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THE FORMATION OF CRYSTALS IN GELS.*

BY

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THE general properties of gels—or jellies—are familiar to us, but their inner structure is a matter of some dispute. J. M. van Bemmelen, Bütschli, and many others consider gels to be two-phase systems—a more concentrated solution as a network of cell-walls enclosing a more dilute solution of the same substance. The whole system is solid or semi-solid and extremely viscous. In the opinion of von Weimarn, the ultimate structure is minutely granular—even crystalline—and any coarser network is a secondary formation.

Emulsoids are two-phase liquids closely related to gels. In fact, emulsoids may change to solid gels by evaporation, cooling, or a change in the distribution of water, for example, between the two phases, thus altering their relative concentrations. Hot fluid emulsoids of agar or gelatine with water “set” to gels on cooling, but silicic acid gels set on the mere mixing of cold-water solutions of sodium silicate and a suitable acid. After standing some time the silicic acid forms two phases with the water, one more concentrated than the other, and when the proper distribution is reached solidification results. Manganese arsenate gels

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so rigid they hold their shape, unaided, as well as any fruit jelly also set without cooling or evaporation. The gels of ferric arsenate and ferric phosphate set on dialysis—a removal of acids, bases, and salts.

As a preface to a study of crystal formation in any of these gels we must note their retarding the rates of diffusion of acids, bases, and salts, and their prohibition of diffusion of colloids. The mesh structure of gels must be practically equivalent to a network of capillary channels filled with the less concentrated phase. It follows, then, that the presence of substances affecting the distribution of water between the two phases must affect the size of these channels and change the rates of diffusion above mentioned. For example, Hatschek states that such salts as citrates and sulphates produce more rigid gels, but iodides and sulphocyanates retard or prevent gel formation. Bechold adds that sulphates, glucose, alcohol, and glycerol retard diffusion, while urea, iodides, and chlorides accelerate it.

The influence of certain gels—or jellies—on crystal growth is illustrated by many crystalline minerals. It is very probable that gelatinous silicic acid was the ancestor of quartz and by gradual dehydration became hard silica rock. In the gelatinous medium reactions took place under conditions favoring the formation of crystalline veins. For example, the reduction of gold salts produced crystals of gold, veining the gel, which later became quartz. A convincing part of this development can be reproduced in the laboratory.

To the geologist a working method of duplicating many such processes of Nature must be of great value. To the chemist a study of reactions in gels gives a useful control of relative concentrations and velocity of reactions. The pathologist finds in the subject some relation to the formation of crystalline material in animal tissue.

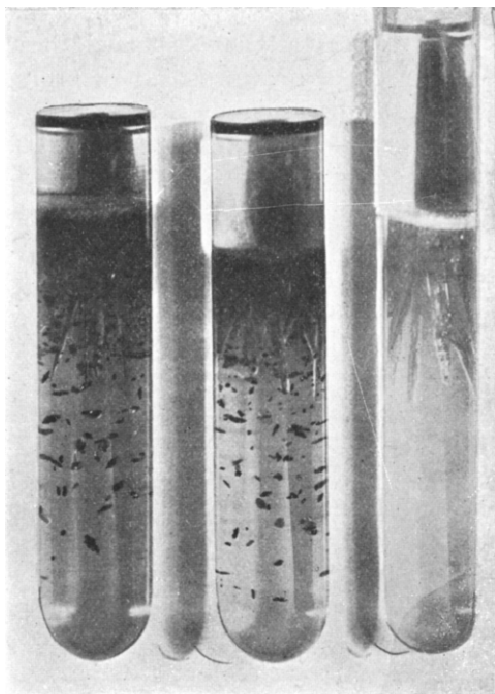
Silicic acid gels are discussed in this paper more than any other, but other gels function in a similar, though usually less effective, manner.

HISTORICAL.

E. Hatschek ¹ did much important work in this field, attracted doubtless by the experiments of R. E. Liesegang. The latter ob-

¹ *Kolloid Z.*, 8, 193 (1911); *Ibid.*, 10, 77 (1912); *Ibid.*, 10, 124 (1912); *Ibid.*, 10, 265 (1912).

served that if a drop of silver nitrate solution was placed on a film of gelatine gel containing potassium dichromate the precipitated silver dichromate was formed in concentric rings separated by clear intervals. This "rhythmic banding" of "Liesegang's rings" will be discussed in a later paper. Whether a disk of gel or a tube partly filled with a gel be used, the essential feature is that one substance shall diffuse into a gel containing another



Mixed crystals of silver sulphate--silver chromate with silver dichromate below.

substance, with which it reacts to form a rather insoluble compound. Rhythmic bands may form or, under different conditions, separate crystals of remarkable size and shape.

Hatschek and Simon² reduced gold salts in silicic acid gels by the use of oxalic acid, ammonium formate, ferrous sulphate, sodium sulphite, carbon monoxide, sulphur dioxide, hydrogen, ethylene, etc. When illuminating gas was used as a reducing

² *Kolloid Z.*, **14**, 115 (1914); *J. Soc. Chem. Ind.*, **31**, 439.

agent a black deposit of carbon always appeared mixed with the gold. Since graphite sometimes occurs with gold in quartz veins, this experiment is suggestive.

Hatschek's usual method of work was to make a 5 to 20 per cent. gelatine gel or a 1 to 5 per cent. agar gel containing, for example, a small amount of potassium dichromate. This was allowed to solidify in a test-tube and covered with a solution of silver nitrate. The silver ion slowly diffusing down into the gel reacted with the dichromate ion to form silver dichromate in small crystals. In 1911 Hatschek reported these crystals 0.5 mm. long in 10 per cent. gelatine; lead dichromate 0.03 mm. long in 2 per cent. agar; lead chloride 2 mm. long in agar; barium carbonate 0.1 mm. long in 5 per cent. gelatine; potassium sulphate 0.2 mm. long in 5 per cent. gelatine. He also prepared a number of other crystalline compounds, such as lead iodide, lead sulphate, lead chromate, calcium sulphate, and barium silicofluoride. Later he used silicic acid gels as the media for diffusion, and obtained larger crystals. In 1913 he reported lead chloride crystals 15 mm. long. He was unable to make crystalline sulphides in gels.

His reduction of gold chloride in silicic acid with oxalic acid yielded beautiful crystalline gold and, by varying the conditions, colored colloidal gold.

Hatschek held that the concentration and nature of the gel determined the form and size of the crystals. The inelastic gels like silicic acid, he thought, were superior to the elastic organic gels like agar and gelatine. He wrote of "the practically universal tendency to form spherical bodies in agar and gelatine," although he did obtain some crystals in these media.

Hatschek³ made gels of silicic acid by mixing sodium silicate solutions with hydrochloric acid. The diffusion of a lead salt into this gel formed crystals of lead chloride. In similar fashion he treated sodium silicate with sulphuric acid and caused lead or calcium salts to diffuse into the gel, thus forming crystalline sulphates of lead or calcium. With phosphoric acid gels he obtained crystalline phosphates of copper, calcium, and strontium.

Simon⁴ grew the well-known "lead tree" in a silicic acid gel containing lead acetate. A bit of zinc or tin was pressed into the

³ *Kolloid Z.*, **10**, 77 (1912).

⁴ *Ibid.*, **12**, 171 (1913).

top of the gel. I found that if the gel is about 0.02 N with respect to lead acetate a splendidly branching tree grows and may be handled roughly, since it is supported on all sides by a solid.

Pringsheim⁵ states that when two salt solutions diffuse into a gel in opposite directions the reaction does not proceed beyond a thin film if the solutions are isotonic. A hypertonic solution continues to diffuse into a hypotonic, and any precipitate formed is deposited in the latter. In accord with this idea, Hatschek often added indifferent substances to the solution on top of the gel in order to insure reaction below the gel surface.

