XXXV.—*The Liesegang Phenomenon and Stratification.**

By MAURICE COPISAROW.

THE present study of colloidal and stratified calcium carbonate, not only completes the investigation on the heteromorphism of this substance (J., 1923, **123**, 785), but also shows that neither organised life nor organic hydroxy-compounds, and—more remarkable still—neither colloid, at least of a permanent character, nor suspended matter, is essential in the formation of strata. Nevertheless, although only hydration is necessary for the stratification of calcium carbonate, yet, as is shown later, the presence of colloids and salts and experimental conditions, such as temperature and pressure, which influence hydration, greatly affect the nature of the product. Thus, whilst hydrocalcite ($CaCO_3,5H_2O$) (Copisarow, *loc. cit.*) represents the maximum state of hydration under normal conditions, a hexahydrate is obtained in sugar solution, etc. (Pelouze, *Compt. rend.*,

---

* Publication of this work, which was carried out during 1923—24, long before the appearance of Ganguly's paper (J., 1926, 1381), has been delayed owing to the illness of the author.

1865, **60**, 429; Mackenzie, J., 1923, **123**, 2409). Again, whilst ordinarily the dehydration of calcium carbonate * is complete at 18—20°, yet in the case of mother-of-pearl (formed in presence of "conchiolin") apparently a dihydrate persists up to 50°, at which temperature the mother-of-pearl loses its iridescence, becoming "dead." †

Cohesion, hitherto elusive, not only in synthetically prepared calcium carbonate of the stratified variety, but also in all cases of Liesegang ring formation, is certainly dependent upon velocity of formation and pressure. The influence of pressure upon cohesion is well illustrated by the synthesis of marble and alabaster (Copisarow, *loc. cit.*). Unfortunately, owing to lack of facilities, the study of pressure and the time factor upon Liesegang rings in general, and rings of calcium carbonate in particular, could not be carried out.

Considering the peculiarities of the stratification of calcium carbonate itself, we find that it is the first case in which (*a*) Liesegang rings, (*b*) opacity bands, and (*c*) tree formation make a joint appearance. This combination of occurrences may be regarded as an extension of the Liesegang phenomenon, rather than an anomaly of it.

The fibrillar structure of the colloidal calcium carbonate formed *in situ* supplies the necessary framework for the ring formation, and at the same time accounts for its peculiar physical properties. The presence of colloidal calcium carbonate and the general mild conditions explain the formation of opacity regions, which, being the outcome of the mild effect of an electrolyte upon a colloid, may be regarded as very diffused Liesegang rings. This formation of opacity bands of colloidal calcium carbonate (the concentrations of which progress in opposite directions to one another) is identical with the observations of Holker (*Proc. Roy. Soc.*, 1923, *A*, **102**, 710), the distinguishing feature between the two being that Holker's whole series of test-tube experiments is naturally embodied in one phenomenon, taking place in one vessel. The tree formation, as an extreme case of spiral deformation of Liesegang rings, may be regarded as being due, on the one hand, to strong diffusion and, on the other, to the transformation of a semipermeable membrane to an impermeable one owing to the dehydration of calcium car-

---

* Hydrocalcite, $CaCO_3,5H_2O$ (Pfeiffer, *Arch. Pharm.*, 1879, **15**, 212; Copisarow, *loc. cit.*), and subhydrocalcite, $CaCO_3,3H_2O$ (Ivanow, *Z. Kryst. Min.*, 1908, **44**, 87; Copisarow, *loc. cit.*), are the only mineral hydrated forms of calcium carbonate. $CaCO_3,2H_2O$ (mother-of-pearl ?) and $CaCO_3,6H_2O$ are formed in presence of organic matter only.

† Clément and Rivière (*Compt. rend.*, 1922, **174**, 1353) gave the following analysis of mother-of-pearl :

$CaCO_3$, 75; H_2O, 25; albumin, 5% ($CaCO_3,2H_2O$ requires H_2O, 26·7%).

bonate. In this case, diffusion takes place at one or more points of least resistance instead of throughout the whole membrane.

Extremes in reactivity and in conditions of experiment are detrimental to the periodic effect. The electrolyte, to be effective, must be strong enough to cause orientation, coagulation, or " salting out " in the medium (electrolyte, colloid, or matter in suspension). Opacity bands, produced by salt solutions acting upon colloids (Holker, *loc. cit.*), by ammonia gas upon gelatin (see later), and by the interaction of calcium chloride with sodium carbonate, indicate the phenomenon of periodicity, but are not strong enough to condense these wide bands to a series of rings or membranes.

