LXVIII. ON THE THEORY OF GELS. III.

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IN earlier papers [1918; 1920, 1 and 2] much evidence has been adduced in support of the hypothesis that the reversible gelation of the natural emulsoids is an extreme case of crystallisation and takes place in conformity with von Weimarn's formula $N = K \cdot \frac{P}{L}$. The very small diffusion constants of the gel substances greatly retard the velocity of crystallisation and determine a large degree of supersaturation, P , in the cooling sols. In this stage the liquid contains large numbers of aggregated particles and is highly viscous. The factor K is, therefore, large. And, since the solubility, L , is small, each factor contributes to a maximum value of N , which corresponds to the formation of ultramicroscopic particles.

The very small rates of diffusion of the natural emulsoids have been attributed, partly, to high molecular weight, and, partly, to a chemical, or other, tendency to molecular aggregation. The colloidal effect of both these causes is exhibited by a great many organic substances, of which examples have been quoted. And, indeed, it has been estimated recently [Lloyd, 1920], that gelatin may have a molecular weight of 10,300, which, alone, would be sufficient to confer upon this substance its colloidal properties. A review of all the phenomena of gelation not only shows them to be compatible with the process of crystallisation, but strongly suggests that the two processes are the same. In two cases, viz., the thermal anomaly and heat of swelling of gelatin, where the recorded properties did not agree with the requirements of the theory, the experimental data were shown to be in error. Moreover, von Weimarn's prediction that colloids have a solid crystalline phase has been verified in certain cases by X-ray analysis [Debye and Scherrer, 1916; Scherrer, 1918].

The question may be asked, however, whether gelatin has a definite solubility which may be used in von Weimarn's formula. An affirmative answer is supplied both by the molecular theory of solution [Bradford, 1919] and by experiment. The electrical structure of matter indicates that all molecules attract one another, whether alike or unlike. And solution is shown to be due to the disintegration of the solid, by the kinetic energy of its particles, when its surface tension has been reduced by the counter-attraction of the solvent in which it is immersed. Aided by this counteracting force, particles at the surface of the solid that acquire a velocity, normal to the surface, above a certain limiting value, will be able to overcome the attraction of

adjacent solid particles and pass into the solvent. On the other hand, those particles of the solute that approach the surface of the solid from solution will be reclaimed, on account of the greater resultant attraction of the solid. Equilibrium will be attained when the numbers of particles entering and leaving the solution are equal. This condition determines the solubility of the solid.

If the ultimate particles of the solute attract one another more than do those of the solvent, usually the adhesion of the unlike particles will be intermediate between these two values. It follows that solutes with a greater molecular cohesion than that of the solvent will be the less soluble the greater their cohesion. The adhesion of solute and solvent is reflected in the changed surface tension of the latter. It is important to notice that the less soluble a substance, the greater its attraction for the solvent. If, as seems probable, these principles apply to colloid solutions, the "lyophile" substances have comparatively little attraction for their dispersion media, and conversely.

Since the kinetic energy of the solute particles varies with the temperature, the equilibrium conditions corresponding to saturation will also change. But, if the excess of solid be removed, entirely new conditions will prevail. A statistical equilibrium between the number of particles entering and leaving the solution will be possible no longer, until, with falling temperature, the solid has been re-formed. This can result, only from the aggregation of the solute particles in consequence of their mutual resultant attraction¹. When two particles of the solute come into collision, aggregation will occur only when their relative kinetic energy is less than a certain limiting value that is sufficient to overcome their mutual attraction. On the other hand, when the internal energy of the associated particles reaches this limiting value, the union will be severed and the particles will be free to pursue their separate paths. Until the stage is reached, when the aggregates become large enough to subside, the problem is similar, analytically, to that of the dissociation of a gas, such as iodine vapour, investigated by Boltzmann [1898]. Analysis shows that the number of re-associated particles increases exponentially as the temperature decreases. Since larger particles may be formed by union of smaller ones, the particles will grow in size with falling temperature until they become big enough to settle. This stage will be reached when the force of gravity on the particles becomes sufficient to dominate the kinetic energy that tends to re-distribute them through the solution. Perrin's calculations indicate that, if n_1 and n_2 are the numbers of particles of radius r , at the heights x_1 and x_2 , the distribution of the particles is given by the equation

$$\frac{n_2}{n_1} = e^{-\frac{N}{RT} \cdot \frac{4}{3} \pi r^3 (\rho_1 - \rho_2) (x_2 - x_1) g}$$

where ρ_1 and ρ_2 are the densities of the particles and of the medium respectively.

