

SECTION II.—THE PHYSICAL PROPERTIES OF ELASTIC GELS

The Introductory Paper to this Section of the Discussion was given by **Mr. Emil Hatschek**.

THE PROPERTIES OF ELASTIC GELS

BY

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The statement that the familiar table jellies (gelatine gel) are typical representatives of the class to be discussed in the present paper will probably, at the outset, be found more useful than an attempt at strict definition. These systems exhibit immediately two of the most characteristic properties of the elastic gel: stability of shape, notwithstanding a very high content of liquid (about 95 per cent. in the case quoted) and perfect elasticity within certain narrow limits.

The gel may be obtained in two opposite ways: either by transformation—which may be reversible or irreversible—of a sol, *e.g.*, by cooling a gelatin sol below a certain temperature; or by allowing the dry substance to “swell” in an appropriate liquid. Practically all substances from which elastic gels may be produced show this capacity of swelling, though to an extent which differs widely. Only certain liquids will cause a given substance to swell, and the relations between the constitution of the solid and the liquid, on which this property is based, are at present quite obscure. Thus gelatine and agar (the former a protein, the latter a mixture of carbohydrates) swell in water at ordinary temperature, but do not dissolve until the temperature is raised. Vulcanised india-rubber swells in various organic solvents such as benzene, toluene or xylene, without dissolving. Finally, the processes of swelling and dispersion or solution may proceed *pari passu*, as with gum arabic at ordinary temperature. At low temperature, a definite stage of swelling may be observed to precede solution.

The elastic gel which can be most easily reproduced and has, accordingly, been studied most frequently and extensively, is that of gelatine. Bodies of any desired shape can be obtained by pouring the gelatine sol into suitable moulds and allowing it to set for a period of not less than 24 hours (*cf. infra*, E. Fraas). The procedure, once chosen, must be rigidly adhered to throughout, since all the properties of a gel depend, not only on its composition, but also to a marked extent on its history, especially its “thermal history,” *i.e.*, the temperatures to which the sol has been exposed and the duration of such exposure. Some of the principal investigations will now be briefly summarised.

ELASTIC PROPERTIES

These have been studied principally by R. Maurer,¹ P. v. Bjerken,² E. Fraas,³ and A. Leick.⁴ All these investigations date back some time, and were undertaken with a view to studying a material with very low modulus and sufficiently transparent for examination in polarised light, rather than with the intention of elucidating such

problems as the structure of gels. Both Maurer and Leick determined Poisson's ratio for gels of various concentrations and find it 0.5 within the limits of error—a result which is not surprising in view of the large percentage of liquid. Maurer studied the elongation of gel cylinders of considerable diameter (2.21 cm.) with small loads, the extensions being measured microscopically. His figures for the modulus are in good agreement with those found by Leick, which range from 2.42 (gm/mm²) for 10 per cent. to 29.4 for 45 per cent. gels. Leick found the modulus E roughly proportional to the *square* of the gelatine concentration; the ratio E/c^2 , however, varies somewhat irregularly, and decreases with increasing c . All the investigators find that the modulus increases with increasing load.

Fraas studied the ageing of gels and found that a constant modulus was not reached until about 24 hours after apparently complete setting. These hysteresis effects are universal in colloidal systems, and the increasing modulus of a gel is paralleled by the increasing viscosity of the sol, when kept at a temperature above the setting point. In the following table one series of Fraas's results is given to illustrate the magnitude of the effect.

Cylinder of 20 per cent. Gelatine Gel

Hours after removal from mould - - -	1	2	3	4	5	6	7	24
Extension produced by 50 gm. weight -	12.5	7.5	7.7	6.5	6.5	6	5	

Maurer, and more particularly Leick, also studied the effect of various substances dissolved in the water on the elastic modulus of gelatine gels; the results are of particular interest from the colloidal point of view, inasmuch as they can be co-ordinated with the well-known effects of such solutes on other properties of the system, *e.g.*, maximum swelling, setting point of sol, &c. Leick finds that the addition of various chlorides lowers the modulus, sodium sulphate is without action, while cane sugar and glycerine raise the modulus considerably. Chlorides also lower the viscosity and setting temperature of the *sol*, while glycerine and cane sugar (generally substances containing hydroxyl groups) raise both constants.

The elasticity of gels is perfect only for small loads applied for a short time, but very little work has been done on relaxation in such systems. A. O. Rankine⁵ maintained gelatine gels of low concentrations (3.4 to 4.5 per cent.) at constant strain and plotted the stress necessary to do this against time. The stress, within the limits of concentration and time investigated, never becomes zero. Breaks occur in the time-stress curves, which are taken to indicate that the elastic limit has been reached. The concentrations employed by Rankine are very much lower than those at which determinations of the modulus, &c. have been made.

Reiger⁶ determined the relaxation time of gelatine gels by optical means (disappearance of the double refraction produced by strain). The investigation was undertaken with the object of testing Maxwell's relation between modulus, viscosity and relaxation time, and was accordingly carried out at 29° C., *i.e.*, at a temperature very near the "melting point" of the gel. In these conditions Reiger found a relaxation time of 10 minutes for 20 per cent., and about 41 minutes for 40 per cent. gel.

