

tion of the work of Mr. F. Reuter, formerly instrument maker to this Laboratory, who built the instrument.

Summary.

1. We have described 2 types of photometer distinguished as vertical and horizontal types for the study of colloids.

2. The vertical plane type easily lends itself to modification for use as a nephelometer, colorimeter, microphotometer, dispersimeter and turbidimeter.

3. The horizontal type is strictly a transmission and scatter photometer of chief utility in determining particle size, comparative turbidities and coagulation velocities.

ROCHESTER, N. Y.

[COMMUNICATION NO. 108 FROM THE RESEARCH LABORATORY OF THE EASTMAN KODAK COMPANY.]

THE ELASTIC PROPERTIES OF GELATIN JELLIES.

BY S. E. SHEPPARD AND S. S. SWEET.

Received January 19, 1921.

In a previous paper there has been described a torsion dynamometer for measuring the mechanical strength of gelatin jellies.¹ In that paper the measure of jelly strength adopted was either the "breaking load" or the $\frac{\text{"breaking load"} \times \text{twist}}{\text{cross section}}$. The "breaking load" or torsional tenacity

marks the end of the stress:strain curve of the material. It is well known² that in general this value is less definitive, less immediately and certainly related to other physical and chemical properties of a material than the typical elastic constants, *viz.*, *Young's modulus* (of stretch), the *modulus of rigidity* (or shearing) and the *bulk modulus*. The torsion dynamometer described by us readily permits the determination of the *modulus of rigidity*. Calling this N , it is defined by the ratio $N = \text{shear stress/shear strain} = g/\theta$.

If θ is the angle of twist in degrees, T the twisting moment in g./mm., l the height of cylinder in mm. and $D =$ diameter of cylinder in mm., then

$$N = \frac{583 Tl}{D^4 \theta} \text{ g./inm.}^2$$

We have found it usually desirable to calculate N in g./mm.², as giving convenient figures.

Experimentally, this expression reduces to the following for our instrument.

¹ S. E. Sheppard, S. S. Sweet, and J. Scott, "The Jelly Strength of Gelatine and Glues," *J. Ind. Eng. Chem.*, **12**, 1007 (1920).

² Cf. A. Morley, "Strength of Materials," Chap. 2 (Longmans Green & Co.), 1911.

$$N = \frac{583 \times 24.085 \times 31.75}{(25.425)^4} \times \frac{L}{\theta}$$

$$= 1.057 L/\theta$$

where L is the load in grams, and θ the angle of twist in degrees. To determine N therefore simultaneous values of L and θ are read off while the torsion is being applied at a uniform slow rate. For this the torsion is applied by a geared down centrifugally governed constant speed motor, the rate of twisting being usually $36^\circ/\text{minute}$. Through a change speed set of gears, other rates of twisting could be used if desired, but when the

rate becomes much greater than $70^\circ/\text{minute}$ it is necessary to have an automatic recorder for the stress strain curve. Such a recorder is being designed, but is not essential for measurements of the curve at low rates of shearing.

Gelatin Jellies are Rigid.

The typical curves, for different concentrations, given in Fig. 1 show that gelatin jellies under torsion follow Hooke's law nearly up to the breaking load;¹ the *limit of elasticity* and the *tenacity* very nearly coincide. (Fig. 1.) Conditions under which this is departed from will be noted later. One consequence of this, however, is that results for jelly-strength on the *tenacity* basis will generally be fairly comparable with those on a rigidity basis.²

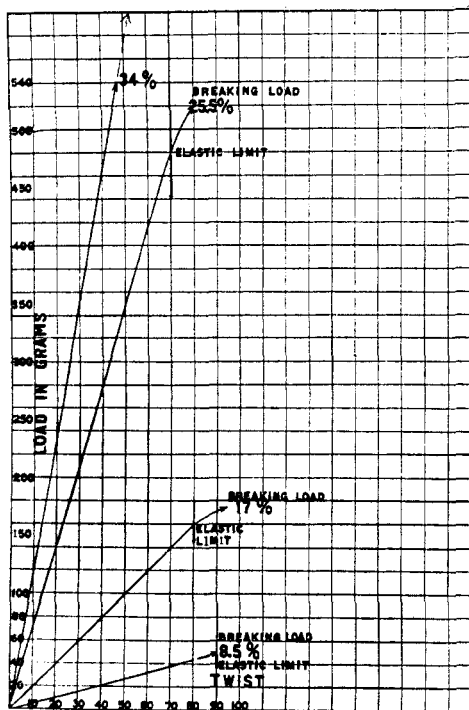


Fig. 1.