¹ There will be, always, a resultant attraction between the particles of the solute whether their cohesion be greater, or less than, that of the solvent.

This gives

$$r = \sqrt[3]{\frac{RT}{N} \cdot \frac{\log \frac{n_1}{n_2}}{\frac{4}{3} \pi g (\rho_1 - \rho_2) (x_2 - x_1)}}.$$

The condition that the particles shall separate is that $\frac{n_2}{n_1}$ shall be small. If we suppose $\frac{n_2}{n_1} = \frac{1}{100}$ when $x_2 - x_1 = 0.1$ cm., and give ρ_1 the value 1.16 which has been adopted below for the density of the gelatin particles, we find

$$r = 0.06 \mu.$$

When particles of the supersaturated solution reach such a size, they will begin to subside. The number of particles which separate will increase rapidly as the temperature falls, and, on these, the excess of solid will be deposited, until, once more, the statistical equilibrium between the solid and its solution has been re-established. Evidently the metastable limit is determined by the rate of aggregation of the solute particles. And, as von Weimarn has already indicated, even a metastable solution will deposit solid in course of time.

From this point of view, every substance must have a definite solubility, however small, in a given solvent, with which it does not combine chemically, without regard to the size of the particles which go into solution; except that the solubility will vary with the dimensions of the particles, in so far as these affect the internal field exerted by them. If, therefore, it be permissible to use the term crystallisation in the most general sense, to imply merely the separation of solid from solution, without necessarily imputing a definite orientation to the particles of the solid aggregates, although there is no definite evidence that any substance is truly amorphous, it may be admitted that there is good reason for regarding gelation as a crystallisation process and applying von Weimarn's formula to it.

The experiments, about to be described, show that gelatin conforms in every way to the principles laid down. Particles of macroscopic size have been obtained by decrease in supersaturation, P . But since the extreme values of K and L remain, the particles occur in the form of spherites rather than of regular crystals.

In the first experiments 0.3 and 0.5 % sols of Nelson's "crystal" leaf gelatin were allowed to evaporate spontaneously in shallow dishes at room temperature with addition of various antiseptics. The clear liquids developed, within a few days, an extraordinarily dense opalescence, which gradually disappeared as a light buff-coloured precipitate was deposited. This consisted of spherites up to 2.8μ . Similar results were obtained by experiments carried out at 31° and 40° . The appearance of an opalescence indicates that gelatin is not completely miscible with water even at the higher temperature.

With the object of avoiding the addition of antiseptics, the experiments were continued by sealing slightly supersaturated solutions in tubes and allowing them to stand at room temperature. In the first place, 0.4 % gelatin solutions were filtered into chemically clean test tubes, quickly heated to

boiling and the ends of the tubes drawn out and sealed. The characteristic opalescence soon made its appearance, though more slowly than when the liquid could evaporate spontaneously. But, after a time, the remarkable fact was observed that the opalescence was slowly subsiding in the tube. The average rate of fall was found to be 0.10 during the first 20 days. A second measurement, five days later, gave a velocity of 0.18, and at the same time the milkiess had considerably increased. Several later observations showed a lower rate of fall about 0.07. Corresponding to the decrease in the velocity of sedimentation, the edge of the surface of the cloudiness appeared to be separating from the side of the tube, and the precipitate had the appearance of having coalesced to a just coherent jelly. On inverting one of the tubes the jelly broke up into flocks. But the unbroken gels continued to shrink and eventually came away from the sides of the tubes.

