

## GELATION OF SILICIC ACID. THE FORMATION OF GAS BUBBLES AND DROPS IN SILICIC ACID DURING GELATION.

BY H. A. FELS AND J. B. FIRTH.

*Received 17th September, 1927.*

In a previous paper the authors described experiments which show that when hydrogen peroxide is added to the sol of silicic acid (prepared by adding sodium silicate solution to hydrochloric acid solution),<sup>1</sup> there is no apparent action. The mixture behaves as a normal gel mixture until a few minutes before setting. Just before gelation, streams of tiny bubbles appear from many points. The viscosity of the mixture changes rapidly near the setting point, and the movement of the bubbles is correspondingly retarded and in a very few minutes the bubbles become fixed, a condition which is coincident with the setting of the gel. The bubbles thus formed are quite small and spherical, but soon begin to increase in size and number. The general appearance of the gel at four stages is shown in Fig. 1.

The authors have shown that<sup>2</sup> the first formed spherical bubbles develop at first by the production of a lenticular belt, passing gradually into flat disc-like bubbles, which become distorted, bending in many planes; subsequently many of the bubbles merge into one another, causing the gel to become broken up into small pieces.

<sup>1</sup> Vide, *J. physical Chem.*, **29**, 241, 1925.

<sup>2</sup> *Proc. Roy. Soc., A*, **114**, 517, 1927.

Hatschek<sup>3</sup> produced bubbles of carbon dioxide in gelatine by the decomposition of small amounts of carbonate whilst Harden<sup>4</sup> produced bubbles by fermentation within the gel.

It appeared to the authors that methods for obtaining bubbles within the gel by chemical, catalytic, or enzyme action, have the disadvantage that there is little or no control over the rate of development of the bubble. Thus, in the case of the effect of the addition of hydrogen peroxide to the gel mixture any subsequent development of the first formed spherical bubble is characterised by the formation of a sharply defined belt.

The form taken up by the bubble during development will be primarily dependent on two factors—the rate of increase in volume of the gas, and the rate of change of the medium in which the bubble develops. If the former is very slow relative to the latter during any particular interval, then some changes in gel structure are not indicated during the subsequent development of the bubbles. On the other hand if a bubble could be produced and developed under control it might be possible to show a sequence of changes which under conditions previously adopted (uncontrolled) would not be indicated.

It was with the object of tracing as completely as possible the changes during the setting and ageing of silicic acid gel that the following experiments were devised.

### Experimental.

Gas bubbles were produced by two methods: (1) Electrolysis, (2) blowing air into the medium through a jet. In order to generalise the phenomena, a further series of experiments was carried out in which drops of non-miscible liquids were introduced into the medium by means of a dropping pipette. Two liquids, mercury and chloroform, were used.

In the case of the electrolytic method it was only possible to control the gas-bubble formation to a limited extent, but in the cases of blowing air bubbles from a jet, or the formation of liquid drops, it was possible to produce a single bubble or drop, at any particular stage of gelation and to develop it (if required) after any given interval. It was further possible to produce a single bubble or drop of a composite nature showing the several stages of gelation.

The details of each series are recorded below:—

(1) *Electrolysis of the Solution.*—A rectangular glass tank was filled with a solution prepared by adding water glass, density 1.178, to an equal volume of hydrochloric acid, density 1.121. Two platinum electrodes were submerged in this (Fig. 2), in such a way that the gas bubbles produced on one electrode would rise through the main portion of the solution. A fairly large volume of gas accumulated on the electrode before a portion was released as a bubble. The first bubbles released were spherical and rose vertically to the surface.

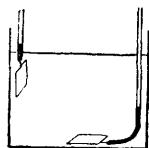


FIG. 2.

These spherical bubbles were formed for a considerable time, but very gradually they changed their shape. As the viscosity increased, the bubbles assumed an elongated shape as soon as they formed. The tendency to become elongated became more pronounced as the setting point was approached, until finally, very flat disc-like bubbles only were formed. These did not rise vertically, but usually took an oblique path to the surface. Once a bubble had passed to the surface, all the subsequent

<sup>3</sup> Koll. Z., 15, 228, 1914.