The Liesegang phenomenon is complex in character, and the actual rings are the outcome of a primary and a secondary cause. The primary cause is the periodic deformation or coagulation of the fibrillar structure of the colloid, under the influence of the electrolyte. The secondary cause, contributing to the viscosity and thickness rather than to the formation of the rings, is the salting out or deposition of the electrolyte on the coagulated membrane. Thus the usual Liesegang rings represent an intimate mixture of electrolyte and colloid. The fact that the secondary cause may be eliminated without interfering with the first or periodic effect, is shown by the action of hydrochloric acid, ammonia, or formaldehyde on gelatin, described later. Not infrequently, cases are encountered where the initial substances taking part in the Liesegang formation are neutral in character, but in these cases we often find hydrolysis or reduction preceding ring formation, acidic or basic bodies being produced *in situ*.

The general study of the Liesegang phenomenon in this paper revealed the possibility of substituting in ring formation the two salt and the one salt–acid systems (Moeller, *Kolloid Z.*, 1917, **20**, 242) by (1) one basic salt (sodium carbonate, baryta, etc.), and (2) a gas or its aqueous solution (hydrogen chloride, formaldehyde, ammonia, etc.).

These facts, together with the observation that Liesegang rings may be formed in an aqueous medium (*e.g.*, solutions of calcium chloride and sodium carbonate), widen considerably the whole aspect of the Liesegang phenomenon and show definitely the inadequacy of any single theory, hitherto advanced, to afford a proper explanation.

The influence of light, studied by several investigators (Davies, *J. Amer. Chem. Soc.*, 1923, **45**, 2261; Tryhorn and Blacktin, *Trans. Faraday Soc.*, 1923, **19**, 433), is to a large extent accounted for by the photochemical changes it induces, but it also involves a milder and much more general effect, that of local activation, or formation of nuclei. Careful study of the tree formation showed that in more than 70% of the cases the direction of the spiral tended towards the illuminated side of the vessel no matter where the trees originated. After fully considering such disturbing factors as the sensitiveness of the trees to traffic-vibration, reflexion, and general difficulty of localising the light, the influence of light upon orientation can scarcely be doubted. This finds ready support in the fact that when sodium carbonate solution acted upon a set gelatin solution of calcium carbonate, the reaction taking place in a glass cylinder of 2·5 cm. diameter, the Liesegang rings were not horizontal, though parallel to one another. The rings seemed to incline invariably towards the illuminated side of the vessel, suggesting that diffusion, and therefore interaction, was more rapid on that side.*

EXPERIMENTAL.

Section I. (With GEORGE ERNEST WILSON.)

Ring Formation with One Basic Salt.

Sodium Carbonate.—Series 1; 1% *solution.* Graduated test tubes (2 cm. × 15 cm.) containing a set solution of gelatin † (5—8 cm. in height) were almost filled with a 1% sodium carbonate solution and allowed to stand. At the salt–gelatin junction, a translucent concave membrane soon formed. On further standing, rings gradually appeared below this membrane, and examination showed them to be considerably thicker than the membrane. Under the magnifying glass, they were seen to consist of a multitude of fine globules, in the form of a gelatinous precipitate, the compactness of packing diminishing upwards. The inter-band distances progressively increased with each succeeding ring. After 7 days, 4 bands appeared, increasing to 6 at the end of 14 days. Measurements by means of a cathetometer gave the following figures: After 7 days, the membrane had moved down 0·2 cm., the curvature of meniscus was 0·1 cm., and the distances from the position of the membrane to the consecutive bands ‡ were 0·4, 0·8, 1·3, and 1·9 cm.,

---

* Some years ago, the author made similar observations on the crystallisation of certain substances from solution. Mere evaporation would scarcely account for the invariable primary appearance of the crystals on the more illuminated side of the vessel. Davies (*loc. cit.*) found that light influenced ring formation in a medium of colloidal gold.

† In all the experiments "Gelatine extra" of Coignet Père, Fils, et Cie. was used, the solutions (usually 5%) being employed within 12 hours of their preparation. The experiments were carried out in a basement having a concrete floor, so as to eliminate as far as possible the effect of light and vibration.