The experiments were continued with solutions of ashless gelatin made from a sample kindly supplied by the Osmosis Co., of which the moisture content was 14.74 % and the ash only 0.02 %. A 1 % sol of this gelatin was prepared by making up 1 g. of material to 100 cc. with water in a stoppered test mixer, allowing to soak over night and quickly warming until melted, by careful immersion in the water-bath. The warm liquid was filtered through Chardin's filter paper into a burette, the first portion rejected, the temperature noted, and small measured volumes run into a number of chemically clean test-tubes. The temperature of the liquid remaining in the burette was again noted and, from the average value, the true volumes at 15° of the gelatin sol used could be calculated: with an average temperature of about 35°, the correction was negligible. The necessary amount of water was then added to the test-tubes so as to make the gelatin contents range from, say, 0.25 to 1.0 % of dry gelatin.

The liquid in the tubes was quickly boiled and the tubes sealed. The actual strengths of the sols, three of each, in a typical experiment, calculated to dried gelatin, were 0.26, 0.30, 0.41, 0.51, 0.77 and 1.02 % respectively. The more dilute sols were quite clear at first, but all became distinctly opalescent within 24 hours, according to concentration, the 0.51 % tubes being very opalescent. During the same time the 0.77 % sols had set to very opalescent and just coherent gels; while the last three tubes were found to contain a slightly stronger jelly that was also still rather more opalescent. In about three weeks a film of clear liquid had collected on the surface of each of these six gels.

The opalescence in the remaining tubes, containing the weaker sols, developed from day to day and, after about ten days, the commencement of the subsidence of the fine particles was observed. The rate of fall was measured from time to time, and the distances fallen plotted against the time. The curious fact was thus brought out that there appear to be three distinct stages in the fall of the surface of the opalescence: (a) a long gradual fall at a uniform rate for from about 20 to 40 days according to the concentration, (b) a sudden

sharp drop taking place within a short time and (c) a slight continuous shrinkage at a slower rate than (a) which was still going on after a couple of months from the time of the sudden coalescence. The photograph, Pl. III, *b-k*, shows the final appearance of two tubes of each concentration, except the highest, after nine weeks from the beginning.

If the volumes of the precipitates are plotted against the concentrations, the curve cuts the concentration axis at the point corresponding to 0.12 g. of gelatin per 100 cc. of solution. This is, evidently, the true solubility of gelatin at room temperature, which remained fairly uniform at 18° during this time. According to the theory discussed, a slightly higher concentration should yield a metastable solution, which would remain more or less permanently supersaturated on account of the low diffusion constant of gelatin. This was found to be the case. A 0.12 % solution continued perfectly clear with no trace of opalescence, while a 0.13 % solution developed, in a few days, a beautiful clear bluish opalescence quite different from the appearance of the more concentrated solutions when in course of precipitation. At the time of writing this opalescence has in some cases persisted for four months, Pl. III *a*. The preparation is evidently a stable aqueous sol of gelatin. With a 0.135 % solution the metastable limit was overstepped and a minimum of flocculent precipitate was deposited.

The long gradual subsidence (*a*) of the surface of the cloudiness appears to correspond to the free fall of the gelatin particles, and the application of Stoke's law should give some indication of their relative sizes. It is interesting to see how these compare with the excess concentrations, *P*, in the light of von Weimarn's formula. In the table below, the radius, *r*, of the particles has been calculated on the assumption that these have a density of 1.16¹.

Reference number	Concentration ($\frac{\text{grams}}{100 \text{ cc. solution}}$)	P ($=C-L$)	$\frac{P}{L}$	Rate of fall (mm./day)	<i>r</i> (μ)	$r \times \frac{P}{L}$
10	0.26	0.14	1.17	0.35	0.10	0.12
11	0.26	0.14	1.17	0.30	0.10	0.11
13	0.30	0.18	1.5	0.17	0.07	0.11
14	0.30	0.18	1.5	0.14	0.06	0.10
16	0.41	0.29	2.4	0.09	0.05	0.12
18	0.41	0.29	2.4	0.08	0.05	0.12
19	0.51	0.39	3.3	0.06	0.04	0.14
21	0.51	0.39	3.3	0.05	0.04	0.14

As has been shown, von Weimarn's formula is still in an indefinite stage. The variable *N* is defined as the precipitate form-coefficient, so that, as *N* increases, the size of the ultimate particles diminishes, until, finally, ultra-microscopic dimensions are reached. But whether *N* represents, inversely, the volume, surface or radius of the particles is uncertain. The last column of the table seems to show that the product of the radius and *P/L* is constant,

¹ By supposing the particles to be half water, this value was derived from the density of the air-dry Nelson's gelatin, $D_4^{15} = 1.3329$ *in vacuo*, determined by weighing in air and in a sp. gr. bottle containing toluene.

indicating that N is really the reciprocal of the radius of the particles. Some hundred experiments in all gave similar results. The investigation is to be continued, a thermostat being used, so that separate series can be run at different temperatures to collect material for the determination of the solubility curve of gelatin, which may throw more light on von Weimarn's formula.