<sup>4</sup> Vide, 3.

bubbles followed the same path. Although by this method bubbles could be produced at any desired stage, the control over the rate of development was limited. It is of interest, however, as a method of bubble formation in silicic acid gel, quite distinct from those previously adopted.

(2) *The Blowing of Air-bubbles Through a Jet.*—(a) A silicic acid sol was prepared, as described in 1, and put in a glass vessel through the base of which passed a fine jet, having an orifice as truly circular as possible. Air could be blown through the solution from the jet by means of a compressed volume of air regulated by a tap. It was thus possible to blow a bubble at any moment, and to have only one bubble in the solution under observation.

Exactly similar results were obtained by this method as by method 1, but the changes in shape could be more easily followed. These changes in shape of the first series of bubbles however could not be photographed, as the bubbles once released from the jet passed through the solution too quickly, and so the method of their production had to be modified. A series of diagrams (Fig. 3) will serve to show the gradual change in the shape of the bubble passing through the gel from the time of mixing to the final setting of the gel. The final setting of the gel was indicated by the formation of disc-like bubbles. Once the gel had set no further changes

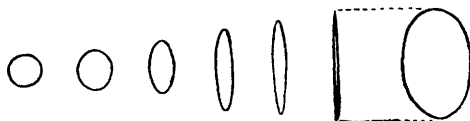


FIG. 3.

could be observed. All subsequent bubbles took the same shape and escaped along the same path (see p. 628).

(b) *Modified Method.*—Instead of allowing the first bubble to release itself from the jet, it was blown so that it remained attached to the jet as a spherical bubble. At intervals of five minutes, the volume of the bubble was increased and the following results were obtained. The enlargement of the first bubble did not give a larger spherical form, but a wing-like extension was produced, and each subsequent enlargement resulted in this outgrowth becoming more extended in distinct stages. At each stage, the "wing" became much thinner, so that finally a composite bubble was formed, showing as many stages as intervals of time passed.

These results can be clearly seen in Figs. 4 and 5. With a solution which required a longer time for gelation, the same type of composite bubble was formed, but each stage was not so well defined. Two other important features were observed during these experiments.

1. If a bubble were produced during the early history of the solution, it assumed a certain form dependent upon the conditions at the moment of its formation. If this bubble were allowed to remain stationary in the medium, until the gelation was complete, it underwent *no change in shape*.

2. If a composite bubble were produced on the end of the jet, the air could easily be withdrawn from it and the bubble would completely disappear. On re-admitting the air, the bubble *assumed its former shape*.

*Pressure Required to Blow the Bubbles.*—A simple manometer was introduced into the air delivery system and the pressure record shown by the manometer, was magnified by a lever attachment, which in turn made a continuous record on a revolving drum. As air was admitted the pressure gradually rose during the formation of the bubble until the bubble escaped

from the jet, at which instant the pressure suddenly fell and, then, gradually increased again during the formation of the next bubble. A typical series of results is recorded in Table I.

TABLE I.

No. of Reading.	Pressure to Blow Bubble in Mm.	Pressure after Bubble Escapes.	Time in Seconds after First Bubble.
1	1.77	0	(20 mins. after mixing)
2	2.95	0	35
3	4.13	0	89
4	4.72	0	129
5	5.31	0	319
6	5.34	0.59	344
7	5.9	1.77	394
8	6.49	2.36	534
9	6.49	2.95	672
10	6.49	4.72	808
11	6.49	5.31	946
12	7.08	5.41	1080
13	54.00	0	(24 hours)

A mixture was prepared of equal volumes of hydrochloric acid  $\Delta 1.121$ , and sodium silicate solution  $\Delta 1.178$ . The pressure required to just keep the jet clear of liquid was taken as zero throughout. The first observation was made 20 minutes after mixing. It will be observed from the table that the maximum pressure developed for this first bubble was 1.77 mm. and when the bubble escaped from the jet, the pressure returned to zero. The pressure required to blow the next four bubbles showed a continuous increase, and in each case the pressure returned to zero. In all subsequent attempts to blow and release a bubble, the bubble was only partially released, and a residual pressure therefore remained. This residual pressure continuously increased as the gel aged.