The curves connecting tenacity with concentration, given in our former paper remain approximately the same if the modulus of rigidity be substituted for the tenacity. (See Fig. 2.) Further, the

¹ Certain deviations were observed for small loads, resulting in a shift of the origin in opposite senses for both low and high concentrations. The method of testing is a dynamic one, and this effect appears to be the resultant of frictional and inertia terms of the instrument, on the one hand, and rate of transmission of stress in the jelly on the other. A separate investigation is being made of the time of relaxation under static loading conditions.

² *Loc. cit.*

quantity $\frac{\text{breaking load} \times \text{twist}}{\text{cross sectional area}}$ taken in the former paper as a measure

of jelly-strength is, in this case of approximate coincidence of the elastic limit with tenacity,¹ proportional to the "proof resilience," *i. e.*, the strain energy stored at the elastic limit. For unit volume this equals $\frac{1}{2}$ (stress \times strain) at the elastic limit. Hence, the values of jelly-strength expressed in the former measure can be converted approximately, into "proof resilientances per mm." by multiplying by $\frac{1}{2} \left(\frac{583 \times 31.75 \times 34.085}{(25.425)^2} \right) = 362$.

Relation of Modulus of Rigidity to Concentration.

As already stated, the relation of N to concentration of gelatin for a given sample will not differ markedly from that found for the jelly-strength values given. We have, however, determined this relation for N for a number of gelatins. Typical curves, plotted from the values as in Fig. 1 are given in Fig. 2. At the same time we are now able to compare our results on the elasticity of gelatin jellies with those of former observers. Previous observations are due to Fraas, Leick, Reiger, Maurer and Bjerken.² In particular, Leick gives values for Young's modulus (of stretch) obtained by stretching moulded blocks of jelly, dimensions $10 \times 6 \times 1.6$ cm³, in relation to concentration of his jellies.³ Leick's values are for the *modulus of stretch*. Calling this E , we may note that E and N are related by the equation

$$N = \frac{E}{2(1 + \mu)}, \text{ where } \mu = \frac{\Delta D}{D}; \frac{\Delta l}{l} \text{ (Poisson's ratio),}$$

¹ Torsional tenacity is referred to here.

² Fraas, *Wied. Ann.*, **53**, 1089 (1894); Leick, *Dend. Ann.*, **14**, 139 (1904); Reiger, *Physik. Z.*, **2**, 213 (1901); Maurer, *Wied. Ann.*, **28**, 628 (1886); Bjerken, *ibid.*, **43**, 817 (1891).

³ Leick states that the gelatin used was of good quality photographic gelatin from Hoechst & M.

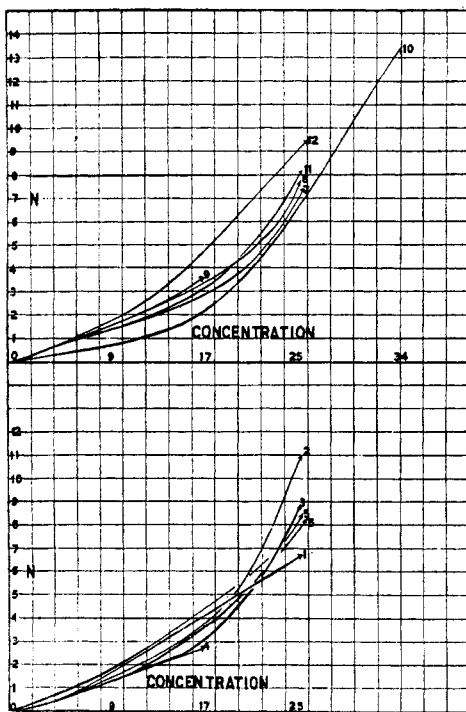


Fig. 2.