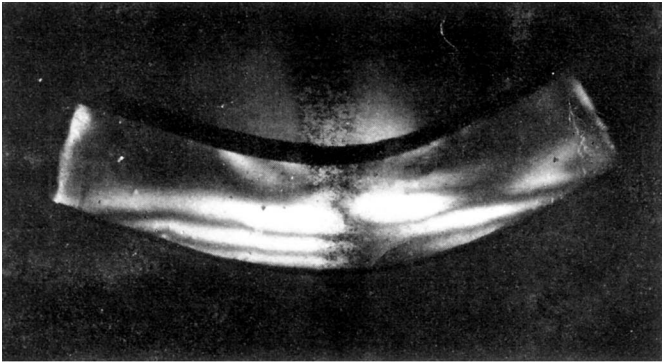


FIG. 1.

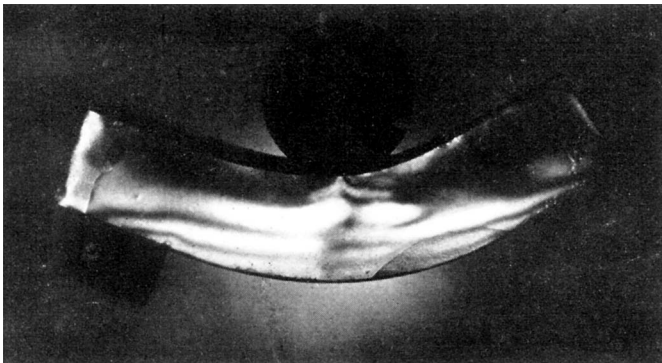


FIG. 2.

That the conditions are entirely different at lower temperatures is shown by experiments by the writer, published here for the first time. Rectangular prisms of gelatine gel (10 per cent.) with 1 per cent. of sodium fluoride, to prevent putrefaction, were cast and allowed to set for 36 hours before removal from the mould. One of these prisms was then bent between three stops fixed on a glass plate, the latter being covered with paraffin oil to prevent adhesion of the gel and consequent irregular deformation. The specimen was then photographed in polarised light (double plate glass as polariser, Nicol as analyser) within 10 minutes of the application of stress at room temperature, about 15° C. This photograph is shown in Fig. 1. The glass plate with the specimen was then placed in a moist chamber for five days, being examined at intervals (visually) without any noticeable change showing itself. At the end of five days the stress had practically disappeared, so that the specimen could be removed without friction and without straightening itself appreciably. It was then again placed on an oiled glass plate and photographed as before, the result being shown in Fig. 2. Considering the extreme sensitiveness of 10 per cent. gel to deformation, it may be said that the appearance is substantially unaltered, and that at any rate the optical anisotropy caused by strain has not disappeared with the removal of the stress. The absence of relaxation in a system consisting to about 90 per cent. of liquid is certainly remarkable and will be referred to again.

OPTICAL PROPERTIES

The double refraction produced by deformation has been referred to incidentally in the preceding paragraph. Quantitative investigation of this property has been carried out chiefly by Leick (*l.c.*). His principal results (obtained with gel plates in tension) are : (1) the double refraction ($D = n_e - n_o$) is, *ceteris paribus*, very approximately proportional to the strain, and (2) for equal relative elongations the double refraction is roughly proportional to the gelatin content.

The refractive index of both gelatine sols and gels has been shown by G. S. Walpole⁷ to be a linear function of the gelatine concentration. If the refractive index is plotted against the temperature over a range containing the setting point, no discontinuity occurs at the latter, *i.e.*, when the sol is transformed into gel.

On the whole, our knowledge of the elastic and the related optical properties of gels must be pronounced slight. As in other branches of the subject, non-aqueous systems have received hardly any attention; their study is eminently desirable, as the enormous complications introduced in the case of a protein like gelatine by the formation of salts, and their electrolytic and hydrolytic dissociation, would be absent. There is a very large literature on the stress-elongation curve of india-rubber, which, however, refers only to the dry material and is not of immediate interest. The writer has found only one reference to a rubber gel in a paper by A. E. Lundal,⁸ who determined the tensile modulus of rubber which had imbibed 133 per cent. of paraffin oil and found it about one-half that of the dry material.

