

on moist fines, and the total cost for roasting low-grade material does not exceed 50 cents per ton. In places where actual smelting is done by reverberatory, it may be possible to use the waste heat of the latter for carrying out a sulphatising roast, as a smelting reverberatory requires an intense heat throughout its entire length to liquify the charge, and the fire gases on leaving it carry more than the degree of heat required for effecting calcination.

3. Leaching. A cheap solvent is the main consideration; it is possible for a smelter to supply its own want of acid by erecting a bye-pass flue leading to absorption towers filled with coarse coke down which water is trickling. The acid so obtained is very dilute, but strong acid is undesirable in leaching. As another source of acid I would suggest the fume from the stack end of the flue, which always contains more or less sulphuric anhydride. Thus in one case I found more than 15 per cent. SO_2 , and of this material there were many tons available. On mixing with water and decanting, a strong acid is obtained which may be used to strengthen the liquor from the tower. The roasted slime would require but little acid as a considerable part of the copper is soluble in water. Thus in Expt. 21, 70 per cent. of the recoverable copper was present as sulphate. The roasted material is dropped quite hot into a weak liquor, raising its temperature and assisting solution.

4. Precipitating. The chief source of expense is the iron required for cementation; this may be considerably reduced by using broken-up low-grade matte to precipitate the copper. If necessary the precipitation is completed with scrap iron in a separate launder.

5. Refining the precipitate. In the majority of cases the impure precipitate goes back to the blast-furnace to be converted into matte.

Cost of process. It is of course impossible to make a general statement as to costs, as expenditure varies greatly according to the country or even district. At Natrona (Pa.) the total cost is \$1.87 per ton of ore; at another plant in the Western U.S. it amounts to \$2.96.* These two plants use the Longmaid-Henderson process on pyritic cinders. This is done at the same temperature as the sulphatising roast and in a reverberatory or muffle furnace. No acid is needed, but the amount of salt required is $7\frac{1}{2}$ to 20 per cent. of the weight of ore treated. An approximation of the cost may be arrived at by compiling statements of cost of the various operations and of the initial cost of the plant divided by the number of tons treated in one year:—

	Per ton.
Initial cost of plant	\$1.50—3.50
Collecting slimes	0.20
Roasting	0.40—0.60
Leaching	1.60
Precipitating and collecting	0.60
Smelting, refining	0.10

By taking the average of these figures, the total expenses are found to be \$5.60. Thus, assuming that all the acid and iron had to be purchased and making the plant pay for itself at the end of the first year, there would remain a profit of \$1.60, and for the succeeding years \$4.10 per ton of the material experimented upon.

Concerning the time required for treatment, roasting and leaching can be done in 24 hours, while precipitation takes one day or more, according to capacity; and while there is necessarily an accumulation of slimes about equal to the quantity required to fill one settling-pond, the plant can cope with the slimes at the rate at which they are produced in the mill; it is really part of the latter.

In conclusion, I may mention that I have applied roasting and leaching by nitric acid to the copper assay of pyritic ores. 10 grms. are roasted in a porcelain dish over a Bunsen burner for 20 minutes with occasional stirring. After cooling the dish is covered, 15 c.c. of strong nitric acid added and most of the acid evaporated. The roasted ferric oxide remains unattacked. Take up with 10 c.c. nitric acid (1:1), add hot water, transfer to a graduated 200 flask, fill up, filter 100 c.c. and electrolyse.

* Greenawalt, The Hydrometallurgy of Copper.

On account of the ferric oxide retaining a little copper the results are about 0.02 per cent. low, but keeping this in mind the method is very rapid and has proved extremely useful in technical work.

Meeting held at Burlington House on Monday, June 2nd, 1913.

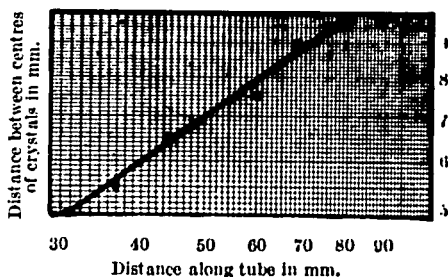
PROF. W. R. E. HODGKINSON IN THE CHAIR.

REACTIONS IN AQUEOUS AND COLLOIDAL SYSTEMS.