‡ In all measurements, the edge of the membrane was taken as an indication of its position, as, owing to diffusion and osmotic pressure, the mem-

respectively. After 14 days, the membrane had moved down 0·5 cm., the curvature was 0·25 cm., and the distances from the *new* position of the membrane to the consecutive bands were 0·7, 0·9, 1·4, 2·1, 2·8, and 3·5 cm., respectively.

The number of bands formed after 7 and 14 days, given above, does not really indicate the rate of formation of bands, as the membrane in its movement downwards first depresses the bands and then absorbs them. But even after 3 months, when the diffusion was complete, the adhesion of the remains of the bands to the walls of the tube was sufficiently strong to leave a record of their original position.

Series 2; 5% *solution.* When experiments were carried out as in series 1, but with a 5% solution of sodium carbonate, the texture of the bands was more compact, and the inter-band spaces were comparatively smaller.

After 2 days, 7 bands had formed; membrane (concave) had moved down 0·5 cm. from original position; curvature of meniscus, 0·1 cm.; distances from membrane to consecutive bands were 0·6, 0·9, 1·2, 1·5, 2·0, 2·5, 3·1 cm., respectively.

After 7 days, 9 bands had formed; membrane had moved down 0·9 cm. from original position; curvature of meniscus, 0·4 cm.; distances of bands from new position of membrane, 1·0, 1·2, 1·5, 1·9, 2·4, 3·0, 3·7, 4·5, 5·4 cm., respectively, the bands reaching the bottom of the tube.

After 14 days, 8 bands remained; membrane had moved down 1·5 cm. from original position; curvature, 0·8 cm.; distances of bands from membrane, 1·0, 1·3, 1·6, 1·9, 2·4, 3·0, 3·7, 4·8 cm., respectively (see Fig. 1).

After 3 months, the membrane had moved down 2·4 cm.; the bands were very distinct, and composed of coarse, spherical granules in a clear space, the inter-band space being cloudy. After 6 months, the membrane had reached the bottom of the tube, leaving the remains of the bands adhering to the walls (as rings of cloudy gelatinous matter) on pouring out the solution.

Series 3; 10% *solution.* Formation of bands was similar to that in series 2, the bands being closer together and still more solid in texture. After 7 days, 7 bands had formed, and the concave meniscus of the membrane (curvature, 1·0 cm.) actually penetrated the first band. After 14 days, 10 bands were formed, and reached the bottom of the tube; membrane concave; curvature, 0·9 cm.

---

branes were in all cases convex or concave. (*Note.* A water–air meniscus is regarded as concave.)

In measuring the inter-band distances, the bottom of a band was taken, as this was quite definite, whilst the top was practically always diffuse.

Fig. 1.

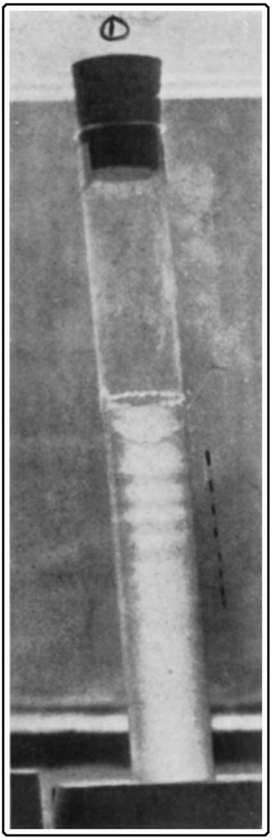
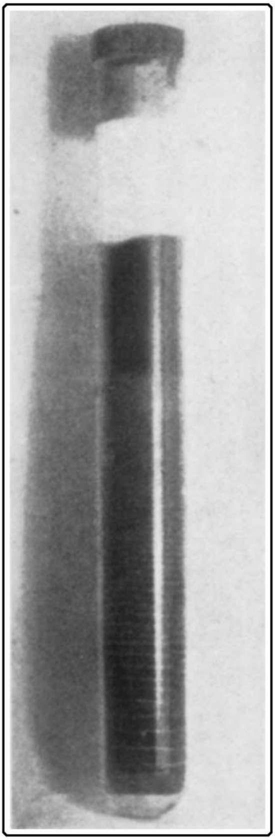


Fig. 2.



[*To face page* 226.]

Series 4; 15% *solution.* Gradual formation of bands, 2 mm. in thickness, and inter-band distance gradually increasing from 1 mm. to 3 mm.

