydration factor, *i. e.*, the number of grams of solvent associated with each gram of solute and therefore withdrawn from solution. Substituting this value in (1) we have⁹

$$\log \frac{\eta}{\eta_0} = \Theta \frac{100 p}{100 - (n + 1)p} \quad (3)$$

$$\text{and } n + 1 = \frac{100}{p} - \frac{100}{\log \frac{\eta}{\eta_0}} \quad (4)$$

$$n + 1 = \frac{100}{p_1} - \frac{100 \Theta}{\log \frac{\eta_1}{\eta_0}} = \frac{100}{p_2} - \frac{100 \Theta}{\log \frac{\eta_2}{\eta_0}} \quad (5)$$

$$\Theta = \left(\frac{1}{p_1} - \frac{1}{p_2} \right) \div \left(\frac{1}{\log \frac{\eta_1}{\eta_0}} - \frac{1}{\log \frac{\eta_2}{\eta_0}} \right) \quad (6)$$

This gives us a method for solving for Θ on the assumption that the gelatin is hydrated in solution at 40°. By combining the values for a 1% solution with each of the others and solving for Θ in Equation 6 we obtain values for Θ as follows: (1%-2%), 0.1796; (1%-3%), 0.1816; (1%-4%), 0.1838; (1%-5%), 0.1834; average, Θ 0.1821. Substituting this value in Equation 4 we obtain values for n as follows: 1%, -0.43; 2%, +0.23; 3%, -0.31; 4%, -1.18; 5%, -1.01. These values are well within the experimental error in determining viscosity and indicate that when gelatin is hydrated in solution at 40° the degree of hydration is very slight, cer-

³ Bingham, *Bur. Standards, Bull.*, **298**, 74 (1917).

⁹ Hatschek, *Biochem. J.*, **10**, 325 (1916).

tainly not greater than 1%. The agreement between the calculated and observed viscosities in Table III indicates the same fact because these values were calculated on the assumption that the gelatin is not hydrated.

Hatschek¹⁰ has proposed the formula $\frac{\eta_0}{\eta} = 1 - \sqrt[3]{\phi}$ where η as usual is the viscosity of the solution, η_0 that of the solvent and 100ϕ is the volume per cent. of the dissolved substance with its associated solvent. Regarding this formula Smoluchowski¹¹ says: "It may be an interpolation formula of a certain use in many cases, but it is probably of no general significance, as it is impossible to give it a rational foundation." Hatschek⁹

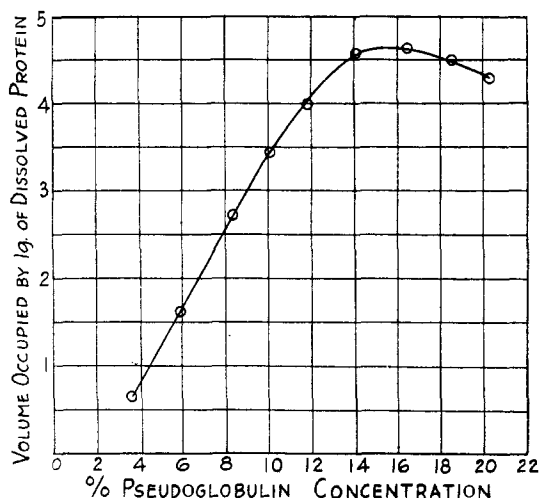


Fig. 5.—From Chick.

calls attention to the application of his formula by Miss Chick¹² to some of her results on various proteins and emphasizes the fact that where the dissolved substance with its associated solvent occupies more than 50% of the total volume the formula holds very well. Arrhenius⁶ shows that Hatschek's equation does not give constant values for the degree of hydration even under the conditions imposed by Hatschek. Arrhenius also suggests that it is improbable that a continuous function such as the degree of hydration of these various proteins should be represented by an equation for a discontinuous function. In Fig. 5 we have plotted the values obtained by Miss Chick for pseudoglobulin. In selecting her values for the hydration constant she chose points at the top of the curve. This is the only point where Hatschek's formula can possibly

¹⁰ Hatschek, *Kolloidchem.*, **8**, 34 (1911); **11**, 284 (1912); **12**, 238 (1913).

¹¹ Smoluchowski, *Kolloid Z.*, **18**, 190 (1916).

¹² Chick, *Biochem. J.*, **8**, 261 (1914).

give anywhere near constant values. Generally the solutions become so viscous that few values can be determined on the descending portion of the concentration-volume curve.