BY W. P. DREAPER, F.I.C.

The precipitation of insoluble compounds in solutions, under conditions which somewhat resemble those previously obtained in gels, has been considered in order to see if the results in the gels are dependent upon, or confined to conditions which involve precipitation in such media.

The experiments now recorded involve precipitation in solutions where the reacting substances are contained in glass capillary tubes, preferably set in a horizontal position. Disturbing influences (cross currents, etc.), are thus reduced to a minimum, and the course of the reactions can be conveniently followed under the microscope. Certain insoluble salts are produced by slow diffusion in aqueous solutions of suitable concentration. One solution is drawn up into the capillary tube to its total length, and the top end sealed. The open end is then inserted into a second and larger one containing the other solution. This outer tube has a bulb blown at its closed end, which acts as an additional receiver for the necessary supply of the second solution.



The results obtained under these conditions, indicate that the formation of stratified layers is not necessarily due to the reaction taking place in a gel, but that the diffusion process itself is primarily responsible for it. The strata obtained in aqueous solutions may be thus as clearly defined as in a gel. Precipitation in the form of spherulites has not yet been observed in the absence of gels.



FIG. 1.

Lead chloride.—A capillary tube contained a 3 per cent. lead acetate solution, and the outer one a 5 per cent. solution of hydrogen chloride. At the open end of the capillary tube, the lead chloride gradually precipitated in long needle-shaped crystals at certain intervals. Their length and position in the direction of the length of the

capillary tube, is indicated in the tables given below. These were followed at definite intervals by single crystals of lead chloride, the intervening spaces being free from precipitate. The form of the crystals obtained is shown in the accompanying photo-micrographs Figs. 1, 2, the direction of flow of the outer solution being indicated by an arrow. Following the long needle-shaped crystals formed at the distance mentioned, from the entrance of the tube, the single crystal (Fig. 1) was observed, which nearly filled the tube. Possibly owing to this, the next crystal (Fig. 2) took the distinctive form observed, which is also fully developed in the next and final crystal. In Fig. 3 are seen original crystals as subsequently removed from the tube.

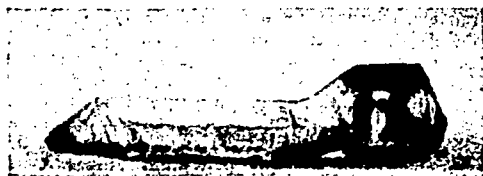


FIG. 2.

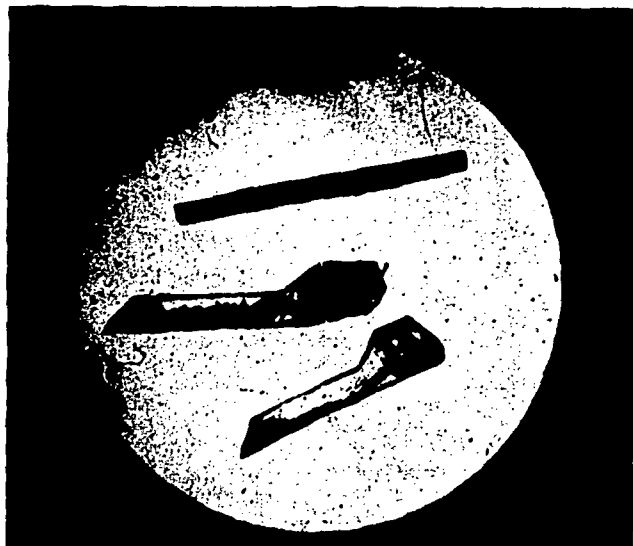


FIG. 3.

The distances between the centres of the crystals in the direction of the length of the tube, are given in the case of two typical cases in the accompanying tables and curve on double log-squared paper. The reaction in the tube was generally complete after an interval of five to six days.

TABLE A.

Lead chloride in capillary tube. Diam. 0.66 mm. (internal).