i. e., the relation of the relative alteration of diameter to the relative alteration of length. According to experiments of Maurer, Bjercken and others, the volume of a gelatin jelly is practically constant even for relatively large stretching loads. Hence μ can be taken as equal to $1/2$, and hence

$$N = E/3 \text{ or } E = 3N.$$

We have converted our values of N for a typical "hard gelatin" into E -values and get, for comparison with Leick's, the following table,

Leick.			Sheppard and Sweet.		
Concentration. %	E . g./mm ² .	E/C^2 .	Concentration. %	E . g./mm ² .	E/C^2 .
10.0	2.42	2.4	8.5	1.98	2.8
10.2	2.66	2.6	17.0	6.5	2.3
18.6	9.78	2.8	25.5	18.4	2.8
18.9	9.77	2.7	34.0	38.1	2.3
30.0	15.45	1.7			
32.0	21.57	2.1			
45.0	29.44	1.5			

It will be seen that the agreement as regards actual values is as near as is likely for a material giving such variable results from one grade to another. On the other hand, we are unable generally to confirm Leick's conclusion that the elastic modulus is proportional to the square of the concentration.

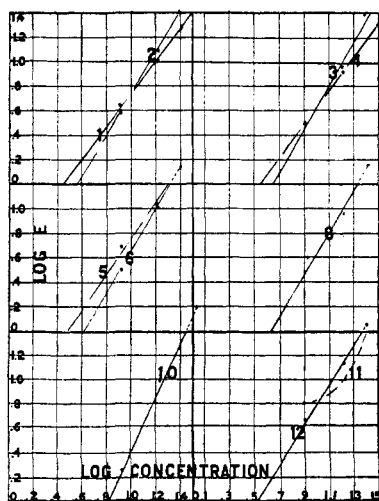


Fig. 3.

In fact, when a large number of different brands of gelatins are investigated, our results indicate that even if the relation of the elastic modulus to concentration be representable by a function of the type $E = k c^n$ for a certain range, n may vary from one sample to another. To test this we have plotted $\log E$, or $\log N$, as ordinate against $\log C$ as abscissa. It will be seen that the general function of the type considered gives $\log N = \log k + n \log C$. Our results show that on taking a wide variety of commercial gelatins: (Fig. 3) (a) some gelatins give good approximations to a straight line relation of the above type, (b) in others the curve is definitely concave to the x-axis, (c) in the case (a) the value of n may be less than or equal to 2. Leick's result, therefore, appears to be either a special case or a limiting condition.

It has been generally accepted that the properties of different gelatins depend in a large measure upon the ratio of hydrolytic products to unal-

tered gelatin. Recently Bogue¹ has shown that "a most clear-cut relation exists between the nitrogenous constituents and the jell-strength, which may be summarized as follows: (1) the protein nitrogen varies directly as the jell-strength; (2) the proteose and peptone nitrogen vary inversely as the jell-strength; (3) the amino-acid nitrogen shows a slight tendency to vary inversely as the jell-strength."

It is possible, and this will be investigated further, that the variability of the function $N = f(c)$ depends upon the proportions of these components. Before considering this more thoroughly, however, it appeared desirable to ascertain the effect of certain other factors upon the elastic modulus, with a view to securing jellies of different gelatins in corresponding or comparable states.

Effect of Hydrogen-ion Concentration.