A glance at Fig. 6 indicates why Hatschek's formula gives more nearly constant hydration values above 50% than below. Up to the point where $\phi = 0.5$ or where the solute with its associated solvent equals 50% of the total volume the viscosity increases only to 4.858 times that of the solvent. As ϕ increases from 0.5 to 1 the viscosity increases from 4.858 to infinity. In other words, over that portion of the curve up to $\phi = 0.5$ the viscosity increases fairly uniformly with the total volume occupied by the solute with its associated solvent. Beyond the point

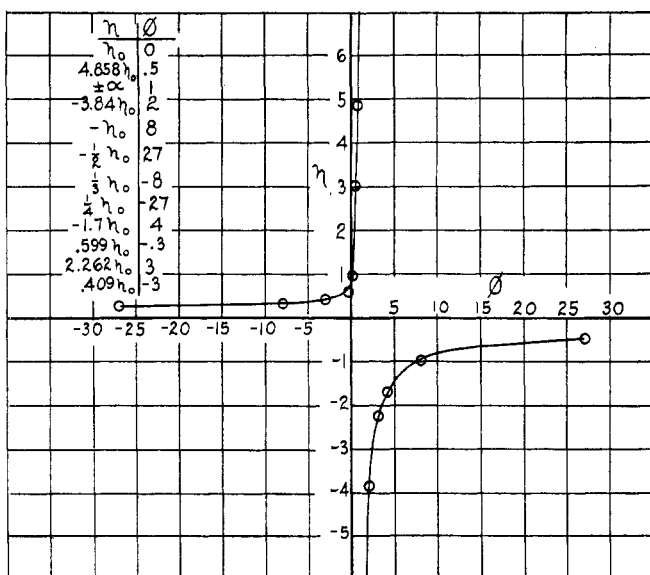


Fig. 6.—Graph of Hatschek's hydration formula $\frac{\eta_0}{\eta} = 1 - \sqrt[3]{\phi}$, assuming $\eta_0 = 1$.

where $\phi = 0.5$ the formula would have the viscosity increase out of all proportion to ϕ if ϕ continued to increase at a uniform rate. Now the experimentally determined viscosity does not increase as rapidly as is demanded by the formula so that ϕ must change from an increasing to a decreasing function. That section of the curve where ϕ is undergoing a change of direction will indicate a more constant value for the degree of hydration. Beyond this point the degree of hydration will decrease rapidly. Since most solutions are too viscous to manipulate on this downward part of the curve (Fig. 5) by selecting values above $\phi = 0.5$ they necessarily come on this flat section.

When Hatschek's formula is applied to the results in Table III it gives

the following values for ϕ and for the volume occupied by 1 g. of gelatin with its associated water.

Concentration of gelatin. Weight per cent.	ϕ	Volume occupied by 1 g. of gelatin plus associated water
1	0.0407	4.07
2	0.1917	9.58
3	0.3781	12.60
4	0.5333	13.33
5	0.6741	13.48

B does not even approach a constant value until ϕ is greater than 0.5. We have just seen that from the nature of the equation this is exactly what is to be expected and the formula apparently has no general application. Instead of each gram of solute associating itself with an increasing amount of water with decreasing concentration of water (increasing concentration of solute) we would expect the reverse to be the case. Hatschek was at first enthusiastic over Miss Chick's results because they gave a constant hydration factor. He then proceeds to apply the formula to Para rubber-benzene solutions. A 0.5% solution of Para rubber in benzene gives an association factor of 62%. Obviously a 1% solution must give a lower factor. It seems certain then that Hatschek's formula when applied to these solutions gives no information as to their behavior, while Arrhenius' equation expresses the results within the experimental accuracy. Naturally Einstein's formula $\eta = \eta_0 (1 + 2.5\phi)$ does not apply, for the viscosity is increasing more rapidly than the equation permits. As Smoluchowski¹¹ points out "For the sphere this value ($k = 2.5$) has evidently a minimum value. There is no excuse for Hatschek's higher values. K decreases with increasing diameter of the spherical particles." Hess¹³ under the title "Theory of the Viscosity of Heterogeneous Systems"

has proposed the formula $\eta_s = \frac{\eta}{1 - aK}$ where η_s is the viscosity of the

suspension, η the viscosity of the fluid dispersion medium, K is the volume of the suspended particles and a is a characteristic constant for each substance and always greater than 1. The formula was tested with suspensions of blood corpuscles which offer the advantage of great uniformity. For cattle blood, a is 1.6-1.52; for pig blood, 1.42; for sheep blood, 1.52.

Before considering the application of this formula to the data under discussion let us consider its relation to Einstein's formula.

Hess' equation is

$$\eta = \frac{\eta_0}{1 - aK} \quad \text{or} \quad \frac{\eta}{\eta_0} = \frac{1}{1 - aK};$$

¹³ Hess, *Kolloid Z.*, 27, 1 (1920).