It has been shown (p. 625) that once a bubble has been formed it produces a kind of mould, such that the air, (or liquid) can be withdrawn and returned at will, the identical form of the bubble being re-assumed. It will be apparent therefore that any increase in pressure will be that required to produce an enlargement of the bubble. Owing to the peculiar shape of the later expansion of the bubble the internal forces act unequally on the walls, with the result that there is always a tendency for the last segment to break away (*i.e.* to break away at the junction *a* in Fig. 6).



FIG. 6.

As the last segment approaches film-like dimensions this phenomenon becomes more pronounced, and ultimately it is mainly the last film-like extension which is released.

The results show clearly the gradual and continuous increase in the cohesive forces within the gel. Finally a passage of air through the gel can only be obtained by the application of a considerable pressure (54 mm.), which produces a permanent rupture from the jet to the surface. The fracture produced is usually conchoidal in character.

The significance of the foregoing observations will be discussed after an account has been given of the experiments with liquid drops in the gel.

3. *The Formation of Chloroform Drops.*—Chloroform, in which iodine was dissolved so that the drops could be easily seen, was allowed to run from a narrow jet into a solution of water glass and hydrochloric acid.

Water-glass of density 1.180, and hydrochloric acid of density 1.142 were used in equal volumes.

When the mixture was freshly prepared, the drops of chloroform were spherical, and sank to the bottom. As the viscosity increased, the drops required a longer time to reach the bottom, but remained spherical. After this stage a drop could be formed which did not sink to the bottom, but remained suspended in the gel. The drops now assumed an ovate form, and beyond this point the chloroform tended no longer to fall, but to rise to the surface round the jet.

Attempts were then made to produce a composite drop. A spherical drop of chloroform was suspended from the jet and more chloroform was run into it at intervals of five minutes. The drop increased in size just as in the case of the air bubble. The similarity of the composite drop and composite bubble will be seen by comparing Figs. 7 and 4.

In a further experiment with chloroform, a drop was allowed to remain suspended in the gel until a well marked stage had been reached in the process of gelation, and the tube was then immersed in hot water. This caused the chloroform to be vapourised, but instead of the spherical drop increasing uniformly in size, the gas escaped as a very thin film, making a path for itself towards the surface. When all the chloroform had been vapourised, the skeleton of the drop remained, the original spherical shape with a very thin film protruding from it (Fig. 8).

4. *The Formation of Mercury Drops.*—Mercury was dropped into a silicic acid medium as in Method 3 and, again, the primarily formed drops were spherical. The usual series of changes in shape was observed again, but the earlier stages were difficult to see, as the drops of mercury sank to the bottom very quickly. With the later stages, however, the very flat disc-like drops took an oblique course and, consequently, they were fixed in approximately a horizontal position. A few were actually fixed as flat discs in a vertical position (Fig. 9). Fig. 10 shows a disc of mercury which was produced in a horizontal position, but owing to the mobility and high density of the mercury, a well marked plane was made by it in which it was free to move. This plane was clearly marked from the rest of the gel as it was more transparent and apparently was filled with a watery liquid.

A curious but interesting modification of this production of a clear-looking plane of cleavage can be seen in Fig. 11. A drop of mercury was allowed to fall through a gel before gelation had proceeded very far and, instead of dropping obliquely, a spiral path was taken. The shape of the containing vessel probably affected the ordinary oblique path which would have been taken had the body of the gel been sufficiently large. The spiral path taken by the drop was not at first very noticeable, but the same path was taken by all subsequent drops. After standing for about 12 days, this path became very clearly marked, being far less opaque than the rest of the gel, and containing a watery fluid. (See Fig. 11).