The advantage of using gelatin, rather than a mixture of salts in a double decomposition, for the further investigation of this expression is that the undoubted influence of the varying concentrations of the several reaction components on the solubility and metastable limit of the precipitate is eliminated. Moreover, on account of the very low velocity of crystallisation of gelatin, the disturbing effect of the concentration of the substance to be precipitated on the velocity of the condensation is largely avoided. This concentration affects not only the rate of growth of the crystals after they are started, but also the rate of precipitation of the initial nuclei. With high concentrations the great velocity of precipitation may prevent the calculated value of the supersaturation being reached. Above a certain limit, precipitation may be practically instantaneous, and no further increase in concentration could increase the actual supersaturation. This may explain the constant dispersity of condensed water particles above a certain degree of supersaturation [Wilson, 1911, 1912].

The more or less sudden fall (*b*) of the gelatin particles corresponds with the formation of an apparently coherent jelly. It is not advisable, at present, to speculate on the exact causes of this coalescence, except to suggest that it may be due to an attractive force between the particles. This seems also to afford a possible explanation of the gradual shrinkage (*c*) of the jelly, that follows, as being due to a gradual rearrangement of the jumble of particles resulting from the sudden fall together. The hypothesis has the advantage of suggesting a physical cause for the syneresis, and seems preferable to the mere application of the term "dehydration." The mutual attraction of the particles may also be the origin of the opposing elastic force that must be assumed in cases of imbibition; as the attraction between the gel particles and those of the liquid, together with the capillary effects, is the origin of the swelling.

Microscopic examination of the precipitates in the tubes gave the appearance of particles just too small to be differentiated, like sand collected in ridges. There were also a few small round grains just large enough to be seen. Some of these were aggregated in clusters of two or three or more. With 0.2 % gelatin the ground-work of undifferentiable particles was marked, and the few larger grains reached nearly $1\ \mu$ in size. With increasing concentration the sand-like appearance diminished in intensity and the larger grains became smaller, more aggregated and more numerous. With 0.3 % gelatin the ground-work was still clearly visible, while there were a good many larger particles just differentiable, mostly aggregated in clusters. With 0.4 % the sand-like appearance was only just to be made out, and the larger granules were

numerous, only just distinguishable and often aggregated into large clusters or bundles of fibrils.

Thus the hypothesis that the natural emulsoid gels have a granular structure like that of a pile of shot receives further confirmation. The individual spherites would seem either to be aggregated crystallographically, or to adhere by their mutual attraction. It will be admitted, however, that, with such very small particles, there can be little difference between these two methods of attachment, since, in either case, the union would be due to the forces between the few molecules in the surface of contact. The coupling would be unstable in the case of only two grains, but would become firm as more grains were added.

To avoid the possibility of bacterial influence, Prof. Paine very kindly steamed some preparations three times on consecutive days after sealing. Although some of the gelatin was destroyed by the process the same series of effects was obtained. The 0.2 % solutions remained perfectly clear, the 0.35 % preparations produced opalescent metastable solutions, or sols, one of which persisted for some months. While the 0.85 % tubes developed a precipitate comparable in bulk with that in the 0.26 % unsteamed tubes.