Liesegang⁶ found that the older opinion that growth of a precipitate in a gel was limited to one side of the initial precipitation film did not hold for quinol on silver nitrate. I confirmed Liesegang's finding by several new examples. He also obtained silver crystals in gelatine by reducing silver nitrate with ferrous sulphate.

Gerhart⁷ placed a solid reacting substance in a test-tube, covered with a mixture of water-glass and a suitable acid before the gel set, and, after it became solid, poured a solution of the second reacting substance on top. Both salts then diffused into the gel and met. Gerhart found alum and potassium nitrate to have considerable influence on the form of crystals deposited.

Hausmann⁸ obtained crystalline halides of thallium in gelatine.

Dreaper⁹ dispensed with a gel as a medium for reactions and used a single capillary tube. For example, a capillary tube filled with 3 per cent. lead acetate was immersed in 5 per cent. hydrochloric acid. Crystals of lead chloride nearly 1 mm. long formed in the capillary. Sand in wide tubes functioned the same as a single capillary. Dreaper considered relative rates of diffusion and concentration of the incoming solution the determining factors.

Ernest Marriage¹⁰ studied the arrangement and size of lead iodide crystals in fruit gels and jams. The various fruit jellies and jams influenced the precipitation of lead iodide in different

⁵ *Z. phys. Chem.*, **17**, 473 (1895).

⁶ *Kolloid Z.*, **17**, 141 (1915).

⁷ *Tsch. Min. Mitt.*, **28**, 347 (1908); *Ibid.*, **29**, 185 (1910).

⁸ *Z. anorg. Chem.*, **40**, 110 (1904).

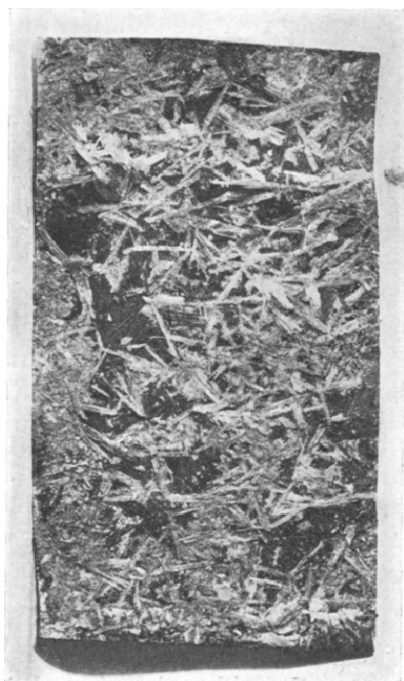
⁹ *J. Soc. Chem. Ind.*, **32**, 678 (1913); *Kolloid Z.*, **14**, 163 (1914).

¹⁰ *Kolloid Z.*, **11**, 1 (1912); *Sci. Am. Sup.*, **77**, 375 (1914).

ways, and use was made of this fact in detecting adulteration of commercial products.

De Schulten,¹¹ by the slow admixture of extremely dilute solutions of barium chloride and sulphuric acid, obtained crystals of barium sulphate that in a month measured 5 mm.

Deiss¹² prepared a gel of MnHAsO_4 by mixing equal volumes of 10 per cent. MnCl_2 and KH_2AsO_4 . On standing three



Zinc-ammonio chloride crystals lining a dry cell.

months, rose-colored crystals of the same composition as the gel separated.

Kohler,¹³ in a study of "rhythmic crystallization of sulphur," states that "the viscosity of the liquid must be so great that the rate of flow towards the crystallizing part is slower than the rate of crystallization." This compares with slowness of diffusion in a gel.

¹¹ *Compt. rend.*, 136, 1444 (1903).

¹² *Kolloid Z.*, 14, 139 (1914).

¹³ *Ibid.*, 17, 10 (1915).

Shulansky and Gies¹⁴ observed that "in the putrefaction of meat crystals of ammonio-magnesium phosphate appear early and accumulate rapidly," due to bacterial activity. This paper and a similar one by Perlzweig and Gies¹⁵ may have some bearing on the subject because of the hydrated colloid nature of animal tissue.

Creighton¹⁶ added the influence of a weak current of electricity to the process of diffusion in gelatine. Using an iron anode and a gel containing potassium ferricyanide, Turnbull's Blue appeared in stratified layers—not crystalline, however. Braun¹⁷ believed that certain phenomena attending the formation of sulphides and the deposition of copper in capillary spaces previously noted by A. C. Becquerel are of an electrochemical nature, as Becquerel¹⁸ had suggested: "Sur des nouveaux effets chimique produits dans les action capillaire." These phenomena are partly dependent, according to W. Ostwald,¹⁹ on the semipermeability of precipitated membranes.

In a paper on "Electrostenolysis," H. N. Holmes²⁰ reported on electrocapillary action in insoluble powders.

The observation of Henri Becquerel that solutions of copper sulphate and sodium sulphide meeting by diffusion through a fine crack in a glass tube formed minute crystals of copper sulphide relates to Dreaper's experiment with the single capillary.

Cornu's great series of papers²¹ on the significance of gels in geology are an important part of the literature.

As will be shown elsewhere in this paper, slow diffusion processes in the earth's crust have much to do with the formation of crystalline mineral deposits. John Clark,²² in "A Chemical Study of the Enrichment of Copper Sulphide Ores," gives a suggestive account of the reducing action of hydrogen sulphide and amorphous sulphur.

¹⁴ *Biochem. Bull.*, 3, 45 (1913).

¹⁵ *Ibid.*, 3, 69 (1913).

¹⁶ *JOURNAL OF THE FRANKLIN INSTITUTE*, 182, 745 (1916).

¹⁷ *Ann. der Physik und Chemie*, 44, 507 (1891).

¹⁸ *Compt. rend.*, 64, 919 (1867); *Ibid.*, 65, 51, 720 (1867); *Ibid.*, 66, 77, 245, 766, 1066 (1868); *Ibid.*, 67, 1081 (1868).

¹⁹ *Z. phys. Chem.*, 6, 75 (1890).

²⁰ *J. Am. Chem. Soc.*, 36, 784 (1914).

²¹ *Kolloid Z.*, vols. 1-5.

²² *Bull. Univ. of N. Mex.*, 1, 79 (1914).

W. H. Emmons,²³ in a similar paper on "The Enrichment of Sulphide Ores," remarks, "To the chemist this paper is an appeal for more experimental data on the important mineral syntheses involved in the process."

P. Krusch²⁴ investigated primary and secondary ores with especial reference to the gel and the rich heavy metal ores.

Interesting changes in glass structure are given in U. S. G. S. Monograph 32, on "Spherulites and Lithophyse," and in a paper published by George H. Williams in an early issue of the *Johns Hopkins Circular*.

Johnston, Merwin, and Williamson,²⁵ discussing "The Several Forms of Calcium Carbonate," state that "aragonite is precipitated, as is well known, even at ordinary temperatures in a solution of a salt from which a carbonate isomorphous with aragonite may be precipitated. Aragonite is precipitated in the presence of a lead salt formed around nuclei of cerussite (PbCO_3) in parallel orientation." It seems to me that these authors might well try the precipitation of calcium carbonate in a neutral gel containing a lead salt. Crystals of unusual size might be obtained and thus facilitate their study.

Doelter²⁶ considers that practically all substances are colloidal when first precipitated. What we call amorphous bodies are very close to the crystalline. The tendency to pass from the colloidal to the crystalloidal condition is greatly influenced by pressure, shock, light, and long-continued heating. Doelter proved his point by laboratory experiments. He was led to declare that minerals whose formation was once thought to require high temperatures may easily be formed without such temperatures.