The investigations of a number of workers, notably Wo. Pauli,² H. R. Proctor,³ J. Loeb,⁴ Sørensen,⁵ and Clark,⁶ on the physical chemistry of the proteins, and not least of gelatin, point to the hydrogen-ion con-

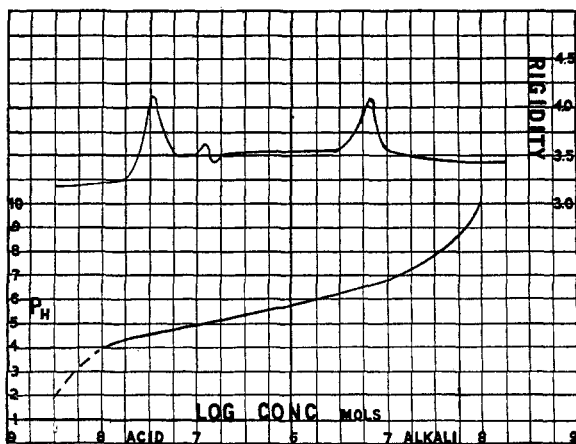


Fig. 4.

centration being an essential factor, indeed the controlling factor, for the greater number of both chemical and physical reactions of these substances. Hence, before investigating the influence of other electrolytes,

¹ R. H. Bogue, "Properties and Constitution of Glues and Gelatines," *Chem. Met. Eng.*, **23**, 5-12, 61-67, 105-113, 154-159, 197-205 (1920).

² Cf. "Kolloid Chemie der Eiweisskörper," H. 1 (Heinkoff, Dresden and Leipzig, 1920).

³ Proctor, *Trans. Chem. Soc. (London)*, **105**, 313 (1914).

⁴ Loeb, *J. Gen. Physiol.*, **1**, 39 (1918).

⁵ Sørensen, *Compt. rend.*, Lab-Carlsberg, **9**, 1 (1917).

⁶ Clark, "The Determination of Hydrogen Ions." Williams and Wilkins, Baltimore, 1920.

it appeared essential to determine the effect of hydrogen-ion variation. It is known that different commercial gelatins, and different batches of the same brand, vary in "acidity," but in view of the great sensitiveness of proteins it is evident that we can only get a useful comparison of different gelatins when placed on an equivalent hydrogen-ion basis.¹

The values obtained with different gelatin concentrations (5, 10, 20%, air-dry basis)² varying the concentration of the acid and alkali are shown in Fig. 4.

We have also determined the value of P_H for the gelatin in question at 2% and 5% concentrations at each relative change of acidity. These

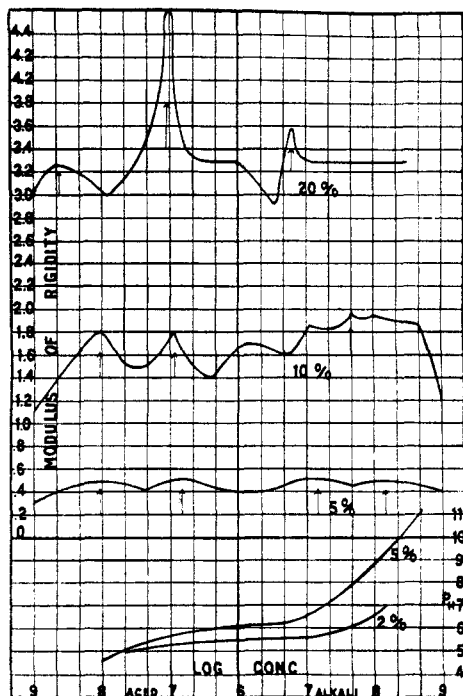


Fig. 5.

curves, similar to Patten and Kellems' for commercial gelatin³ show that the changes of elasticity of the gelatin jellies with acid and alkali are not a simple function of the actual hydrogen-ion concentration, or of P_H . While the decline in elastic strength at either end of the series may be attributed to hydrolysis of the protein superposed on salt formation the maxima and minima between do not at present appear to be entirely explainable in terms of the present theories of gelatin as an ampholyte. Similar variations are obtained with other commercial gelatins but with positions and intensities somewhat altered. (See Fig. 5.) It appeared possible that part of the phenomena here might be due to imperfect adjustment of equilibrium. The procedure in preparing the jellies was as follows: (1) weighed amount of gelatin is swollen in cold water for 15 minutes; (2) acid or alkali solution to bring up to desired strength is added; (3) heated

¹ The sensitiveness is of the same order as changes of color of indicator dyes, but is shown as change of mechanical strength instead of visible color. We consider it possible that the "ionic dissociation" side of this is probably just as secondary to catalysis of tautomeric changes of constitution as for color changes with indicators. That does not affect the present argument, however.