Similar experiments were made with agar that had been dialysed in the stick form for ten days in the presence of a trace of camphor. These behaved in the same manner, but the opalescence was much weaker. A solution corresponding to 0.05 % of air dry agar became just opalescent and deposited a trace of precipitate in 14 days. This consisted mainly of spherites up to $2\ \mu$. With 0.075 % agar the opalescence was still only just noticeable and a small quantity of flocculent precipitate collected at the base of the tubes. A 0.1 % solution gave a more distinct opalescence which gradually subsided and the opalescent portion eventually set to a jelly that occupied just two-thirds of the original volume after four months, Pl. III, *l*. With 0.125 % agar, the whole set to a just coherent gel that showed syneresis and contained some, more or less rounded, more cloudy portions. The 0.05 % jelly also showed syneresis, was opalescent and contained bands of more cloudy gel at 2.1, 2.35, 3.25 and 3.35 cm. below the surface. The 0.2 % jelly was more coherent and nearly homogeneous.

These experiments establish that gelatin, and presumably agar, behave to water exactly as do other substances in regard to suitable solvents. Gelatin has a definite small solubility at room temperature. At a slightly higher concentration it forms an ordinary metastable solution which tends to be permanent because of the very slow rate of diffusion of the substance. This solution is beautifully opalescent on account of the size of its solute aggregates and may be regarded as a typical sol. With further increase in concentration, a precipitate is produced, and the bulk of the precipitate increases with the concentration until, as in many other cases, it fills the solution. Concurrently with increasing concentration, the particles of the precipitate grow smaller, as required by von Weimarn's theory, until, when their distribution is sufficiently dense, they form an apparently homogeneous gel.

A further test of the theory is readily suggested. Substances which form gels only under suitable conditions revert, more or less rapidly, to the ordinary crystalline state; while the natural emulsoids appear to persist in the gel form. The difference must be due to the slow diffusion constants of the latter substances that retard their re-crystallisation. Therefore, if such gels be kept for a sufficient time, signs of re-crystallisation should be developed. Actually the presence of microscopic spherites in aged silicic acid gels has been described on several occasions. And some geological specimens of sponge spicules have a radiating definitely crystalline structure. Very likely this has developed in the course of ages from the opaline silica of which, probably, the spicules were originally composed.

It is easy to test the theory in the case of gelatin. A 5 % solution, made from Nelson's "crystal" leaf gelatin was filtered, boiled and sealed in tubes. The gels had the usual appearance, showing practically no opalescence and were perfectly clear. But, after keeping for three months, a distinct opalescence had developed, which grew from month to month, until at the time of writing, after ten months, it has become very marked and almost as deep as that of the 0.13 % metastable solutions of ashless gelatin. Microscopic examination of one of the gels after four months showed an almost clear field in which some tiny round particles were just to be seen. With lapse of time the visible particles gradually developed in size and number, and, now, numerous spherites may be observed from just distinguishable up to $1\ \mu$. These must have grown from the larger amicroscopic grains of the gel at the expense of the still smaller ones, just as in the case of any ordinary substance in contact with a solvent.

Using the term in the general sense, the case for the crystallisation of gelatin appears to be fairly complete. But the exact nature of the ultimate particles of the gel remains to be determined. When large enough to be seen, gelatin, agar, silicic acid and starch particles are invariably spherical. Since the radiating structure is evidently that most readily assumed by crystallising substances, complex bodies may be expected to take this form if they crystallise at all, and this is found to be the case, generally, with complicated organic substances. But spherites are known in every gradation from the obviously crystalline form, built up of coarse radiating crystalline needles, separately visible, through stages showing only a more or less radiating formation, but which give the well-known shadow cross in polarised light, to apparently homogeneous spherical bodies giving no definite evidence of crystalline structure. This limiting stage may, or may not, be crystalline. In the case of gelatin, Scherrer's analysis does not show, necessarily, that the amicroscopic spherites are not crystalline. Their tiny radiating filaments would have a cross section of, perhaps, not more than two or three molecules, and could hardly be expected to give interference with monochromatic X-rays. Moreover, neither the complex structure of the molecule, nor the mixed chemical composition of the substance would favour a positive result.

Spherites of starch have been described by a number of observers. The writer obtained them, in a similar way to Bütschli, by the spontaneous evapo-

ration of carefully filtered, boiled aqueous solutions of starch. They showed no shadow cross [Meyer, 1914] and appeared to consist of aggregates of tiny "drops." But there is not much doubt that natural starch grains are actually crystalline, and Bütschli [1898] has prepared artificial grains exactly resembling them. It seems likely, therefore, that the tiny drops, or smallest particles, composing the globular aggregates of starch may be crystalline.