DIFFUSION IN GELS

This phenomenon has, for various obvious reasons, received a considerable amount of attention. Thos. Graham already used dilute gels instead of pure aqueous solutions in the study of diffusion, and found the rate approximately the same in both. This, however, only holds good of gelatine gels up to, say, 3 or 4 per cent. and agar gels

under 1 per cent. In more concentrated gels the rate of diffusion decreases markedly with the concentration, but no quantitative relations have, so far, been determined. The rate of diffusion for a given solution and gel concentration can be affected by various solutes in the latter. Among the earliest investigations on the point are those of H. Bechhold and J. Ziegler⁹, who found NaCl and NaI without effect; Na_2SO_4 and several non-electrolytes as dextrose, glycerin and alcohol reduced the rate of diffusion of certain solutes. A certain—though not exact—parallelism shows itself between the effect of solutes on the elastic modulus and the rate of diffusion: substances which increase the former reduce the latter. The experimental difficulties are very considerable and are explained in the literature. Among more recent papers on the subject are those by O. v. Fürth and F. Bubanovic,¹⁰ and by W. Stiles.¹¹

The fact that both the swelling and the drying of gels are controlled by diffusion involves some consequences which, considering that they may have an important bearing on histology and related subjects, have not yet received adequate attention. If a body of gel is bounded by a surface in which the radius of curvature changes very quickly or (as in polyhedra, cylinders bounded by plane ends, &c.) discontinuously, diffusion to or from regions adjacent to tracts of surface with low or zero-radius takes place more rapidly than from the rest. The result is that a body of gel does not remain similar to itself during swelling or drying, but undergoes successive deformations which may be considerable. The effect is particularly marked in drying; thus, cylinders with plane ends at first dry more rapidly round the circular edges, which contract, the profile becoming that of a barrel with convex ends. As the material forming the edges becomes less permeable, the large surfaces dry more quickly, and the final shape is, approximately, a single-shell hyperboloid with concave ends. On allowing such a body of dry gel to swell again, the original shape is not necessarily restored; the reason for this alteration in the capacity of absorbing water is obscure.¹²

The foregoing summary—though necessarily restricted by considerations of space—may give the reader unfamiliar with the literature some idea of our present knowledge. The two great problems to be solved must now be set forth briefly. They are (1) the elucidation of the structure of elastic gels, and (2) the explanation of the phenomenon of swelling. As regards the former, there is at present a fundamental divergence of opinion, inasmuch as some authors (H. Procter, W. Pauli, and J. R. Katz) maintain that elastic gels are *homogeneous* systems, *i.e.*, solid or (H. Procter) “semi-solid” solutions. The evidence for this view is set forth at length in a very exhaustive monograph by Katz.¹³ The other school (W. B. Hardy, W. Ostwald, Wo. Ostwald, S. C. Bradford, Dorothy J. Lloyd) consider gels to be heterogeneous systems, but differ regarding the state of aggregation of the phases. Ostwald, in particular, considers gels to be *systems of two liquid phases* having an interfacial tension, while some of the other investigators incline to the view that the properties of gels are best accounted for by assuming some sort of network or cellular arrangement of *solid* phase permeated by liquid. Speaking generally, these rival theories are based on the consideration of a limited number of selected properties, and a great deal of further work is required, probably on quite novel lines, before a definite conclusion commanding universal acceptance can be reached. The author feels, in particular, that the elastic properties have received insufficient attention, and

has attempted, as a first step, to examine whether they are compatible with the assumption of two liquid phases possessing interfacial tension,¹⁴ the result being negative if the assumptions necessary to allow of mathematical treatment are granted.

As regards the phenomenon of swelling, we have at present no explanation whatever why certain substances swell in a comparatively limited number of liquids. In the case of proteins, which have received the greatest attention, conditions are enormously complicated through salt formation and electrolytic and hydrolytic dissociation, and here, as in other problems of colloid chemistry, substantial progress is to be expected only from the study of non-aqueous systems, of which a large number is certainly available. This is also the view expressed by Katz in the monograph already quoted: "Swelling in organic solvents would, perhaps, be more important for an investigation in the service of pure physical chemistry than swelling in water." It is greatly to be hoped that the present discussion may induce competent workers to examine this—equally neglected and promising—field.

¹ R. Maurer, *Ann. d. Phys.*, **28**, 628, 1866;

² P. v. Bjerken, *ibid.*, **43**, 917, 1891.

³ E. Fraas, *ibid.*, **53**, 1074, 1894.

⁴ A. Leick, *ibid.* (Drude), **14**, 139, 1904.

⁵ A. O. Rankine, *Phil. Mag. Ap.*, 1906, 447.

⁶ R. Reiger, *Phys. Zeitschr.*, **2**, 213, 1901.

⁷ G. S. Walpole, *Koll. Zeitschr.*, **13**, 241, 1913

⁸ A. E. Lundal, *Ann. d. Phys.*, **66**, 741, 1898.

⁹ H. Bechhold and J. Ziegler, *Zeitschr. phys. Chem.*, **56**, 105, 1906.

¹⁰ O. v. Fürth and F. Bubanovic, *Biochem. Zeitschr.*, **90**, 265; **92**, 139, 1918.

¹¹ W. Stiles, *Biochem. Jl.*, **14**, 58, 1920.

¹² E. B. Shreve, *Science*, **48**, 324, 1918; *Jl. Frank. Inst.*, 187, 319.

¹³ J. R. Katz, *Die Gesetze der Quellung*, *Koll. Zeit.*, IX., 1917.

¹⁴ E. Hatschek, *Trans. Faraday Soc.*, Vol. XII., Part 1, 1916.