Length of crystals in mm.	Space from centre to centre of crystals.	Actual space between crystals.
(1)..3 mm.	(1-2)..6.5 mm.	(1-2)..3 mm.
(2)..4 mm.	(2-3)..8 mm.	(2-3)..4 mm.
(3)..4 mm.	(3-4)..5.75 mm.	(3-4)..2.5 mm.
(4)..0.7 mm.	(4-5)..5.85 mm.	(4-5)..3.3 mm.
(6)..0.5 mm.	(6-7)..6.0 mm.	(6-7)..5.5 mm.
(7)..1.0 mm.	(7-8)..7.75 mm.	(7-8)..6.5 mm.
(8)..1.5 mm.	(8-9)..7.05 mm.	(8-9)..6.5 mm.
(9)..0.6 mm.	(9-10)..8.2 mm.	(9-10)..7.5 mm.
(10)..1.0 mm.	(10-11)..11.75 mm.	(10-11)..9.0 mm.

TABLE B.

Lead chloride in capillary tube. Diam. 0.42 mm. (internal).

Length of crystals in mm.	Space from centre to centre of crystals.	Actual space between crystals.
(1)..0.5 mm.	(1-2)..4.0 mm.	(1-2)..2.5 mm.
(2)..1.5 mm.	(2-3)..5.25 mm.	(2-3)..3.5 mm.
(3)..1.5 mm. (2 crystals)	(3-4)..5.75 mm.	(3-4)..4.5 mm.
(4)..0.5 mm.	(4-5)..6.0 mm.	(4-5)..5.5 mm.
(5)..1.0 mm. (2 crystals)	(5-6)..9.5 mm.	(5-6)..8.5 mm.
(6)..0.5 mm.	(6-7)..7.0 mm.	(6-7)..6.0 mm.
(7)..0.5 mm.	(7-8)..6.0 mm.	(7-8)..5.5 mm.
(8)..0.5 mm.	—	—

Hatschek has stated (this J., 1911, 30, 257) that aggregates of lead salts of 1.0 mm. diameter have been obtained in gels and that "how enormous this size is, need hardly be pointed out to anyone familiar with the microscopic appearance of lead compounds precipitated from aqueous solutions." The crystal (3) in Table A of lead chloride had a length of 4.0 mm. so that such figures may be equalled, if not exceeded, in aqueous solutions under the conditions now recorded (see Fig. 3).

Lead ferrocyanide.—In a capillary tube of 0.6 mm. diam. precipitation rapidly takes place, and for some distance into the tube the deposit is granular rather than crystalline. (Fig. 4.) A more or less sharp change then takes place and the lead ferrocyanide precipitates in well-formed crystals up to a length of 0.8 mm. which in some cases seem to occur in stratified bands. In a finer tube of 0.42 mm. diam. stratification was more pronounced, and ultimately the precipitate became strongly crystalline. There is a tendency for this heavy precipitate to fall to the bottom of the tube in a granular state, and partly obscure the stratification.

Lead sulphate.—When this salt is formed by the diffusion of 5 per cent. potassium sulphate into 2 per cent. lead acetate solution, stratification is very pronounced. On standing for two months a further change is observed. The original stratified area is seen changing into a more crystalline form in Fig. 5.

Silver salts.—Up to the present time no very definite result has been obtained with silver chloride, but in the case of silver ferrocyanide distinct stratification has been observed.

Barium sulphate.—Distinct stratification has been observed when using a 2 per cent. solution of barium chloride in the capillary tube, and a 5 per cent. solution of potassium sulphate in the surrounding one. In this case the intervening spaces are not entirely free from precipitated barium salt, but the stratification is very distinct. At a rough estimate, the proportion present in the space might be 10 per cent. of that present in the rings. After a certain period the precipitate seems to become crystalline.

In this case the reaction proceeds differently to that in the lead chloride experiments. Working with potassium sulphate the barium sulphate may be precipitated in an extremely finely divided, or even gelatinous, state. There is no tendency for it to settle to the bottom of the tube. It occupies the whole area and does not appear crystalline, but granular under a fairly high power (250 diam.). When this precipitate has formed to a length of possibly 80 mm. distinct stratification may occur within this area. This experiment presents conditions possible in nature where the substance precipitated may itself act as a gel or its equivalent in inducing stratification on further precipitation, within that area. It is interesting to compare these results with those obtained with lead chloride.

Barium carbonate.—The results obtained in this case are typical, as the intervening clear spaces may be practically free from deposited barium carbonate. (Fig. 6.)