Probably the difficulty in preparing definitely crystalline grains of gelatin may be due to the fact that it is not a chemically pure substance. Since the spherites show much resemblance to the grains of mastic and gamboge prepared by Perrin, it seemed useful to try to grow some of these large enough to be examined in polarised light, though, again, neither of these substances is a definite body.

Prof. Perrin very kindly supplied the information that large grains, up to $10\ \mu$, could be obtained by slow diffusion of the alcoholic solutions into water. The nose of a dropping funnel containing the clear filtered 4 % alcoholic solution was passed through a cork into a small 50 cc. cylinder full of water, and diffusion allowed to continue for about five weeks. The resulting grains were washed by decantation and examined with a $\frac{1}{16}$ " objective.

Beautiful mastic particles were obtained of all sizes up to about $9.2\ \mu$. The smaller particles, up to about $3\ \mu$, appeared translucent, but the larger ones had a mosaic appearance, as if built up of aggregates of the very small particles that were also present. The latter showed fairly vigorous Brownian movement and appeared to be attracted by the larger spheres. But some cause, possibly the energy of their motion, seemed usually to prevent their coalescence, though occasionally a small particle might be seen to be captured.

The gamboge grains were slightly larger, up to $10\ \mu$, and mostly quite clear, though some appeared mosaic. In this case there were very few of the smallest particles, and this suggests the possibility that the mosaic appearance of the mastic grains may have been due to a surface layer of captured granules.

In the moist state neither kind of grain gave any appearance in polarised light. But, after the slide had become dry, the mastic particles showed a shadow cross, particularly towards the edges of the grains and when the microscope was focussed slightly above their equators. The appearance vanished again on wetting the slide and seems to have been due merely to light polarised by reflexion at the edges of the spheres. Consequently the crystalline nature of the grains cannot be affirmed.

Similar experiments were made in test-tubes with aqueous solutions of from 0.12 to 0.33 % of gelatin, which were sufficiently dilute not to set for a time, the alcohol being carefully floated above the solutions. On account of the small solubility of gelatin, only small particles were obtained about $1\ \mu$ in size. The precipitate showed a tendency to form in layers, and, with the most dilute solution, a good banded precipitate of gelatin floating in water was produced by the gradual diffusion of the alcohol down the tube. The effect lasted a week, slowly disappearing as the precipitate fell to the base of the

tube. Presumably the gelatin particles were so small, or so light by adsorption of alcohol, as to remain suspended in the liquid. Since the bands settled so slowly, they could not have been produced by different rates of subsidence of the particles, and appear to have been due to the same causes as ordinary banded precipitates in gels.

SUMMARY.

Further evidence is adduced that the reversible sol-gel transformation of the natural emulsoids is an extreme case of crystallisation and solution.

Experiments are described which demonstrate that gelatin behaves to water as does any substance to a suitable solvent. It has the definite solubility in water at room temperature (18°) of 0.12 g. per 100 cc. of solution. At 0.13 %, gelatin forms a metastable solution, with a beautiful bluish opalescence, which is a typical sol. With slight increase in concentration the metastable limit is reached and the gelatin deposited as a gelatinous precipitate, consisting of particles mostly just below microscopic size together with a few spherites reaching $1\ \mu$. As the concentration is increased, the bulk of the precipitate grows, and the particles decrease in size, until, at about 0.7 %, the precipitate fills the solution and forms a white cloudy jelly.

Similar results were obtained with agar, and small spherites of starch by Bütschli's method.

The prediction was verified that clear gelatin gels should become opalescent and develop microscopic spherites when kept for a long time.

The experiments confirm the view that gelatin, agar, starch and silicic acid gels have a granular structure like that of a pile of shot. In other cases, the form of the ultimate particles may vary according to the crystalline habit of the gel substance.

Large granules of mastic and gamboge were grown by slow diffusion. These substances are not chemical individuals, and the grains gave no indication of crystalline structure.

An attempt to prepare smaller gelatin granules by the same method led, also, to the preparation of a banded precipitate of gelatin, which remained suspended in water for several days.

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