Stephen Taber,²⁷ in "The Origin of Veins of Asbestiform Minerals," makes a valuable contribution to the study of crystal growth. "The shape of a growing crystal is controlled by one or more of three independent factors, namely: (1) The tendency to assume a regular polyhedral form because of the forces of surface tension and molecular orientation; (2) the relative and absolute magnitude of the external forces resisting growth in

²³ *Bull. U. S. G. S.*, No. 529, 11.

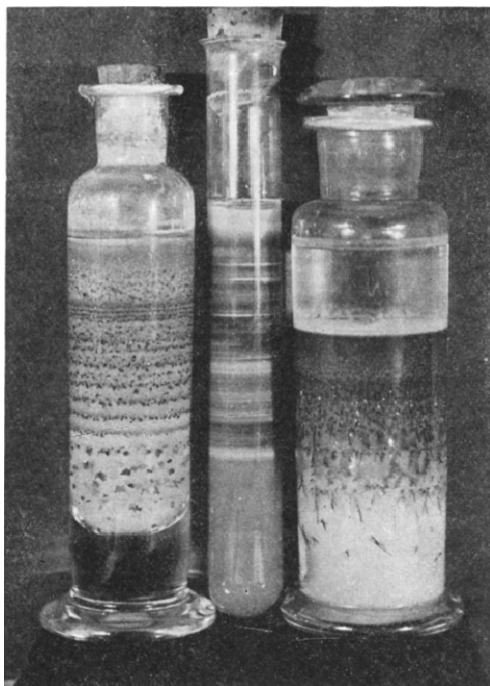
²⁴ *Min and Sci. Press*, 107, 418 (1913).

²⁵ *Am. J. Sci.*, 41, 473 (1916).

²⁶ *Kolloid Z.*, 8, 29, 86 (1911).

²⁷ *Nat. Acad. Sci.*, 2, 659 (1916).

different directions; and (3) the accessibility of the material from which the crystal is built. As a result of the first factor some substances normally crystallize in slender, acicular or hair-like forms, but an asbestiform structure is never produced without the assistance of one of the other two factors. Crystal growth under unequal pressure undoubtedly explains the development of fibrous structure in some instances. The solubility of most substances increases with the pressure, and therefore crystal growth



Basic mercuric chloride in silicic acid containing an excess of base.

may be limited to the direction of least pressure. This hypothesis is not applicable, however, to fibres that develop normal to the walls of the vein. Moreover, the veins frequently intersect and run in all directions through a given rock mass. Such occurrences of abnormal fibrous structure must therefore be attributed largely to the circumstance that the material for growth was accessible only in one direction."

In another paper on "Pressure Phenomena Accompanying the

Growth of Crystals" Taber²⁸ remarks: "Crystallization is retarded or prevented in supersaturated solutions which occupy small capillary or subcapillary spaces; therefore crystals may be supplied with material for growth by diffusion through solutions occupying such spaces, and the increase in volume due to the entrance and deposition of new material must result either in the expulsion of part of the solution or the enlargement of the space occupied by the growing crystals. . . . Crystals grow in directions in which external forces oppose growth whenever the surfaces under pressure are in contact with a film of supersaturated solution, and it is possible to supply the material for growth by slow diffusion through subcapillary spaces, as great resistance is offered to the expulsion of solution from such openings. The conditions requisite for crystal growth under pressure commonly obtain in the rocks of the earth's crust, and many phenomena connected with the metamorphism of rocks, the growth of concretions, and the formation of mineral deposits are difficult of explanation under any other hypothesis than that growing crystals have made room for themselves by exerting pressure on the surrounding material."

METHODS OF WORK.

I found it convenient to mix equal volumes of solutions of sodium silicate and some acid, pouring the water-glass into the acid and mixing quickly and thoroughly. Before the silicic acid set to a solid one of the reacting salts was mixed with this solution, which was then poured into test-tubes. After the gel set, the other salt solution designed to react with the first was poured on top. The solution on top should have a greater osmotic pressure than the gel to insure reaction within the gel instead of above the surface.

The water-glass used was a commercial grade known as "water white," with a density of 1.375. The ratio of the Na_2O to the SiO_2 was 1 to 3.5. When diluted to a density of 1.06 and titrated against hydrochloric acid, using phenolphthalein as an indicator, it was equivalent to 0.51 N acid. With methyl red as indicator the normality was 0.57.

This particular water-glass was used at the 1.06 density for many experiments because weaker solutions were too slow in the

²⁸ *Ibid.*, 3, 297 (1917); *Am. J. Sci.*, 41, 532 (1916).

set of the silicic acid. With this concentration an equal volume of N acetic acid was suitable for most of the experiments. Such a gel set over night and contained a small excess of acid. It was reasonably clear. This rather arbitrary selection really marked the lowest concentration limit for working convenience. Acetic acid, 0.75 N, serves as well and gives less excess acid. Several other acids were used for special purposes, but the time of set varied with the acid. A partial list follows:

- 1.06 density sodium silicate with equal volume N acetic acid set in 6 hours.
- 1.06 density sodium silicate with equal volume N formic acid set in 36 hours.
- 1.06 density sodium silicate with equal volume NN phosphoric acid set in 10 minutes.
- 1.06 density sodium silicate with equal volume N hydrochloric acid set in 10 days.
- 1.06 density sodium silicate with equal volume N sulphuric acid set indefinite.
- 1.06 density sodium silicate with equal volume N nitric acid set in 4 weeks.

This applies only to the particular water-glass described above. Considering convenience in time of set, clearness of the gel, and failure to split as the gel contracts, the following table will be found more useful, except in respect to acetic:

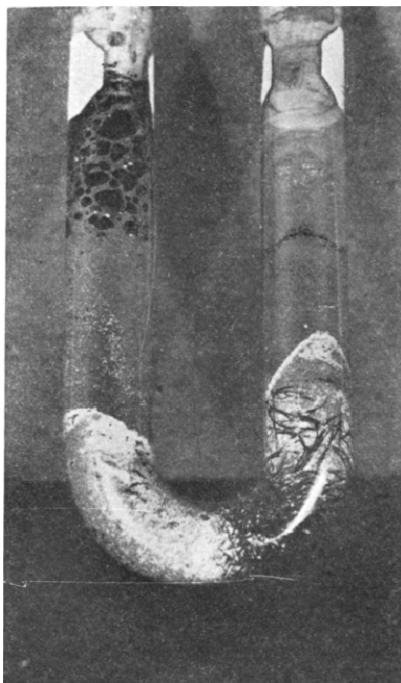
- 1.16 density sodium silicate with equal volume 3 N acetic acid set in 1 hour.
- 1.08 density sodium silicate with equal volume of 3 N formic acid set in 48 hours.
- 1.06 density sodium silicate with equal volume 2 N hydrochloric acid set in 5 days.
- 1.06 density sodium silicate with equal volume 6 N sulphuric acid set in 1 day.
- 1.10 density sodium silicate with equal volume 2 N nitric acid set in 2 days.

Temperature changes affect the time of set considerably. I made a few tests with water-glasses of different composition and found it possible to get good results with them also. In one the ratio of Na_2O to SiO_2 was 1 to 2, its density 1.69, and, diluted to 1.06, the solution was equivalent to 0.67 N acid with phenolphthalein as indicator. In another the ratio of Na_2O to SiO_2 was 1 to 4, the density 1.34, and, diluted to 1.06, the solution was equivalent to 0.46 N acid.

New tables of time of set should be constructed on the basis of the normality of the particular water-glass at hand. For

example, a 1.06 water-glass equivalent to 0.67 N acid must be mixed with an equal volume of more than N acetic acid to give results similar to those in the table.