Change of physical state in insoluble precipitates.—In the presence of a third substance (electrolyte or colloid) in sufficient quantity, certain results have been obtained which it would be difficult to observe in a test tube where the additional cross-sectional area would obscure the effect. Two cases may be cited:—

(a) The inner tube contained 2 per cent. barium chloride solution saturated with ammonium chloride. The outer tube 5 per cent. potassium sulphate saturated with ammonium chloride. At the start a copious and opaque precipitate of barium salt formed, extending to 8 mm. into the capillary tube. After 24 hours, this first area up to 10 mm. was apparently quite free from any visible precipitate of barium sulphate although the next section of the tube contained insoluble salt. It is probable that this is not due to actual migration, but is due to a change in the physical state of the precipitate.



FIG. 4.

(b) When 2 per cent. gelatin was present in the 2 per cent. barium chloride solution, similar effect was observed, except that an 8 mm. opaque section of precipitated salt appeared to gradually migrate up the tube. This effect was found to take place against the force of gravity, for when the capillary tubes were in a vertical position, the section progressed in the same manner. This might be due to (a) direct migration of the precipitate; (b) to the precipitate re-dissolving or (c) changing its physical or chemical state.



FIG. 5.

A short capillary tube, 15 mm. in length, containing a column of the above gel and barium chloride was immersed in 5 per cent. potassium sulphate solution. The usual deposit (8 mm. in length) formed within a few hours. This advanced along the tube leaving an apparently clear space behind it, until it reached within 1 mm.

of the surface of the gel which remained permanently clear. On further standing, the opaque area gradually shortened in length, and ultimately disappeared. Under the microscope, the main area of the tube contained well defined large crystals except that the last 1 mm. in which the precipitate (opaque) had never formed, was free from them. This experiment indicates that the opaque area probably contains a colloidal, or at least a finely divided precipitate of an insoluble barium salt of such a nature, that it does not deposit. This is gradually changed into a crystalline salt, and the appearance of migration through the column of the solution or gel of this opaque area is illusory. The actual change is a rapid one and may occur at any one spot within an hour.

In a further experiment where the opaque column was allowed to "advance" into the tube for a distance of 20 mm. the capillary tube was then removed from the outer solution of potassium sulphate. The 8 mm. column had remained opaque and non-crystalline at 200 diam. after 14 days, and did not continue its advance into the tube. Opaque sections were cut out of similarly treated capillary tubes, and placed in a 5 per cent. solution of potassium sulphate. This change to the crystalline state took place in the presence of this further excess of potassium sulphate. An opaque section placed in 2 per cent. barium chloride solution remained opaque, and non-crystalline. A photo-micrograph of the opaque area indicates an exceedingly finely divided precipitate. (Fig. 7.) Further action of diffused potassium sulphate solution is shown in Fig. 8. The absence of any finely divided precipitate in the clear space following the opaque area indicates the complete change which has taken place in the physical state of the deposited salt. Fig. 9 greatly enlarged, shows a peculiar formation of the barium salt which for optical or other reasons may appear in star-like formation.

There is no actual migration, but a progressive formation of an 8 mm. band or column of an extremely finely divided, and apparently non-crystalline precipitate, which in the presence of further potassium sulphate, spontaneously changes into a strongly crystalline one. As the opaque section progresses into the capillary tube, and consequently reaches a point, where the potassium sulphate solution, diffusing up the tube is more dilute, it increases in length in some cases up to 30 mm.

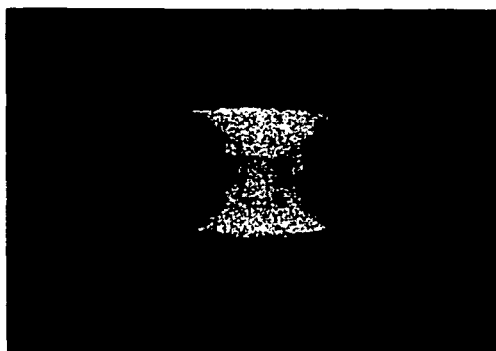


FIG. 6.

This is an interesting record of a change in an insoluble inorganic substance from the amorphous to the crystalline state, within a short period, although similar changes which occur in organic substances have often been observed and have been studied by Hatschek and others. This reaction adds further weight to the argument, that crystalline minerals such as quartz may have been formed

from a gel of silicic acid. It has been observed as the opaque area advances into the capillary tube, that it may increase from 8 mm. to 30 mm. if the solution in the tube becomes very weak in potassium sulphate.