Series 5. *Concentric ring formation with sodium carbonate.* A crystal of sodium carbonate was allowed to penetrate the whole thickness of a set 5% gelatin solution contained in a Petri dish. Concentric rings were formed similar to the bands described above. The same effect was obtained by filling with sodium carbonate solution a cylindrical hole bored through the whole thickness of the gelatin. On the contrary, placing a drop of the sodium carbonate solution on the surface of the gelatin gave no definite rings, the horizontal diffusion not being simultaneous through the whole depth of the gelatin. No bands were obtained on substituting agar-agar for gelatin.

Sodium Hydrogen Carbonate.—The presence of sodium hydrogen carbonate exerted an inhibiting effect on ring formation. The salt itself showed but small tendency to stratification, the bands being few and imperfect.

Sodium Hydroxide (4% *solution*).—The membrane had a concave meniscus, and faint, imperfect bands were formed, a brownish gelatinous precipitate separating.

Barium Hydroxide.—Series 1; 3·5% *solution.* A flat membrane was formed at the junction of the barium hydroxide solution and the gelatin. After 7 days, a cloudy space of about 1 cm. below the membrane was observed, followed by a space of 1·4 cm. occupied by 10 fine rings. After 14 days, the membrane had moved down 2·5 cm., this space being occupied by 25—30 fine bands. Below the membrane a space of 5·0 cm. contained 17 bands. No further change was observed after 21 days.

Series 2; 7% *solution.* After 7 days, the flat membrane had moved down 2·0 cm. from its original position, and above it were very fine, close, film-like bands in two layers: (*a*) upper layer, about 40 equidistant bands occupying 1·8 cm.; and (*b*) lower layer, about 30 equidistant bands, occupying 2·0 cm. Below the membrane was a slightly cloudy region of 2·4 cm. containing 14 distinct bands.

After 14 days, the membrane had moved down 5·4 cm. from its original position, this space being occupied by about 60 bands, the inter-band space increasing from 0·3 mm. to 1·0 mm. towards the membrane. Below the membrane 6 bands were formed, occupying 2·1 cm.

After 21 days, the membrane had reached the bottom of the tube, and below the original position of the membrane the tube was filled with bands, gradually increasing in thickness and distance apart towards the bottom of the tube. After the contents of the tube had been poured out, the rings adhered to the walls as a white precipitate (see Fig. 2).

The peculiarity of the bands above the membrane, in so far as they differ in appearance and structure from those below, would simply show that they were formed after the passage of the membrane.

Series 3. *Agar-agar medium* (1%). (*a*) Barium hydroxide, 3·5%. A concave membrane was formed, moving down 0·2 cm. in 7 days. A heavy precipitate was found on the membrane, below which was a clearer space of 1·2 cm. followed by a thick band of a distinct yellow colour. Below this the gel was of a green tint.

(*b*) Barium hydroxide, 7·0%. Membrane had moved down 0·1 cm. in 7 days. A very heavy precipitate was on the membrane, below which was a clearer space of 0·3 cm. then one very thick band of yellow colour. Below this, the gel was green.

Ammonium Hydroxide.—Series 1; 5% *solution.* A convex membrane, moving up 1·1 cm. in 7 days, was formed at the junction of the 5% solutions of ammonia and gelatin. This membrane had a rough surface, composed of feathery particles. No bands were observed. After 3 months, the membrane had moved up 5·8 cm., having become flat and indistinct. One band, composed of coarse particles, had appeared 0·3 cm. below the new membrane. The rest of the gel was cloudy. With ammonia solution (*d* 0·880), the diffusion was similar but slower.

Series 2. *Ammonia gas.* Test tubes containing set 5% gelatin solution were filled with ammonia gas and allowed to stand hermetically closed. The gelatin solution liquefied.

Series 3. *Gaseous ammonia–nitrogen mixture.* A 100 c.c. measuring cylinder, containing 75 c.c. of 5% set gelatin solution, was connected to a nitrometer containing a mixture of ammonia gas and nitrogen in the ratio 1 : 3. After 30 minutes, a cloudy membrane was formed, complete liquefaction occurring within 24 hours; the column of liquid presented the appearance of opacity bands, extending throughout the liquid, the band thickness and inter-band distances (equal) being 2·4 cm. (approx.). The opacity bands gradually disappeared, nothing except a general turbidity remaining after 3 hours. On increasing the proportion of ammonia, ordinary liquefaction occurred as in series 2.