Pouring the mixture before it solidifies into the bend of a U tube gives the experimenter excellent control of conditions. The two reacting solutions poured separately into the arms of the U tube slowly diffuse through the gel and meet, often forming a



Silver dichromate crystals in alundum powder.

sharp precipitation band. Any amount of either solution can be used in this method.

Hatschek, in some of his work, directs that the mixture of water-glass and acid be dialyzed to free it from excess acid and salts. Addition of very little ammonia sets the gel. In other experiments he did not dialyze. I do not find it necessary or desirable to dialyze out the acid and salts. Their influence on crystal formation or development of banding is beneficial in most instances. In a number of experiments I used a large excess of

acid, and in others added salts or non-electrolytes to secure certain effects.

Doryland ²⁹ suggested that a mixture of water-glass and just enough acid to make a neutral solution would set to a gel in minimum time. Traube and Kohler ³⁰ came to a similar conclusion in regard to the effect of acids and bases on gelatine. This led me to make basic gels by using less acid than enough to neutralize the sodium silicate. In this way a very profitable field of investigation was opened up. Basic salts, for example, may not be studied in gels containing excess acid. A mixture of equal volumes 1.06 density water-glass and 0.5 N acetic acid is very slightly basic and sets in about three minutes. Other water-glasses must be titrated to get similar figures.

EXPERIMENTAL PART.

Hatschek's gold was so interesting and spectacular that it seemed advisable to vary his methods. He used a sodium silicate-hydrochloric acid gel with oxalic acid as a reducing agent. Phosphorus in ether, as well as a number of other reducing substances, was also tried by Hatschek.

After duplicating a number of his results I varied the acid used in making the silicic acid gel and secured by far the most spectacular effects when the gel was made by mixing sodium silicate with sulphuric acid. That this was due in part to the presence of sulphate was proved by comparing an oxalic acid reduction of gold chloride in a water-glass-acetic acid gel with a similar one containing, in addition, considerable sodium sulphate. The first gave very little crystalline gold—mostly the colored colloidal form. Addition of soluble sulphate developed a few color bands in the second.

To secure a dazzling display of gold crystals which gleam brilliantly in the sunlight, I found the best way was to mix equal volumes of 1.06 density sodium silicate and 3 N sulphuric acid. To 25 c.c. of this mixture 1 c.c. of 1 per cent. gold chloride was added. This gel set in about one week. Then the solid gel (in a test-tube) was covered with 8 per cent. oxalic acid solution. In several hours the crystal growth was marked, and in a few days at its best.

²⁹ Private communication.

³⁰ *Intern. Zeitsch. phys.-chem. Biol.*, 2, 42 (1915).

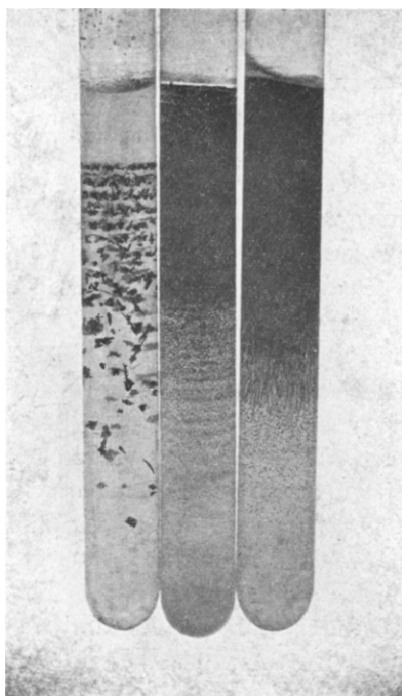
A remarkable difference appeared when 1.16 density water-glass was used instead of 1.06 with the 3 N sulphuric acid. With the same reducing solution—8 per cent. oxalic acid—a series of splendidly colored bands of colloidal gold was obtained. The upper layer of the first bands was red, below that blue, and below that green. A comparatively clear gap below this was followed by another red-blue-green zone. Usually after the first few rainbows the red was omitted. A dozen or more such bands in an ordinary test-tube were not uncommon—the upper bands measuring about 1 cm. in depth. Golden crystals were dispersed all through these gels, but it should be noted that the 1.06 water-glass-3 N sulphuric rarely developed colored colloidal gold—only the yellow crystals.

Many variations in concentrations were tried. Excellent results were obtained with 0.5 c.c. of 1 per cent. gold chloride in 25 c.c. of gel, but 2 c.c. was not so good, and with much less than 0.5 c.c. the gold was too thin. Even 2 per cent. oxalic acid was effective as a reducer, but a saturated solution—about 8 per cent.—was most satisfactory. A very little gum tragacanth mixed with the gel to reduce the gold chloride resulted in blue colloidal gold uniformly distributed.

Copper.—Perfect tetrahedrons of metallic copper were obtained in a 1.06 water-glass-N acetic acid made 0.05 N with respect to copper sulphate. The gel was covered with a 1 per cent. solution of hydroxylamine hydrochloride. In a week or two the tetrahedrons were large enough to observe with the unaided eye. Those formed near the surface were much smaller than those at greater depths. Of course, the farther the reducing solution diffused into the gel the more dilute it became. In a beam of sunlight the faces of the tetrahedrons gleamed with a splendid copper lustre. In nearly all experiments one or more groups of overlapping tetrahedrons were noted. These formed in three radiating lines, making angles of 120 degrees, or in some instances of 60, 120, and 180 degrees. This arrangement of copper crystals is found in mineral deposits. All the other reducing solutions tried were inferior to hydroxylamine.

The presence of small amounts of glucose, cane-sugar, alcohol, or glycerol in the gel caused the formation of a good deal of red feathery stuff. The presence of sodium sulphate aided crystallization.

With a basic gel very different results were obtained. Glucose—a few grammes of 25 c.c.—was mixed with a 1.08 water-glass-0.5 N acetic acid gel and covered with 0.5 N copper sulphate. After a few months close bands of rather amorphous cuprous oxide extended down the gel for a distance of about 12 cm. At first the bands were yellow, but as they aged they turned to a dull red. At one time both colors were in evidence, the newer



The influence of chlorides on the distribution of mercuric iodide. The tube at the left contains sodium chloride—the others do not.

bands yellow. Near the surface of the gel a blue deposit of cupric hydroxide formed. This reaction is suggestive of Fehling's test for glucose. Of course, no copper complex is used here, but evidently slow diffusion permits the reduction from cupric hydroxide to cuprous oxide.

It has been suggested that this method gives opportunity for studying a reaction in its various stages. The control of concentrations and the rates of diffusion pave the way.

Using a U tube containing a 1.10 water-glass-0.5 N acetic acid gel in the bend and 0.5 N copper sulphate in one arm and 1 per cent. hydroxylamine in the other, blue-white bands with a yellow front appeared, later red cuprous oxide, and, finally, red tetrahedrons of metallic copper.

Silver Dichromate.—A 1.06 water-glass-N acetic acid gel was set in the bend of a U tube and the arms filled with 0.1 molar silver nitrate and 0.1 molar potassium dichromate. Minute dark-red crystals soon formed. In one test-tube experiment a single crystal of silver dichromate measured $5 \times 5 \times 1$ mm. This was after a few months' growth. In a U tube experiment a thin red sheet, 1 cm. long, was found—so thin that it was a clear red by transmitted light. Thicker crystals were almost black. The presence of very little gum tragacanth or starch in one of these gels hindered the formation of good crystals and favored the development of spherulites.