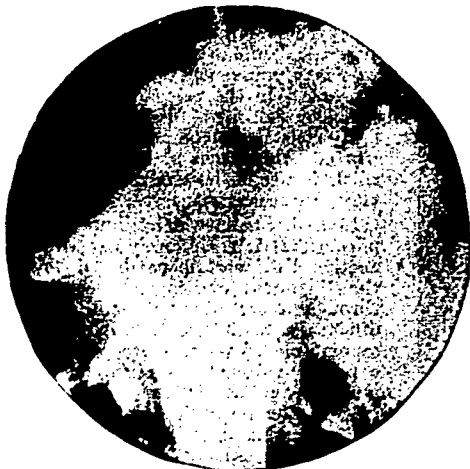


FIG. 7.

An opaque section, as it occurs in stratification in a 3 mm. diam. tube was cut out and immersed in potassium sulphate. In a short time the opaque substance changed into a crystalline one. The rate of change being obviously measurable under the conditions present. As it has been generally acknowledged that the transparent sections in gels, actually contain precipitated salt, it may even be that in some cases an equal amount of the salt is present in a highly crystalline form, as is evidently the case in the one now quoted.

In the presence of a 5 per cent. solution of sodium chloride no further change in the opaque area took place during 10 days. After that time a change occurred of a different order, which indicated that the barium salt had either taken a state of greater aggregation, as judged by the transparency test, or had been removed by solution or otherwise. Under the microscope no actual crystals could be observed. A certain degree of stratification was noticed in the original opaque section which has now become translucent. This was not noticed when the same area was opaque, although it may have been present.

When a solution containing 2 per cent. barium chloride and 1 per cent. gelatin was set to a length of 30 mm. in a 3 mm. tube, and 5 per cent. potassium sulphate solution allowed to react on both surfaces of the gel from each end of the tube, two ordinary 8 mm. opaque sections were first formed. These gradually advanced towards each other, until they were divided by a distance of 3—4 mm. (see Fig. 10). No further action took place, except that each 8 mm. opaque section gradually shortened in length, and was replaced by a practically transparent area containing the usual crystals. No precipitation of any kind occurred in the 3—4 mm. central section. When this was cut out, and placed in a 5 per cent. potassium sulphate solution, it was found to be entirely free from barium chloride. It must have lost its original content of this substance by diffusion in the direction of the incoming sulphate solution. This action may in some way or other also be related to the action which produces stratification.

In another case where 2 per cent. barium chloride was present in a 0.6 mm. tube, and both this and the 5 per cent. potassium sulphate solution outside were saturated with NaCl, precipitation apparently took place for a distance of 50 mm.

The change in crystalline state is evidently not due to the action of an electrolyte, as such, as on the first precipitated barium sulphate, for if this was so, barium chloride should have a more rapid action than potassium sulphate, while in practice the effect produced is hardly observed in the former case, and only very slowly when sodium

chloride is present. It is practically confined to the original potassium sulphate used, under the conditions recorded. This is an interesting fact, when visual stratification is in question. It is possible that some additional chemical change may even be involved, and be responsible for the change in crystalline state. It may be ultimately found, that an acid barium sulphate $BaH_2(SO_4) \cdot 2H_2O$ may take some part in this reaction, or else the double barium potassium sulphate $BaK_2(SO_4)_2$ is at some stage formed. Under ordinary conditions the latter is prepared by actual fusion. The possibility of the formation of a double salt of potassium or sodium is eliminated where sulphuric acid itself is present in the outer tube and barium chloride in the inner one. A similar effect is produced in this case, but the action is a slower one. The matter is being followed up in detail.

When gelatin is replaced by sodium chloride, a clear space actually replaces the first formed precipitate (10 mm.), but this does not subsequently extend beyond a certain point into a tube of 0.6 mm. diameter, and the deposit formed is obviously in a different physical condition to that obtained in gels.