² Moisture in this gelatin was 15.0%, ash 1.16%.

³ Patten and Kellems, *J. Biolog. Chem.*, **39**, 363 (1920).

for 5 minutes at 60°; (4) cooled for suitable viscosity, to 30-35° and poured into molds; (5) set and chilled.

Experiments showed that while time of chilling beyond 6 hours had little or no influence, duration and intensity of the heat-treatment 3 had considerable effect.

The results shown in Fig. 6 for another gelatin¹ illustrate this. The full curve is for the gelatin (at 10% air-dry basis) treated as described above, the broken curve for a similar series, but with a 5-minute cooking at 98-99° superposed on Stage 3. It will be seen, that the general outline is substantially the same, the salients in the curve being rather more sharply emphasized.

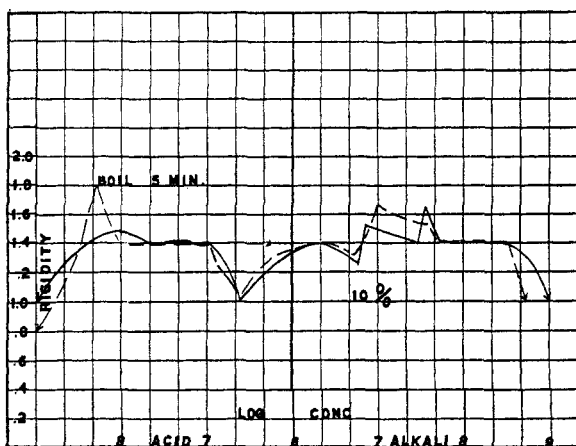


Fig. 6.

ance, inasmuch as for small relative changes in the acidity the jelly-strength shows an over-all variation from 100 to 150, inside the limits when obvious break-down is occurring. The investigation of these effects is being continued, concurrently with the study of viscosity. The results detailed above were obtained with hydrochloric as acid, and sodium hydroxide as alkali; the effect of weak (organic) acids and bases is being investigated.

Effect of Alcohol on Elastic Modulus.

The effect of non-electrolytes miscible with water, is likely to be different, according as they are strong precipitants for gelatin, or not. We have taken ethyl alcohol as representative of the first type, and obtained the following results: the modulus of rigidity, and the jelly strength, increase slowly at first, with increasing alcohol content up to about 25% alcohol. See lower curve, Fig. 7. Up to about 40%, the jellies broke normally. Above this concentration an elastic limit was reached, above

¹ Edible gelatin in powder form (Cox).

which alcohol and water were squeezed out of the jelly, the diameter contracted progressively, the residual jelly went transparent, and gave now nearly unlimited twist. This expulsion of alcohol and water from

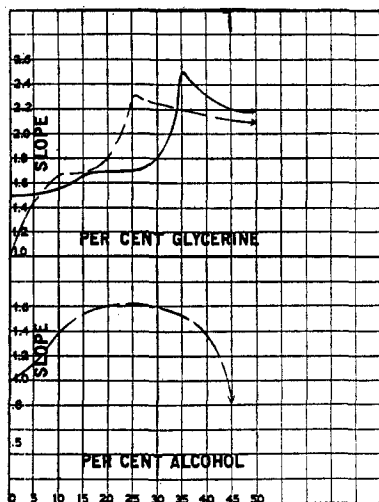


Fig. 7.

algogels of gelatin by pressure or shearing has already been observed by Hardy.¹ The apparatus used by us makes possible, however, a more quantitative study of the relation of the shearing stress to this separation; and further work is in progress on this, as contributing to the theory of the structure of so-called elastic gels. In this connection it was observed that the jellies with considerable alcohol, as also the jelly from which alcohol had been expressed, were noticeably more tacky than the straight water jellies. This is very possibly due to extraction of a hydrolyzed part of the gelatin. It appears possible that apparent incidence of plastic yield with the high alcohol content jellies is associated with a sort of phase reversal of position, the hydrolyzed portion becoming external to the non-hydrolyzed protein.