Einstein's equation is

$$\eta = \eta_0(1 + 2.5\phi) \text{ or } \frac{\eta}{\eta_0} = 1 + 2.5\phi;$$

whence

$$\frac{1}{1 - aK} = 1 + 2.5\phi.$$

and

$$1 + aK + a^2K^2 + a^3K^3 + \dots = 1 + 2.5\phi.$$

Einstein's 2.5ϕ represents the summation of $aK + a^2K^2 + \dots$ and since neither holds except for dilute solutions $aK = 2.5$ and the identity of the two equations is evident. Hatschek¹⁴ proves the identity of Hess' formula and his own. It would seem then that Hatschek's formula as well as that of Hess is identical with Einstein's, although Hatschek does not even mention Einstein in his article.

Variation of Viscosity with Temperature

The viscosity of 1% solutions of 3B gelatin of P_H 8.0 was investigated over a temperature range of 25° to 60°. These results are plotted in Fig. 7 together with the viscosity of water over the same range. It will be seen from the figure that the viscosity is not a simple function of the temperature. At 40° and above, the viscosity of the solutions did not change with age. Above 65° Arisz¹⁵ has shown that glycerine-water-gelatin solutions decrease in viscosity with aging of solution. The higher the temperature the more rapid the decrease. We have shown¹ that the same is true for water-gelatin solutions and that this decreasing viscosity is due to hydrolysis of the gelatin. Arisz suggested but did not prove this point. We also showed that hydrogen and hydroxyl ions catalyze this hydrolysis and established the concentrations of these ions necessary to hydrolyze gelatin solutions below the limit set by Arisz. Furthermore, even at 25° certain concentrations of hydrogen and hydroxyl ions caused a continued hydrolysis of gelatin. Northrup¹⁶ has studied this question in minute detail over the entire range of hydrogen-ion concentration. He finds that the hydrolysis is 10 times as rapid at 65° as at 40°. Inasmuch as our measurements were made at P_H 8.0, hydrolysis had too slight an effect to make itself felt in the results.

It will be seen from Fig. 7 that the viscosity is not a simple function of the temperature. Above 40° the viscosity of the solutions did not change with age. At 35° and below the viscosity increased with age. This increase in viscosity with aging of solution accounts for the curve

¹⁴ Hatschek, *Kolloid Z.*, **27**, 163 (1920).

¹⁵ Arisz, *Kolloidchem. Beihefte*, **7**, 1 (1915).

¹⁶ Northrup, *J. Gen. Physiol.*, **3**, 6, 715 (1921).

being steeper below 35° than it is above 40° . Below 35° the gelation factor manifests itself while above 40° this factor is absent. By prolonging the curves at 35° and 40° as dotted lines they are found to cross at 38° . The transition point of gelatin should lie close to this point.

Variation of Viscosity with Hydrogen-ion Concentration at 40°

It has been pointed out in a previous article¹ that at 25° the forms of the hydrogen-ion concentration-viscosity curves will differ considerably,

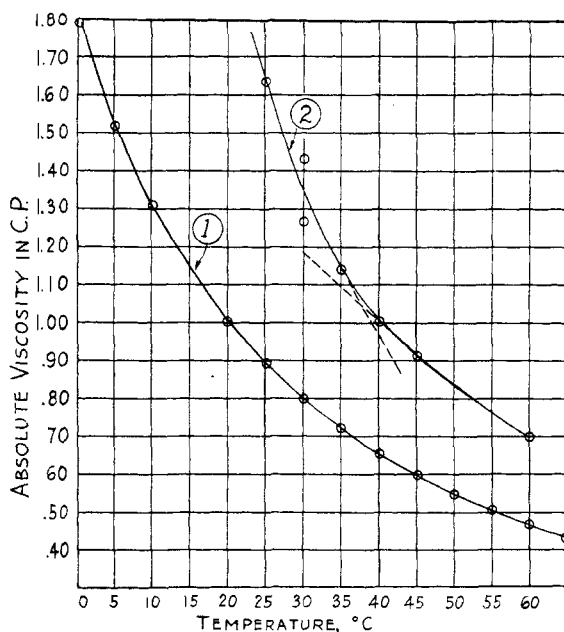


Fig. 7.—Variation of viscosity with temperature, 1 = water, 2 = 1% gelatin solution 3B, $P_H = 8.0$.

especially on the alkaline side of the iso-electric point, depending upon the age of solution at which the viscosity is determined. In that paper data were given showing that the form of the curve meant little unless the age of solution and the time rate of increase in viscosity were given. Since the viscosity of gelatin solutions does not increase with age at 40° it seemed desirable to determine the effect of different acidities at this temperature.