Cause of stratification.—The ease with which examination is possible in capillary tubes, and the low viscosity of the solutions which can be employed by this method, renders it possible to show that unequal or stratified precipitation is not apparently dependent upon local conditions, i.e., surface tension induced by the walls of the capillary tubes. After diffusion has proceeded so far that a series of stratified sections of lead chloride crystals have been deposited in a hermetically sealed capillary tube, the system was heated to 80°C., when the lead chloride re-dissolved. On slow cooling, re-crystallisation took place, but stratification was absent. The lead chloride precipitated in what might be termed a continuous manner. Thus a general state of super-saturation does not in itself induce stratification in the absence of a direction of flow of at least one of the reacting solutions.

Hatschek states (*ibid*) that the concentration and nature of the gel "is undoubtedly the factor which determines the form and size of the crystals." This may undoubtedly be true, but crystals of varying size can also be obtained in the absence of any secondary gel when working in capillary tubes, and in that case, as possibly in the case of gels, the relative rate of diffusion and concentration of the incoming solution seems to be the determining factor.



FIG. 8.

Rate of diffusion.—The rate of diffusion has therefore a distinct bearing on the physical condition of the precipitated salt. It is naturally slow under the conditions set out. This may be shown, and actually determined if required, by using a solution of say methyl orange, in the capillary tube, and hydrogen chloride in the outer one. The influence of the size of the bore of the capillary tube, and consequently of the surface action of the walls of the

tube itself in terms of diffusion, may also be studied. Where a more or less dense or colloidal precipitate is formed, this may materially retard the process of diffusion. This was noticed in the case of barium sulphate.

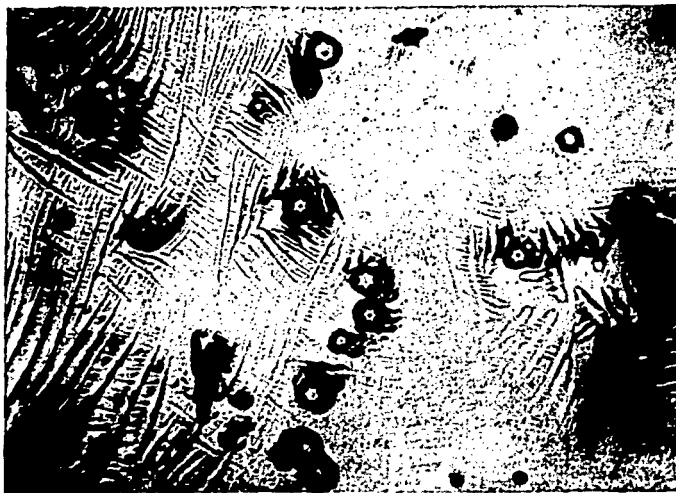


FIG. 9.

General conclusions.—The above results support the suggestion that the actual physical state of the precipitate is primarily due to modifications in the rate of diffusion of the incoming solution, such as is known to take place in gels of varying concentration, and which also occurs in aqueous solutions in capillary tubes under the conditions now indicated. That although certain variations may be due to some inherent property in the structure of the gel itself, the presence of an added gel is not essential to the occurrence of certain phenomena which have been observed. Such a change of condition under which the precipitate is formed may also modify results, in aqueous solutions as seen in the case of lead ferrocyanide where the precipitate is first granular and then further up the tube, entirely crystalline (Fig. 4). Such a change may be due to the increasing dilution of the solution, reduced rate of diffusion, or both. It is possible that this has some bearing on the action of dyeing, the ripening of photographic emulsions, setting of cements, and other similar reactions, where subsequent changes in physical state may come into play.

Ultimately the presence, or absence, of spherulites in a mineral deposit may determine whether a gel was present or not, when certain mineral deposits were produced, but it is now shown that a substance when precipitated may in itself cause stratification. Further attempts to produce these spherulites in the absence of secondary and inactive colloids are being made, especially in saturated solutions of non-reacting electrolytes, which will not interfere with the reaction causing precipitation.

In one case mentioned a deposit of lead sulphate in a capillary tube, has shown after a period of 5 weeks distinct indications of such a formation, which has entirely replaced the original finely divided precipitate over an area of about 5–6 mm. Whether this will extend is at present unknown.

The effect of the diffusion of salts into, or through, a permeable medium (such as sand) may in view of the above experiments be actually anticipated. It may now be assumed that stratification will occur under such conditions. Such experiments are possible where the interstices of the sand in the same correspond to the bore of the capillary tube now used. Experiments are in progress in this direction, with such tubes as have previously been used by Dreaper and Davis (this J., 1912, 31, 100) in other directions, and they should give further direct evidence that such an action is possible. The possibility of such an action has been already suggested by Hatschek

and Simon. Such conditions overcome difficulties which present themselves on gel theory lines in estimating the subsequent effect of contraction of the gel area on dehydration.