Calcium Hydroxide (*Saturated solution*).—A transparent, convex membrane was formed, moving up 0·3 cm. in 14 days. Below the membrane was a cloudy region of 3·2 cm. containing 2 broad bands.

Ring Formation with One Acid.

Series 1; 5% *solution of hydrochloric acid.* A concave membrane composed of fine particles was formed, moving down 3·6 cm. in 7 days. Above the membrane was a cloudy region. As the membrane moved down, faint bands were formed below it. After 3 months, diffusion was complete, the liquid being cloudy. In contrast to those with sodium carbonate, the bands were only of a temporary nature, gradually disappearing. Weaker acid solutions gave no definite bands.

Series 2; 10% *solution.* A concave membrane was formed, moving downwards. After 5 days, very fine translucent bands were formed, slightly resembling the sodium carbonate bands, but farther apart. After 3 months, the diffusion was complete and a white precipitate was at the bottom of the tube. Using 15% and 32% hydrochloric acid, and hydrogen chloride gas (as in the case of ammonia gas) neither membrane nor bands were formed, diffusion increasing with strength of acid.

Experiments with a series of other acids, both organic and inorganic, and also with single salts were carried out, but no definite ring formation was observed. It is noteworthy that, in the majority of cases, inorganic acids gave a concave meniscus moving downwards, whilst organic acids gave a convex one moving upwards.

Bromine Water (*saturated*).—A flat membrane was formed, below which was a thick, opaque mass, followed by a cloudy region. After 11 days, the membrane had moved up 0·8 cm. with an opaque region of 2·1 cm. beneath, and then 2 bands in a cloudy space.

Silver Nitrate (1·7% *solution*).—*In the light.* In place of the ordinary membrane, a dark, wide band was formed. 0·3 Cm. below the first band another wide, dark band was formed, followed by about 2 cm. clear space, and then well-defined bands similar to those in the sodium carbonate experiments.

After 3 months, the membrane band was deep red, and stationary. At the bottom of the tube were 6 distinct bands, 7·6 cm. from the membrane band. A grey deposit on the tube, forming a mirror in places, was seen above the membrane band.

In the dark. Concave membrane.

No bands formed at first. After 14 days, the membrane was still stationary; below it were a dark brown region of 1 cm. and, at the bottom of the tube, faint bands (5 bands in 2·1 cm.).

After 3 months, the membrane was solid and red. The solution was reddish-brown, and the gel red; 7 distinct bands were at the bottom of the tube, 7·0 cm. from the membrane, the intermediate space being clear. No mirror.

No bands were observed on substituting agar-agar for gelatin.

Silver Nitrate and Formaldehyde (0·5% Solution of silver nitrate in 5% gelatin solution, and 40% formaldehyde above).—*In the light.* Membrane reddish-brown, steeply concave, opaque, and 0·2 cm. thick. Beneath the membrane a clear space of 3 cm. with one band. Gelatin below slightly opaque, and reddish-brown.

After 3 months, membrane was steeply concave (0·8 cm.) and 3 bands were seen in the gel, taking the same shape as the membrane.

In the dark. Membrane white, opaque, steeply concave, and 0·1 cm. thick.

Above the membrane was a cloudy layer about 1 cm. thick. No bands of clear space.

After 3 months, the gel was dark brown. No bands or mirror.

Formaldehyde (40% *solution*).—A hard, horny, concave membrane was formed, still stationary after 3 months. The appearance of the gelatin remained unchanged, but on careful examination it was found that its consistency had altered completely, having become hardened throughout in layers. Under the pressure of a glass rod, the layers could easily be distinguished as separated by clear, hard membranes. The gelatinous mass bore a remarkable resemblance to the crystalline lens of an eye. The formaldehyde solution became weaker. Similar results were obtained by employing the 20% solution.

No optical examination could be made of this interesting experiment.

Similar experiments with absolute ethyl alcohol or acetone resulted in the formation of slightly concave, parchment-like, non-permeable membranes. No change was observed after 3 months' keeping.

Section II. (With HUBERT CAWOOD HILLARY and HOWARD BRAITHWAITE STENT.)

Calcium Carbonate and the Liesegang Phenomenon.