Lead Iodide.—Lead iodide crystals had been made by other investigators, but merited further study. This is one of the easiest to make and most spectacular of all the crystal exhibits. A 1.06 water-glass-N acetic acid mixture containing 2 c.c. of N lead acetate to every 25 c.c. was poured into test-tubes. After the silicic acid gel set firmly it was covered with 2 N potassium iodide. A compact layer of lead iodide quickly formed on the surface, followed very soon by crystallization below the surface of the gel. In a few days fern-like fronds grew down into the gel, mixed with many hexagonal plates. These concentrations may be varied with interesting results, and the lead salt may be used above the gel with the potassium iodide in the gel. The first order is much better. Magnificent golden fern fronds, 8 cm. in length, and nearly perfect hexagons, 5 mm. in diameter, were obtained in some experiments. In one or two tubes six hexagons grouped around a centre much like the arrangement in some snow crystals. On standing in direct sunlight for several months the lead iodide crystals blacken somewhat.

Using an excess of the lead acetate as compared with the potassium iodide, for example, in U tubes pouring 0.25 N lead acetate in one arm and 0.1 N potassium iodide in the other, with a gel separating the solutions, yellow-white needles and blocks of basic lead iodide formed. Some of the needles were 2 cm. in

length. Watts³¹ states that if lead acetate in excess is mixed with potassium iodide the basic iodide forms unless sufficient acid is present to prevent. With lead nitrate the ordinary lead iodide results. When formed very slowly, the yellow-white needles and blocks gleam brilliantly and seem to have a high index of refraction. Star-shaped groups and crossed stick arrangements were common. This is not the white double salt ($\text{PbI}_2 \cdot \text{KI} \cdot 2\text{H}_2\text{O}$) made by Remsen and Herty³² by the action of excess potassium iodide on lead iodide.

In U tube experiments such concentrations as 0.25 N lead acetate and 0.1 N potassium iodide formed both the ordinary yellow hexagons and, in the arm nearer the lead acetate, the white-yellow basic crystals. In fact, these concentrations could be so varied as to give, first, only the yellow crystals of lead iodide, with a later formation of the white-yellow basic iodide. As the lead acetate diffused through the gel and met the potassium iodide these yellow hexagons formed, and later, as excess lead acetate diffused into this zone, the white needles or blocks developed. Often a basic crystal formed, touching the edge of a yellow hexagon, and apparently "ate it up" as the excess lead acetate reached that point. With such proportions in the U tube as 0.25 lead acetate and N potassium iodide only the yellow hexagons of the normal iodide form.

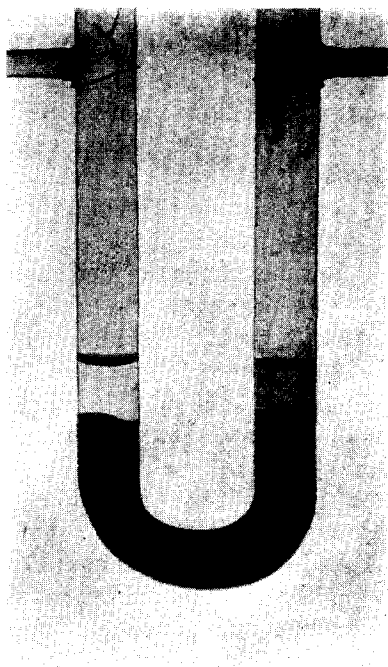
In a slightly basic gel, such as 1.06 water-glass-0.5 N acetic, the formation of the white needles of the basic iodide was greatly favored. Dropping acid on these basic crystals instantly turned them yellow, forming the normal iodide. Using 0.25 N solutions of both lead acetate and potassium iodide in a U tube, a 1.06 water-glass-0.5 N acetic acid gel developed white needles in two days, growing to a length of 2 cm. in one week; a 1.06 water-glass-N acetic acid gel developed yellow hexagons in two days, and in one week white stars also appeared; a 1.06 water-glass-2 N acetic acid gel developed yellow hexagons in two days, and in several weeks no white crystal of the basic salt appeared. The last gel was too acid for a basic salt, while the first gel had a slight alkaline reaction.

A little starch paste mixed with a 1.06 water-glass-N acetic acid gel produced a most interesting result. The gel turned blue

³¹ Dictionary of Chemistry, iii, 127.

³² *Am. Chem. J.*, 14, 107 (1892).

around the individual crystals, proving the release of free iodine. It cannot be urged that the excess acid formed hydrogen iodide which was oxidized by dissolving oxygen, for in that event the gel would have turned a solid blue. It is possible that the starch intimately mixed with the lead iodide as it formed reduced part of it to lead subiodide. There is no question about the existence of a subiodide of lead as recently proved by Denham.³³



Rhythmic bands of mercuric iodide in a silicic acid gel.

A very little gum tragacanth in the silicic acid gel caused the appearance of spherulites of lead iodide and greatly hindered crystallization. In scores of experiments lead iodide showed no tendency to band in silicic acid gels, although in agar well-marked bands of crystalline aggregates were the rule. Hatschek reports bands of lead iodide in silicic acid gels when he used tap-water in preparing solutions, attributing the effect to the bicarbonates present in the water.

³³ *J. Chem. Soc.*, 29 (1917).

Lead bromide in white twin crystals was prepared by experiments similar to those with lead iodide.

Mercuric Iodide.—A 1.06 water-glass-N acetic acid gel with a 0.1 N content of potassium iodide was covered with a saturated solution of mercuric chloride—approximately 0.5 N. At once a layer of red mercuric iodide formed on the surface of the gel, and later scarlet needles in a more or less banded arrangement, depending on relative concentrations. Some of these needles grew to one centimetre in length. Separate cubes of mercuric iodide were observed in some tubes. With a suitable concentration of potassium iodide in the gel, the growing mass of red crystals developed a yellow front, bounded by a sharply marked surface. This zone of yellow needle crystals advanced down the tube. In reality a new yellow zone formed and the old turned red.

An excess of mercuric chloride reacted with the red mercuric iodide to form a somewhat soluble double salt. As a result, the first zone of red crystals formed in the upper part of the gel finally disappeared as the excess of mercuric chloride from the solution above reached this zone. Reversing the order, mixing the mercuric chloride in the gel and allowing the potassium iodide to diffuse down into the gel, produced a mass of red crystals as before, but the red zone advanced down the tube at a rapid rate. In reality a new front formed and the excess potassium iodide readily dissolved the rear of the mercuric iodide column.

With suitable concentrations wonderful banding of red mercuric iodide was obtained. Some tubes contained 40 bands in a distance of 8 cm. The spaces between the denser bands contain scattered crystals. The U tube method was very useful here. Red bands advanced around the bend as the excess of mercuric chloride diffused into the gel. When sufficient mercuric chloride was supplied the red bands finally disappeared, leaving alternate opaque white and clear spaces in a replica of the original banding. Mercuric nitrate diffusing into similar gels produced much better banding than did mercuric chloride, possibly due to the difference in ionization. The presence of sodium nitrate aided banding considerably, as did sugar.

Sodium chloride showed a striking influence on the arrangement and form of the crystals of mercuric iodide. In proportion to the amount of sodium chloride added to the silicic acid

gel the crystals of mercuric iodide became much larger and more like cubes than needles. They were farther apart, and less of the banding arrangement was noticeable. In another series of experiments the acetic acid was dispensed with in making the gel. Water-glass of 1.06 density and 2 N hydrochloric acid made 0.1 N with respect to potassium iodide was poured into tubes, and, after the silicic acid became solid, was covered with saturated mercuric chloride. The red crystals of mercuric iodide formed were very large, relatively, far apart, and no bands could be seen. This change was due to the influence of chlorides, for sodium chloride was formed in the reaction making the gel and, in addition, an unusual excess of hydrochloric acid was present. With less of the same acid the change was not so marked.