Effect of Polyhydrols on the Elasticity.

While monohydrols (alcohols and phenols) precipitate gelatin from aqueous solution, this is not the case with polyhydrols, such as glycerol, sugars, etc. It is known that these substances increase the jelly strength, and in working toward a theory of the structure of colloid jellies it appeared desirable to investigate this action quantitatively. Curves are given for 2 different gelatins (see upper half, Fig. 7) at the same concentration of gelatin. It will be seen that while the general shape of the curves is the same, the maximum occurs earlier in one than in the other. This effect is now being studied over a wide range of both gelatin concentrations, different gelatins, and different P_H adjustments.

The Structure of Gelatin Jellies.

The present results appear to us to indicate that gelatin jellies cannot be attributed to an identical structure independent of their conditions of formation and their composition. Rather does it seem that every transition exists between a 2-phase type of structure with elements submicroscopic but not necessarily molecular in period² and a type in which the

¹ W. B. Hardy, *Proc. Roy. Soc.*, **66**, 95 (1900).

² Cf. W. B. Hardy, *loc. cit.*, "The Mechanism of Gelatin in Reversible Colloid Systems."

mechanical strength must be attributed to solution forces, the system being physically homogeneous down to molecular and submolecular dimensions. A more complete survey of the elastic constants, particularly of the time of relaxation, in relation to composition and treatment, is now in progress, both mechanical and optical methods being used. It is believed that the comparison of mechanical and optical methods will permit a more definite allocation of the respective types of structure.

Summary.

1. Measurements of the rigidity of gelatin jellies are given, showing that the jellies follow Hooke's law nearly up to the breaking point.
2. The relation of the modulus of elasticity to the concentration of gelatin is discussed; it is found that a function of the type $E = kc^n$ is valid for a certain range, but the constants k and n may vary from one grade of gelatin to another.
3. The influence of acidity and alkalinity on the elasticity has been followed quantitatively. P_H measurements show that the observed variations of elasticity are not a simple function of the actual hydrogen-ion concentration.
4. The influence of alcohol and glycerin in different concentrations on the coefficient of rigidity has been measured.

ROCHESTER, N. Y.

[CONTRIBUTION FROM RESEARCH LABORATORY OF WESTINGHOUSE LAMP COMPANY.]

VAPOR PRESSURE OF WHITE PHOSPHORUS FROM 44° TO 150°.

BY DUNCAN MACRAE AND C. C. VAN VOORHIS.

Received January 20, 1921.

1. **Purpose.**—In connection with another investigation in this Laboratory, measurements on the vapor pressure of white phosphorus between 50° and 150° having an error of not over 2 or 3% were desired.

2. **Previous Measurements.**—Measurements have been made on the vapor pressure of phosphorus by the following investigators: Schroetter,¹ from 165° to 287.3°; Hittorf,² from 230° to 530°; Troost and Hautefeuille,³ from 360° to 550°; Joubert,⁴ from 5° to 40°; Jolibois,⁵ from 145° to 312°; Centnerszwer,⁶ from 20° to 40°; Smits and Bokhorst,⁷ from 169° to 409°.

The results of these measurements together with our own are given

¹ Schroetter, *Wien. Ber.*, **1**, 130 (1848).

² Hittorf, *Pogg. Ann.*, **126**, 193-228 (1865).

³ Troost and Hautefeuille, *Ann. chim. phys.*, **2**, 145 (1874).

⁴ Joubert, *Compt. rend.*, **78**, 1853-5 (1874).

⁵ Jolibois, *ibid.*, **149**, 287 (1909); **151**, 382 (1910).

⁶ Centnerszwer, *Z. physik. Chem.*, **85**, 99-112 (1913).

⁷ Smits and Bokhorst, *ibid.*, **91**, 249-312 (1916).