As already indicated (J., 1923, **123**, 785), the formation of hydrocalcite ($CaCO_3,5H_2O$) was brought about by forced double decomposition *en masse* of calcium chloride and sodium carbonate. On the other hand, when the interaction was allowed to take a more natural course (*i.e.*, the velocity of reaction was dependent on the rate of diffusion), a series of new and interesting phenomena were observed. To prevent the reaction being instantaneous, advantage was taken of the fact that concentrated solutions of calcium chloride and sodium carbonate differ widely in specific gravity.

On carefully running 600 c.c. of 7% solution of pure sodium carbonate on to 200 c.c. of a 38% solution of pure calcium chloride contained in a 1000 c.c. glass cylinder, both solutions being at room temperature, a gelatinous semipermeable membrane of hydrocalcite was formed. After 2 hours, the membrane had increased in thickness, the bottom part of the calcium carbonate (the original membrane) showing distinct signs of changing from the translucent gelatinous (hydrocalcite gel) condition to an opaque white crystalline solid (calcite). After 4—5 hours, the membrane had increased in opacity and thickness, showing the solid to be uniformly distributed asbestos-like layers, which in the course of 2 or 3 days spread to a depth of 1·2 cm. Simultaneously with the hardening of the membrane, one or more protuberances or hillocks were observed on the upper layer of the solid. The hillocks soon resembled miniature volcanoes, the eruptions taking the form of fine streamers extending nearly to the surface of the liquid in straight, though not always vertical, chains of gelatinous particles of calcium carbonate. The shot-out streamers, on reaching the surface of the liquid, appeared to bend over and then gradually vanish, giving rise to the remarkable phenomenon of opacity bands or rings, distributed uniformly throughout the upper part of the sodium carbonate solution. In place of the streamers trees began to grow, taking their origin from the protuberances. The trees had the appearance of a wavy, white line or column in a spiral form, the corrugated surface of the column recalling stalagmites or icicles. Not infrequently, the trees were imperfect in their spiral form, being confined almost to one plane. In these cases, the wave maxima invariably coincided with the opacity bands.

After 12—20 hours, the trees extended to the surface of the liquid, often creeping along the walls of the vessel. On nearly reaching the surface, the trees spread into a growth resembling sea plants. This foliage, or calcium carbonate in layers, gradually fell on to the membrane, carrying with it some of the trees, and completely destroying the opacity regions, already disturbed by the growth of the trees. The phenomenon of layers and tree formation persisted apparently indefinitely, provided that experimental conditions remained constant. The trunks of the trees were found to be hollow, a horizontal section of the walls showing concentric rings when magnified.

On long keeping, the bottom part of the laminar membrane gradually broke up and fell to the bottom of the vessel in the form of a fine, crystalline powder of calcite. The edges of the remaining opaque and hardened layers assumed in course of time a zig-zag shape. No appreciable difference was caused by varying the diameter of the vessel or the height of the columns of solution.

On diminishing the concentration of the sodium carbonate, the whole phenomenon of ring and tree formation became fainter. Reduction of the concentration of the calcium chloride solution, *i.e.*, bringing its specific gravity nearer to that of the sodium carbonate solution, prevented the formation of a membrane and resulted in rapid diffusion.

Experiments were carried out with sodium carbonate and calcium chloride in (*a*) tap water, (*b*) distilled water, (*c*) boiled solution cooled under reduced pressure, (*d*) in the dark, and (*e*) in sunlight; the actual tree growth was unaffected by these modifications of conditions.

Influence of Temperature.—On carrying out the experiments at 0—3°, no tree formation took place, so long as the membrane remained gelatinous. Only on the transformation of the gelatinous membrane (hydrocalcite) to the opaque crystalline layers (calcite), did it become impermeable to diffusion, the force of osmosis breaking through at one or more places of least resistance, forming protuberances, and finally trees. But even at low temperatures some streamers were formed, giving rise to well-defined opacity bands, having a spacing of approximately 0·9 cm. and being ultimately destroyed by the tree formation, on raising the temperature. Above 30°, no Liesegang rings or trees were formed, owing to rapid diffusion and to the fact that at this temperature hydrated calcium carbonate has not even a temporary existence. The semipermeable character of the membrane was well illustrated by colouring the sodium carbonate solution with phenolphthalein or potassium permanganate. In each case, no coloration could be observed below the membrane. Similar results were obtained by colouring the calcium chloride with potassium permanganate.