A little starch paste in the silicic acid gel caused the appearance of blue around the individual crystals, proving—as with lead iodide—the presence of free iodine at the surface of the crystals. This, too, may be a reduction of the mercuric iodide by the starch.

Basic Mercuric Chloride.—In attempting to make mercuric iodide in a slightly basic gel, 1.08 water-glass-0.5 N acetic, magnificent brown-black leaves were observed, some of them 2 cm. in length. These leaves appeared in the arm of the U tube containing the mercuric chloride. They formed very soon before any potassium iodide could diffuse into that part of the gel. Other mercuric salts gave no such result, so to test the matter I poured a basic gel, 1.08 water-glass-0.5 N acetic into a test-tube and with no other added salt covered the gel with saturated mercuric chloride solution. The same shining red-brown leaves appeared. Since they could not be obtained in a gel of acid reaction nor with any salt other than mercuric chloride, they were evidently one of the basic mercuric chlorides. A search of the literature justified this theory. Different basic chlorides are on record, but the description of $\text{HgCl}_2 \cdot 2\text{HgO}$ agrees perfectly with the crystals obtained above.

Gels of different basicity were covered with mercuric chloride solution and the crystals compared. With 1.06 water-glass-0.5 N acetic (very slightly basic) the crystals were more widely scattered and, at a distance of a few centimetres from the surface of the gel, were excellent. This particular gel caused the most remarkable banding of the basic chloride. With a very

basic gel the crystals were smaller and formed in a rather compact mass. A few grammes of glucose in 25 c.c. of a slightly basic gel changed the results decidedly. Instead of the brown-red leaves, a gray mass of closely-packed bands, sharply marked, appeared. In a distance of 8 cm. over one hundred of these bands were counted.

Silver Sulphate.—An attempt was made to produce silver dichromate by allowing N silver nitrate to diffuse into a silicic acid gel containing very dilute potassium dichromate. This particular gel was the result of mixing 1.06 water-glass with 3 N sulphuric acid instead of the usual acetic acid. Immediate formation of bright-red crystals at the top of the gel was observed, and later the usual black-red silver dichromate deeper in the gel. Curiously enough, the bright-red crystals were of an entirely different system, orthorhombic, from the triclinic silver dichromate below. They grew rapidly—in less than one hour their shape was apparent, and over night they grew to a length of one centimetre. In a week or two, by using more concentrated silver nitrate, slabs 3 cm. long were obtained, but in spite of their thickness they were a clear cherry red. Using 0.1 N silver nitrate no such orthorhombic crystals formed, only the ordinary silver dichromate. The gel had to be made with sulphuric acid and water-glass. This suggested a double salt formed with the excess of silver nitrate, but the difficulty was readily cleared by analysis and further experiment. Analysis showed the red orthorhombic crystals to be almost entirely silver sulphate, with a very little silver chromate mixed in.

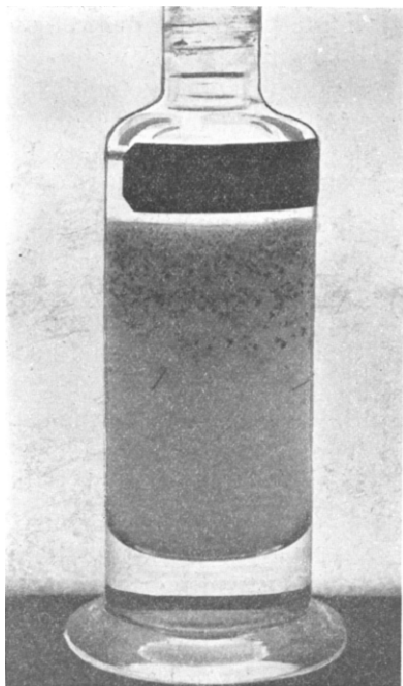
Chamot³⁴ states that both silver sulphate and silver chromate are orthorhombic, hence these must be mixed crystals. Gooch³⁵ and Autenrieth³⁶ observe that silver chromate is formed when excess silver nitrate reacts with a soluble dichromate, hot or cold. To test the mixed crystal explanation, I omitted the potassium dichromate in another experiment and secured colorless slabs exactly like the cherry-red ones in shape and time of formation. Furthermore, by the presence of a single drop of a potassium dichromate solution in a tube of the gel a faint yellow color was made to appear in the slabs. Their depth of color was easily

³⁴ "Elementary Chemical Microscopy," 335.

³⁵ "Methods in Chemical Analysis," 406.

³⁶ *Ber.*, 35, 2057.

made to vary with the concentration of the potassium dichromate. No doubt this experiment could be extended to many other pairs of isomorphous substances. The conclusion is that when approximately N solution of silver nitrate diffuses into a silicic acid gel made from 1.06 water-glass and 3 N sulphuric acid containing any small amount of a soluble dichromate mixed crystals—not a double salt—of silver sulphate and silver chro-



Basic lead iodide in a silicic acid gel.

mate result. As the silver nitrate becomes more dilute at greater depths in the gel only the normal silver dichromate forms.

Silver Acetate.—The silver sulphate experiment is very similar to one with silver acetate. Increasing the concentration of silver nitrate to N in making a silver dichromate, I found that gels made from acid and water-glass soon showed long, colorless slabs or leaves. Omitting the potassium dichromate from the experiment, and simply allowing N silver nitrate to diffuse into a 1.06 water-glass-N acetic acid gel, the same colorless leaves were produced again. Analysis showed them to be silver

acetate. In ten minutes these crystals grew a few millimetres in length, and over night to one centimetre.

By varying the acid mixed with the water-glass in making the silicic acid gel and allowing approximately N silver nitrate to diffuse in, many silver salts can be obtained in crystalline form. This principle was applied by Hatschek to other compounds.

Silver phosphate formed in this manner (1.06 water-glass to 3 N phosphoric acid) grew in irregular yellow fronds, very much like minute ostrich plumes.

Acid potassium tartrate crystals grew rapidly when a 1.16 water-glass-3 N tartaric acid gel was covered with any dilute potassium salt solution. Blocks 5 mm. wide resulted, and in several hours crystals of notable size could be counted on. Changing the concentrations somewhat, wide-branching fern growths were obtained.

Dihydrogen monosodium phosphate crystals formed when about 3 grs. of disodium phosphate were mixed with 10 c.c. of a 1.10 water-glass-2 N acetic acid gel. In a cool room perfect colorless rhombohedrons appeared in a few hours and grew to 6 mm. width in two days. These crystals were so soluble that as the room warmed they dissolved. On cooling in the ice-box they appeared again, but not in such good crystals. Some of the attempts to duplicate this experiment failed. Exact temperature and concentration conditions were not studied.

Urea nitrate crystals of large size formed rapidly when concentrated nitric acid mixed with an equal volume of water diffused into a 1.06 water-glass-N acetic acid gel containing urea.

Lead chromate and basic lead chromate developed in a slightly basic gel such as 1.06 water-glass-0.5 N acetic acid containing a little potassium chromate when lead acetate solution diffused into the gel. In a few weeks a 15-cm. test-tube filled with orange tendrils curling around countless brighter yellow crystals of minute size. In addition, much of the orange material concentrated in regular bands about 5 mm. apart. Near the top of the gel an orange-red band one centimetre deep developed. This, of course, was basic lead chromate. Hatschek formed lead chromate in a gel of acid reaction and thus missed the opportunity of making the basic chromate.

Barium carbonate formed in a basic gel containing some

sodium carbonate. A silicic acid gel was covered with a solution of a barium salt. The crystalline character of the deposit was not apparent for some time. White spherulites appeared to a depth of about 5 cm., and then flower-shaped crystalline aggregates formed. They were very small, but the crystalline character was apparent to the unaided eye.