Accordingly, 1% solutions of 3B gelatin were investigated over a range of P_H values from 1.7 to 12.3. These results are plotted in Fig. 8 and show a very distinct maximum in the viscosity at P_H 3.5. At P_H 11.0 to 12.0 there is another maximum in the viscosity. Due to the very rapid hydrolysis of the gelatin at this temperature and at P_H values greater than 10 the viscosity decreased so rapidly with aging of solution that it was impossible to locate the exact point of maximum viscosity.

The interesting part of this curve lies not so much in the maxima which coincide very closely with those obtained by Loeb¹⁷ as in the minimum point of viscosity which lies between P_H 7 and P_H 8. There can be no doubt whatever that this is the point of minimum viscosity at this temperature, for not only were the viscosities and P_H values checked very carefully, but the slope of the curve on both sides of the minimum agrees with this point. This may very well be the result of absence of the age effect on viscosity; the minimum obtained at P_H 4.7 at 25° would then be an apparent minimum only.

Consider the action of the two major factors affecting gelatin solutions at 25° and in the P_H range 3.5-10.0. Addition of alkali causes

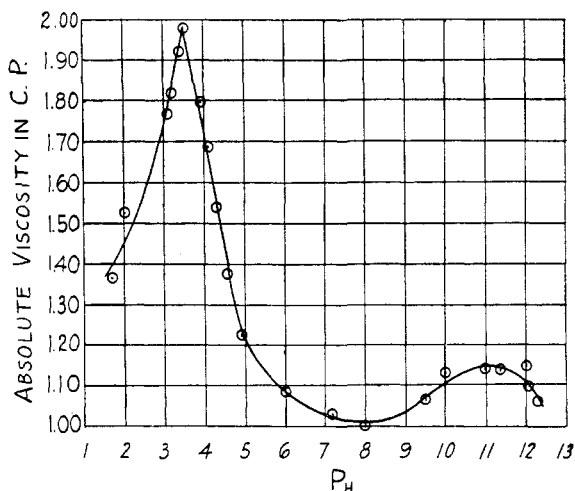


Fig. 8.—Variation of viscosity with P_H ; 1% solutions of 3B gelatin at 40°.

a decrease (R) in viscosity at P_H 3.5. At the same time there is an increase in the rate of gelation (g) caused by the addition of alkali.¹ Where the algebraic sum of these factors $g + R$ equals zero (R being negative at this point) there will be a maximum or a minimum. At 40° this gelation factor is absent; consequently we are getting the true effect of hydrogen-ion concentration on viscosity. It has been suggested that the ash content of this gelatin, which amounted to 0.5 per cent., influenced the point of minimum viscosity. That this is unlikely is seen from the fact that both Loeb and ourselves have repeatedly shown that when the hydrogen-ion concentration remains the same the presence of nonprecipitating salts has no effect other than their effect on the water itself. There may be considerable difficulty in reconciling this minimum viscosity at P_H about 8.0 with the iso-electric point at P_H 4.7.

¹⁷ Loeb, *J. Gen. Physiol.*, 3, 85 (1920).

Summary

1. The density in grams per cubic centimeter of a gelatin solution of any concentration at any temperature is equal to the density of water at that temperature plus 0.00290 multiplied by the percentage concentration of the gelatin by weight.

2. The viscosities of gelatin solutions of various concentrations at 40° conform to Arrhenius' viscosity formula.

3. The viscosity-temperature curve of gelatin shows a sharp deflection at the transition point of the gelatin.

4. There are two maxima in the viscosity-hydrogen-ion concentration curve for gelatin solutions at 40°. These maxima are about equidistant from the neutral point of water and the effect of the iso-electric point P_H 4.7 is not noticeable on the curve.

5. The transition point of gelatin Sol form A \rightleftharpoons Gel form B is at a temperature of 38.03°.

6. A change has been suggested in the method of estimating age of solution for viscosity determinations at temperatures below the transition point of the gelatin

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THE PRESSURE OF OXYGEN IN EQUILIBRIUM WITH SILVER OXIDE

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Introduction

The transfer of oxygen from the chemically combined or bound condition to the free condition is somewhat analogous to the passage of a substance from the solid phase to the gaseous phase. The combined oxygen in an oxide (or the combined carbon dioxide in a carbonate) may be conceived as occupying at any temperature and pressure a definite partial specific volume and regarded as the specific volume of the compound less the specific volume of the metal or other atomic residue. Thus for silver oxide the volume of a gram of oxygen, in the combined condition, obtained from the densities of silver oxide (Ag_2O) and silver, would be 0.6472 cc. at ordinary temperatures, which in fact in this instance is about the estimated volume of 1 g. of oxygen in the free solid condition at -273° .

In the case of silver oxide large pressures of oxygen are obtained at comparatively low temperatures and the gas law $pv = RT$ is insufficient as an equation to calculate the equilibrium volumes of the oxygen. G. N.