Stratification does not always occur at increasing intervals, in capillary tubes. In many cases it occurs at practically equal intervals. In one case (Table B) the intervals may apparently first increase and then decrease. In the presence of a reserve of solution, sufficient to keep the solutions fairly constant in composition, stratification will probably occur at equal intervals, but the influence of the products of the reaction may produce variations.

In the discussion which followed Hatschek's paper (*ibid*) G. T. Holloway suggested in connection with certain natural deposits that the "gradual meeting of two solutions through a gel would explain away many difficulties with which no other theory seems able to cope." By precipitation in capillary tubes, these phenomena may be studied, and the influence of a secondary gel, on the formation of certain insoluble salts *in situ* in colloidal media may be determined. Also whether it is necessary to assume the presence of a gel in explaining the formation of stratification in natural deposits.

Possibly the conditions in nature are more closely represented by drawing up the first solution into the tube to 40 per cent. of its length, and then following this up with the second one for a similar distance. The "band" is then represented by the centre area of precipitation, rather than by a more general stratification as obtained by the other methods. The centre area is also stratified in many cases. If the more general explanation is the correct one, some reason must necessarily be put forward to explain why the "bands" are so far apart in nature. Extreme dilution may be the chief factor.

The presence of stratified bands of abnormal crystalline state which occur in nature, may be of a similar order to those observed in the capillary tubes under the conditions recorded. Thus diffusion is sufficient to account for the phenomena of banded deposits and a very pronounced crystalline state, without necessarily assuming the presence of non-reacting gels.

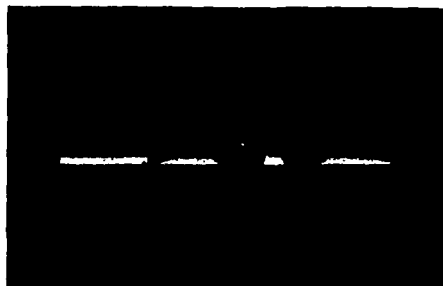


FIG. 10.

The presence of sand or a similarly permeable inorganic medium will naturally allow the cross sectional area of reaction in aqueous solutions being extended indefinitely without materially modifying any tendency to stratification. Thus the diffusion of soluble salts from opposite directions which can by interaction bring about the formation of insoluble salts through or into a porous mineral deposit (or even in the less likely case where the natural deposit contains the second reagent, in a state in which it may be gradually soluble in the first one) with, or without, the actual formation of the precipitate in a gel condition, may offer a simple explanation of the presence of banded deposits. It is, however, evident

that the presence of a colloid in the solution, influences the normal distances between the bands, and the form of the deposits as shown by Hatschek. The experiments in capillary tubes indicate that the presence of non-reacting or secondary gels may in some cases act as an inhibiting agent against stratification, which will not occur within a definite length of the tube in their presence. The influence of colloids in a sol condition are also being investigated.

When working in capillary tubes, the precipitates or crystals may, like those of lead chloride, take a characteristic form, which is obviously influenced by the direction of the flow of the solution entering the tube. This fact may also possibly be applied to the study of the direction of formation of natural deposits. The intervening distances between such crystals as those of lead chloride may certainly increase as in the case of stratified deposits in gels. I am informed by Mr. Hatschek that stratification has not yet been observed with lead chloride in gels.

Stratification has been the subject of much discussion since Liesegang's original observations. The results now obtained agree with the suggestion that this phenomena may be primarily regarded as a diffusion phenomena, and in some way (as suggested by Wo. Ostwald) be influenced by local-supersaturation. A super-saturated column of lead chloride may be first formed, of increasing concentration, which leads to de-solution of the insoluble salt at a certain point in the column of the enclosed liquid. The first crystal as formed supplies a nucleus for further local de-solution. The operation then recommences and by diffusion over a further area in the direction of the tube, causes a flow of the outer solution beyond the first deposit, which would reach a point where further precipitation is inevitable through contact with the inner solution. Even if super-saturation in the ordinary sense of the word does not occur, the lead chloride as formed is obviously soluble, in the first instance, for only in this way can the intermittent nature of the precipitation be accounted for, and the subsequent increase of the single crystals present at certain definite intervals be explained. A condition equivalent to one approaching super-saturation must be assumed, or the salt could hardly be thrown out in the manner indicated. This condition may, or may not apply in the case of very insoluble compounds, *i.e.*, barium sulphate.