Potassium bisulphate crystals of considerable size appeared in a gel formed by the "Hopkins process"³⁷ of obtaining soluble potassium salts and aluminum sulphate from feldspar. Finely ground feldspar was heated at 300° with moist potassium hydroxide. This partial decomposition of the feldspar was then completed by reaction with sulphuric acid. In commercial practice hydrochloric acid is used at this point. Using sulphuric acid in a mere laboratory experiment, a silicic acid gel formed and crystals of KHSO_4 grew in this medium.

Sugar crystals often appear in ordinary fruit jellies. I have a number that measure about $5 \times 7 \times 9$ mm.

Calcium tartrate crystals of great beauty, $20 \times 5 \times 5$ mm., were easily obtained in a U tube containing a 1.06 water-glass-0.5 N acetic acid gel by filling one arm with a solution of calcium chloride and the other with a solution of tartaric acid.

Copper tartrate crystals of perfect shape and clear blue color were made by covering a 1.06 water-glass-3 N tartaric acid gel with 0.5 N copper sulphate.

Zinc-ammonio chloride crystals of several centimetres in length were found in the gelatinous packing next the zinc wall of commercial dry cells. These colorless sheets are of the formula $\text{ZnCl}_2 \cdot 2\text{NH}_3$. They were also obtained by Marignac in a Leclanche cell, but not of such large size. The starch paste or other gelatinous filling next the wall of a dry cell regulates the diffusion rates of the zinc chloride and ammonia formed by the chemical action of the battery on discharge, thus greatly aiding crystal development. On short periods of service, with rest intervals, these crystals were longer than in batteries run down by continuous service. This agrees with the time feature of the theory proposed in this paper.

DEVELOPMENT OF A THEORY.

Early in my work I decided that the most important feature of the favorable influence of gels on reactions forming crystals

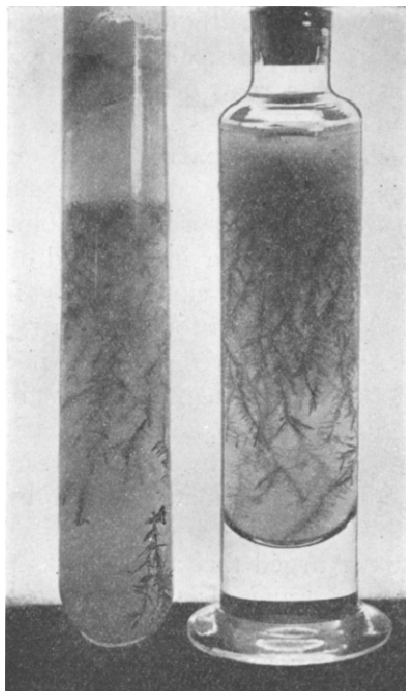
³⁷ Holland, Frazer, Miller, U. S. Patent 1,196,734.

was the capillarity of the gel structure. To test this, I used a layer of finely powdered silica in a U tube, soaked it with water to dislodge air, and filled one arm with a solution of potassium dichromate and the other with a solution of silver nitrate. Slow diffusion of the two salts through the capillary spaces between the silica grains allowed the formation of good crystals of silver dichromate. Later I learned that Dreaper had already developed that idea, using not only a layer of sand, but a single capillary tube. It may be objected that the rather great surface of finely divided silica permits an appreciable solution of silica, thus filling the space pores with a weak gel of silicic acid. Coarse sand did not serve so well.

It seemed worth while to extend somewhat the list of substitutes for gels in this work, so flowers of sulphur was substituted for sand in the above experiment. Some trouble was experienced in packing the sulphur in the bend of the U tube, and many attempts failed from too close packing for free diffusion. A platinum wire was used to dislodge the persistent air bubbles. Finally an excellent band of red crystals of silver dichromate formed where the silver ion met the dichromate ion. Barium sulphate and alundum powder served much better than the sulphur as substitutes for a gel. In fact, the results with alundum were startling. Silver dichromate formed in flat needles one centimetre in length. Closely-packed asbestos gave fair results. Certainly it cannot be urged that any gel was present in the experiments with a membrane of sulphur or alundum or barium sulphate.

Without doubt, any compact mass of insoluble discrete particles with proper sized capillaries will function as a gel in favoring the formation of crystals. Other influences may be present in a true gel. Adsorption, pressure, and solubility effects may greatly influence the capillary space results. A rather amorphous insoluble compound first formed by the meeting of two reacting substances in a relatively narrow channel may so further regulate the rates of diffusion as to give time for crystal formation of more of the same insoluble compound. In this suggestion the geologist may possibly find an explanation of the marked crystalline nature of some mineral veins. The pathologist, too, may obtain some light on the accumulation of crystalline deposits in animal tissue.

To test the theory, the mouth of a small specimen tube was covered with a sheet of goldbeater's skin, holding it on firmly with a rubber band. The tube had first been filled with a solution of 0.1 N potassium iodide. Care was taken to leave no air bubbles on the under side of the membrane and to rinse the outside of the tube. The tube was then immersed in a small beaker of saturated lead acetate solution. At once an almost amorphous



"Lead trees" in silicic acid gels.

precipitate of lead iodide appeared on the under side of the membrane, and in less than a minute crystals of lead iodide fell in a beautiful gleaming shower, rapidly increasing in amount. It is very easy to secure gleaming crystals of lead iodide by cooling its hot solution, but in this experiment the solutions were cold. Mixing the same solutions in a test-tube without the use of a membrane, a yellow powder results.

If the more concentrated solution was placed inside the specimen tube, the crystals formed on the upper surface of the mem-

brane. This is in accord with the osmotic difference rule of Pringsheim. With less difference in concentration of the reacting substances solutions the reaction was much slower.

Separating solutions of silver nitrate and potassium dichromate in this way, it was a simple matter to make a gramme or two of brilliant crystals of silver dichromate settling to the bottom of the tube. Possibly this method may be of some use in the preparation of pure compounds, since the crystals are not mixed with an annoying gel. Other thin, semipermeable membranes serve. Parchment paper is good, but goldbeater's skin is most suitable.

In a number of experiments it was observed that at first a rather amorphous or, at least, fine-grained precipitate formed on the surface of the original membrane, thus forming a new membrane of different capillary structure which exerted a marked influence on rates of diffusion. The result of checking the rates of diffusion of the reacting substances was to give time enough for the growth of minute particles to crystalline size.

Barium sulphate is most annoying in quantitative analysis because of its tendency to form in slow settling colloidal suspensions. It seemed an interesting experiment to precipitate it by the diffusion cup method and observe the rate of settling. I believed that if I placed a dilute solution of a sulphate inside the specimen tube, covered it with a goldbeater's skin touching the surface of the solution, and immersed the tube in a more concentrated solution of a barium salt, the barium sulphate formed on the under side of the membrane would be of much larger crystals than usual and would settle rapidly. It did. Some modification of this experiment may possibly be applied to the determination of sulphates.

To carry the theory further, the only need of the goldbeater's skin is to prevent sudden wholesale mixing of the solutions and mechanically sustain the rather amorphous precipitate first formed, which then functions as the real active membrane. This theory is not universal in its application, for in gels excellent crystals of a number of substances formed without the appearance of a preliminary compact layer of precipitate. In these instances only the gel functions in regulating diffusion. The theory does apply, however, in the absence of a gel and in all instances where a compact precipitation band is formed.

John Johnston's method of preparing crystals of increased size by the slow diffusion of two reacting solutions in a large volume of water at two widely separated points supports the theory above given. De Schulten's experiment, described earlier in this paper, is somewhat similar to Johnston's.