It will be apparent from the foregoing experiment that the shape of a bubble or drop is determined by the stage which has been reached in the medium at the instant of the bubble or drop formation. When certain conditions in the medium are attained the gel "sets." Does this take place uniformly throughout the entire mass at the same instant or are some portions of the medium "not gelled"?

It had been previously observed that, in the formation of bubbles by the decomposition of hydrogen peroxide,<sup>3</sup> the *number* of bubbles increased *after* gelation. In the light of the foregoing experiments it would appear that if the setting of the gel takes place uniformly throughout, then any

bubbles formed after the first formed bubbles had begun to develop a lenticular belt, should be lenticular.

A silicic acid medium to which hydrogen peroxide solution had been added was prepared as previously described<sup>2</sup> and the development of the gas bubbles carefully observed under the microscope. The observations of a portion of the gel are recorded in photographs in Fig. 12. The photographs were taken at intervals of five minutes. In photograph (a) bubble marked 1 is a spherical bubble, as is shown by the subsequent development of the lenticular belt in (b) and (c). The spherical bubble 1 in (a) was formed after lenticular belts had developed on the bubbles in other portions of the gel. Bubble 2 in (a) is not spherical but its appearance is due to the position of observation as is shown by the corresponding photographs of the same bubble in (b) and (c).

It would appear from these observations that after the initial setting of the gel there are still small portions of medium "ungelled," *i.e.*, gelation is not instantaneous throughout the entire medium.

### Discussion.

In the series of experiments herein described, a continuous record of the several stages of gelation has been obtained.

It has been shown that the bubbles or drops produced in the medium prior to gelation are invariably spherical. Gelation is associated with a change in the shape of the bubble or drop which can be produced. The change, however, is very gradual and the various stages from the spherical to the thin film have been recorded. In fact it is suggested that this change of shape of the bubble or drop may be taken as indicative of gelation. Many authors describe gelation in very vague terms, *e.g.* "When the containing vessel can be turned upside down without the gel falling out."

The character of the bubble gives some indication of the internal condition of the gel. It has also been pointed out that once a bubble or drop was formed in the gel, the shape was permanent, *i.e.* a spherical bubble or drop remained spherical, and further, the air or liquid could be withdrawn and replaced at will. Thus any subsequent development of the bubble or drop appears as a growth on the original bubble or drop.

After gelation, up to the condition for the formation of the extremely thin film-like bubble which brought about a permanent fracture in the gel, the only apparent change in the gel was that of continued increase in rigidity. It was only subsequent to this stage that external syneresis was observed. It has been shown that the pressure required to blow a bubble increases as the gel ages, and that once a bubble passes through the gel, subsequent bubbles follow the same path. After a time this path becomes very pronounced, and bubbles pass along it with comparatively little resistance. It has been further observed that where the path terminates in the surface of the gel, liquid exudes. It would appear therefore that the internal pressure produced by the passage of the first formed bubble has caused syneresis<sup>5</sup> to take place at the point of the bubble formation and along its subsequent path through the gel.

When mercury is used this phenomenon is more pronounced owing to the natural weight of the drop, and this is clearly shown in Figs. 10 and 11.

In a previous communication<sup>6</sup> it has been shown that the water present in the gel is of two types, "fixed" water and "free" water. "The

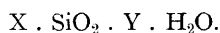
<sup>5</sup> Cf. O. F. Lenher, *J. Am. Chem. Soc.*, **43**, 391-6, 1921.

<sup>6</sup> *J. physical Chem.*, **31**, 1230-36, 1927.