Calcium Chloride, Sodium Carbonate, and a Colloid.

A narrow 100 c.c. cylinder was half-filled with a 5% solution of gelatin containing 3 g. of calcium chloride per 100 g. of gel. When the gel had set, 50 c.c. of a 15% solution of sodium carbonate were slowly poured on. A whitish membrane was formed, and slow diffusion took place into the gel, causing it to become opalescent. The upper solution remained clear. After 60 hours, the diffusion was complete, the white bands being separated by opalescent spaces speckled with calcium carbonate.

A 1% gel of agar-agar in distilled water, containing 2% of sodium carbonate, with a superimposed 10% solution of calcium chloride gave precipitation of a rhythmic character. With 3% of calcium chloride in the agar-agar gel and 10% sodium carbonate solution above, the precipitation was uniform and slow.

In all cases where gelatin or agar-agar was employed, no streamers, trees, or opacity bands were observed, the reason probably being that the transition point hydrated—anhydrous calcium carbonate is considerably raised in presence of colloids (compare mother-of-pearl).

Well-defined concentric rings were obtained by fixing a crystal of sodium carbonate in a Petri dish containing set 5% gelatin, with 3% of calcium chloride in solution. The development of the rings was very similar to that described in the case of sodium carbonate (see Section I).

Influence of Light.—As already stated, the access of light influenced the direction of both the trees and the calcium carbonate rings in the gelatin medium. In the experiments on the effect of light on the tree-orientation, vessels 10—13 cm. in diameter were employed. These were entirely covered with black paper, a narrow slit being allowed to remain on the side facing the light. Sunlight, electric and gas lights were tested, the most satisfactory result being given by sunlight. When precautions were taken to prevent vibration and to keep conditions constant, in more than 70% of the cases the trees tended towards the light, regardless of the position of the protuberances. No such relationship could be observed in the case of streamers.

Interesting results were obtained by using vessels (of diameters varying from 3—12 cm.) enclosed in black paper in which small circular apertures were made at various heights of the sodium carbonate column. The light was admitted through a lens, thus focussing it at any particular point in the vessel. It was invariably found that the trees tended towards the focus, so much so that often several of them met in a point, becoming entangled.

In the experiments with a gelatin medium carried out (*a*) in complete darkness, (*b*) in the light, and (*c*) in a vessel covered with black paper, the light being admitted through a narrow slit, the only difference observed between (*a*) and (*b*) was in the velocity of diffusion, the rings being horizontal and equally spaced; in the case of (*c*), the rings, whilst remaining parallel to one another, were inclined towards the light.

Influence of Hydroxy-compounds upon the Colloidal Condition of Calcium Carbonate.—A series of experiments was carried out on lines similar to those described by Neuberg and Rewald (*Biochem. Z.*, 1908, **9**, 547). Both calcium oxide and calcium metal, suspended in absolute ethyl or methyl alcohol, glycerol,* or mixtures of these, gave colloidal calcium carbonate in presence of carbon dioxide. The stability, viscosity, and concentration of the resulting product depended upon the medium and experimental conditions.

---

* Colloidal calcium carbonate in glycerol may be of therapeutic interest.

Influence of Gelatin upon the Colloidal Condition of Calcium Carbonate.—10 G. of powdered lime were suspended in 200 c.c. of hot 5% gelatin solution. A current of carbon dioxide was passed through for 5 hours, the temperature being allowed to drop to 25°. On keeping, the gelatin solution set to a brownish, opalescent gel, the excess of lime remaining caked at the bottom of the vessel. A white precipitate was thrown down on shaking the gel with water, methyl alcohol, or acetone. Analysis showed the gel to contain 0·67% of calcium carbonate.

No definite results were obtained with agar-agar.

Summary.

(1) The Liesegang phenomenon is a material record of a periodic function, *viz.*, the action of a single substance upon a mobile medium, capable of undergoing either structural deformation or systematic orientation. Such a medium may be a colloid or finely-divided suspended matter. The substance is, as a rule, sufficiently strongly acidic or basic to cause a physical change in the medium. The suitable character of the substance and the condition of the medium may be developed *in situ.*

(2) Opacity bands and tree formation are special cases of the Liesegang phenomenon, the former being produced under very mild experimental conditions, and the latter under the influence of forced irregular diffusion.

THE UNIVERSITY, MANCHESTER.

[*Received, September* 11*th*, 1924.]