The usual gels employed in earlier investigations were agar, gelatine, and silicic acid. To this list I added the insoluble powders above described, and also gels of ferric phosphate and manganese arsenate. Both of these permitted the formation of good crystals of lead iodide, silver dichromate, and mercuric iodide. It is noteworthy that they are inorganic gels like silicic acid. Probably the protective colloid action of organic gels hinders crystal growth.

It is not necessary that this subject be limited to gels. Since the influence of gels on crystal formation is largely that of regulated diffusion, it is permissible to discuss even such structures as steel. Alexander³⁸ holds that graphite in steel is partly in the colloidal form and therefore inhibits crystallization. It would seem that films of colloidal graphite around crystalline nuclei of cementite, for example, must greatly influence the growth of those crystals when steel is cooled from a high temperature. Colloids in general retard diffusion. But, instead of inhibiting crystallization, as Alexander believes, it is conceivable that, although cementite crystals in the steel may form more slowly, they may be larger and of different shape than if formed rapidly.

Ice-cream without egg-white or gelatine or some other protective colloid is grainy. Of course, the lactalbumin in the milk is a protective colloid, but there is not enough of it. In marshmallows crystallization of the sugar is prevented by the protective colloid effect of gelatine or gum arabic.

The reduction of gold or copper salts in plastic glass with the production of a ruby tint is somewhat related to this topic. Possibly new ornamental effects could be obtained by experimenting with diffusion zones while the glass is hot enough to be plastic. Of course, the glass in that condition is not a gel, but it permits slow diffusion.

There seems no good reason why many very viscous substances should not function as gels in their influence on diffusion reactions.

³⁸ *J. Soc. Chem., Ind.*, **28**, 280.

SUMMARY.

1. Good crystals of silver dichromate were obtained by allowing the slow diffusion of solutions of silver nitrate and potassium dichromate through flowers of sulphur. Barium sulphate powder served as well, and alundum was even better. This confirms Dreaper's opinion that diffusion through capillary spaces other than those in a gel may be efficient in aiding crystal formation.

2. An experiment was devised to prove that in many instances the amorphous or fine-grained precipitate formed when two solutions meet acts as a membrane or network of capillaries, retarding further diffusion and favoring the formation of more of the precipitate in larger crystalline particles.

3. Silicic acid gels of alkaline reaction were made by mixing sodium silicate with less than enough acid for neutralization. These basic gels made possible the production of crystalline salts not possible in a gel of acid reaction.

4. Gold in a beautifully crystalline condition was best prepared by mixing equal volumes of a water-glass, 1.06 density, and 3 N sulphuric acid, adding 1 c.c. of 1 per cent. chloride to 25 c.c. of the mixture and, after solidification of the gel, covering with a solution of 8 per cent. oxalic acid.

Startling rainbow bands of red, blue, and green colloidal gold, mixed with scattered crystals, resulted when the water-glass was 1.16 density. Both methods worked readily and gave better results than any yet recorded.

5. Perfect tetrahedrons of copper were secured by using 1 per cent. hydroxylamine hydrochloride to reduce dilute copper sulphate in a silicic acid gel. Peculiar aggregates of tetrahedrons similar to those found in copper deposits in Nature were also observed.

All the steps of the reduction of cupric hydroxide to yellow and red forms of cuprous oxide were shown simultaneously in a series of many bands, using glucose as the reducing agent in a silicic acid gel of alkaline reaction. With 1 per cent. hydroxylamine the same reduction was carried through the cupric hydroxide and cuprous oxide to tetrahedrons of metallic copper. This suggests a method of controlling the different steps of other reactions for study.

6. Lead iodide in perfect hexagonal plates, 5 mm. wide, and

golden, fern-like growths, 8 cm. long, were formed in silicic acid gels. A basic lead iodide in yellow-white needles, 2 cm. long, formed by the action of excess lead acetate on potassium iodide in a slightly acid gel and even better in a slightly basic gel. Iodine was released on the surface of crystals of lead iodide, as shown by the presence of a little starch mixed with the silicic acid. Some reduction of lead iodide must have taken place, possibly caused by the starch.

7. Red mercuric iodide in 2 cm. needles or, in smaller crystals, banding in as many as forty regular bands in a distance of 8 cm. was obtained by the diffusion of a mercuric chloride solution into a silicic acid gel containing potassium iodide. With certain concentration conditions yellow crystals formed in front of the red needles and were finally changed into the red mercuric iodide. Soluble chlorides exerted a striking influence on the size, form, and arrangement of the mercuric chloride crystals.

8. Magnificent red-black crystals of a basic mercuric chloride resulted when a saturated solution of mercuric chloride diffused into a silicic acid gel of slightly basic reaction. In a very slightly basic gel these crystals were grouped in a remarkable series of bands. The presence of a little glucose exerted a marked influence, changing the color and developing over one hundred compact bands in a distance of 8 cm.

9. Silver sulphate crystals appeared in less than one hour when N silver nitrate diffused into a silicic acid gel made by mixing equal volumes of 1.06 density water-glass and 3 N sulphuric acid. In a few days orthorhombic slabs, 3 cm. long, developed. If enough potassium dichromate to make the whole gel 0.1 N molar with respect to this salt only was present, the long slabs were a beautiful clear red. In the presence of excess silver nitrate near the surface of the gel silver chromate was formed, and, since silver chromate and silver sulphate are isomorphous, red mixed crystals resulted. The color of the crystals was made any depth of red by varying the concentration of the potassium dichromate in the gel. Farther below the surface of the gel the silver nitrate became less concentrated, and triclinic crystals of the red-black silver dichromate appeared. In time they grew to a size $5 \times 5 \times 1$ mm.

10. Silver acetate grew in gleaming white sheets, 2 cm. long, when N silver nitrate diffused into a silicic acid gel made from

water-glass and acetic acid. These crystals appeared in a few minutes. Such protective colloids as gum tragacanth, when present in very small amounts, twisted the straight crystals of silver acetate into fantastic shapes.

11. Basic lead chromate was made in crystalline bands by diffusion of lead acetate solution into a silicic acid gel of alkaline reaction containing potassium chromate; urea nitrate in large crystals, by the diffusion of nitric acid into a silicic acid gel containing urea; perfect crystals, 5 mm. wide, of acid potassium tartrate and perfect crystals of copper tartrate in a silicic acid gel made with tartaric acid; and monosodium phosphate in large, colorless rhombohedrons by mixing disodium phosphate in a sodium silicate-acetic acid gel.

12. Dry batteries discharging for short intervals developed colorless slabs, several centimetres in length, of $\text{ZnCl}_2 \cdot 2\text{NH}_3$ next the zinc wall of the container. The gelatinous paste in this part of the cell caused slow diffusion of the zinc chloride, and ammonia formed by the discharge of the cell.

OBERLIN COLLEGE, OBERLIN, OHIO,

July 26, 1917.

Farm Weirs. (*U. S. Department of Agriculture, Farmers' Bulletin No. 313.*)—The value of water has increased in the arid lands of the West with the development of the country to a point where there is now a general demand for accurate devices for the measurement of small streams of flowing water. A "weir" is one of the most commonly used devices for this purpose, and the best known are the rectangular, the Cipolletti, and the 90-degree triangular notch types with free fall, sharp chests, and full contractions. Discharge formulæ for these types are given and are so arranged that if the "head" or depth of water flowing over the weir notch is known, the flow by cubic feet per second can be readily ascertained. A table of hydraulic equivalents enables this flow to be changed into miner's inches or statute inches.

Casting Shells in Permanent Moulds. E. A. CUSTER. (*Proceedings of the American Foundrymen's Association, September 25-28, 1917.*)—One of the remarkable changes that the present conflict has brought about is the spectacle of raining upon the enemy an unheard-of number of high-calibre cast-iron shells. There is nothing new in the use of cast-iron projectiles—before this age of steel they