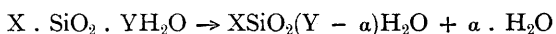


fixed water is a certain varying amount of the total water in the gel, which is definitely associated with the silica. The 'free' water is the remainder of the total water not acting as 'fixed' water. It is free in the sense that it is only enclosed in the meshes or pores of the gel, or interstices between adjacent hydrated particles. It is capable of acting as solvent for the sodium chloride present and can be easily removed by desiccation over sulphuric acid. The 'fixed' water cannot be so easily removed."

When the medium undergoing gelation has almost gelled the amount of water definitely associated with the silica has reached a maximum and the heavily hydrated particles may be represented by the formula



These heavily hydrated particles are still free to move, but the movement is extremely limited as is indicated by the rapid increase in viscosity just prior to gelation. The instant of gelation is the point of maximum hydration and the hydrated silica particles which were originally free to move are now part of a continuous structure, very loose and extended and containing large voids in which the residual free water is enclosed. Then follows a continuous increase in rigidity which is at first fairly rapid. This increase in rigidity is brought about by a continuous change of "fixed" to "free" water, whereby a firmer union between the silica particles results.<sup>6</sup> This change may be represented thus—



where  $\alpha$  is continuously increasing.

It would appear, however, that the foregoing changes do not take place uniformly throughout the medium. It has been shown that in the ungelled medium bubbles and drops invariably take a spherical form, whilst gelation is associated with a change to the lenticular form. On the other hand, the results indicate that whilst lenticular bubbles are produced in the major portion of the gel, there are still sections in which spherical bubbles are formed, *i.e.* even after "general gelation" there exist ungelled portions of the medium. It is suggested that gelation takes place round a series of gelation centres.

The observation of internal syneresis along the path of the bubble or drop, and also when the bubble is withdrawn from the gel, is due to the rupture of what would otherwise be a continuous structure; owing to the comparative rigidity of the gel "free" water rapidly drains into the path or cavity, hence subsequent bubbles are only displacing water (aqueous solution), until the previous state of development has been reached. It would appear, however, that when the bubble is in the nature of a thin film, the surfaces caused by the passage of the bubble come together again so quickly that no syneresis can be discerned, in fact, the film-like bubbles "shoot" through the gel with a distinct "click." Repeated passage of the film, however, finally produces a "syneresis path."

It is not until the gel has reached a stage of rigidity, such that any attempt to blow a bubble produces a permanent fracture, that syneresis at the surface of the gel, accompanied by shrinkage, takes place. The change takes place in such a way, the gel shrinking to such an extent, that the large meshes formed in the semi-rigid gel ultimately become so small in the hard gel as to be of the nature of capillaries.

The hard "dried" friable gel still contains a certain amount of fixed water, very difficult to remove by laboratory methods, which is, however, lost by the influence of time, with the ultimate formation of anhydrous

crystalline silica. The probability of the final production of silica in a crystalline and anhydrous condition was suggested by Zsigmondy,<sup>7</sup> who also showed that the actual crystalline form assumed was that of quartz. This is substantiated by the fact that silicic acid gel was found occurring naturally in the Simplon Tunnel<sup>8</sup> and apparently it was changing gradually into quartz, which was found along with the gel. From a purely theoretical point of view, Arsen's<sup>9</sup> contribution on the tendency to the ultimate formation of a crystal lattice further supports the conception that a process of slow crystallisation is taking place during the ageing of silicic acid gel.

In conclusion, it would appear that the silica gel is always tending to the ultimate formation of crystalline anhydrous silica. This change is accompanied by considerable shrinkage and corresponding expulsion of the free water. It is this tendency of the hydrated silica particles to orientate themselves towards the final production of a crystal lattice, with consequent loss of water, which is responsible for the formation of capillaries in the hard gel.

<sup>7</sup> *Z. anorg. Chem.*, **71**, 336-77, 1911.

<sup>8</sup> *Z. Kryst. Min.*, **34**, 289-90, 1901.

<sup>9</sup> *J. physical Chem.*, **30**, 306, 1926.

*The Chemistry Department,  
University College, Nottingham.*

---