The area of precipitation is continually increasing over the length of the tube and therefore the solutions diffusing under such conditions are less concentrated at any one point as the reaction proceeds. This accounts for the length of the column of the intervening clear spaces increasing before a critical desolution point is reached. In a similar manner the actual area of the opaque precipitate of barium sulphate may increase in length as it proceeds up the tube.

The suggestion put forward by Sir J. J. Thomson and others, that the intervening clear spaces are caused by the presence of soluble products of the primary reaction, which inhibit the formation of the precipitate over a certain area has been dealt with in some experiments by E. Hatschek. In one case now mentioned, the only soluble product formed by the reaction is acetic acid, in which the lead chloride as precipitated is not notably soluble, and in which it is easily formed.

Partial stratification in the absence of gels may be traced in tubes of quite large diameter (3—4 mm. bore) when these are set horizontally. Care has to be exercised as the limit has been seemingly reached at which such action is possible, in solutions of low viscosity.

In the case of very heavy precipitates, such as that of silver ferrocyanide, the precipitate sinks to the lower surface in a capillary tube of even 0.7 mm. diameter. The upper surface of the precipitated salt, however takes the form of a series of peaks running in the direction of the length of the capillary tube, which gives much the same appearance as stratification.

These experiments are being extended. Want of time has prevented them being presented in a more complete form. The results already obtained may, however, have

some general interest. The method employed readily adapts itself to the examination of reactions which are in actual progress.

DISCUSSION.

After some remarks by the Chairman, Mr. HATSCHEK said that the experiments chiefly demonstrated that it was possible to get similar results in a variety of ways. Reactions in a capillary tube and reactions in gels resembled each other, although the capillary in the former case was macroscopic, whereas in gels there was a system of microscopic or ultra-microscopic capillaries. Glass capillaries lent themselves readily to examination, but they had rigid walls, while those of the gel structure were readily destroyed. He thought this factor might explain many of the differences in the results obtained by Mr. Dreaper and by himself, and, particularly, that it accounted for the formation of spherulites, which were so readily obtained in gels, but had not been found in the capillaries. On some minor points he was not inclined to agree with Mr. Dreaper; for one thing, he doubted very much whether the barium sulphate could at any stage be described as amorphous. The magnification used by Mr. Dreaper was quite inadequate to settle this point, as magnifications of about 600 to 700 diams. were necessary to resolve lead and barium precipitates. He imagined the barium sulphate was crystalline even in the earliest stages, and the effect of the added electrolyte was largely the usual coagulation effect. The size of lead chloride crystals was purely a question of degree of dilution, *etc.*, but he had succeeded in obtaining needles of lead chloride 15 mm. long in silicic acid gel. He was much interested in the lead ferrocyanide crystals shown by Mr. Dreaper, as he had obtained an entirely different form in agar, as shown in his paper read before this Section in 1911. These variations were a feature of the work, as one could obtain different forms even by changing the gel, *i.e.*, different in agar and in gelatin. He asked whether Mr. Dreaper had used distilled or tap water for some of his reacting solutions; he had obtained magnificent stratifications of lead iodide if tap water was used, whereas they were not nearly so perfect with distilled water. Possibly there was intermediate formation of lead carbonate, which gave rise to stratifications. To suggest supersaturation or a negative catalyst as a probable cause of stratifications, for neither of which direct experimental proof was possible, seemed to him simply a verbal solution, or evasion, of the difficulty. Of course the simpler the arrangements, and the more disturbing factors were eliminated, the more hope there was of getting at the truth, and since Mr. Dreaper could get stratifications without using a gel, that was a step in advance. Stratifications by diffusion in much wider tubes had been obtained by an Italian observer (published in the *Kolloid-Zeitschr.*). These were transient and due to the different rates of diffusion of the two ions of a highly dissociated salt, a solution of which was placed in the bottom of a long tube and covered with water. As regarded slow reactions, there were also the experiments by one of the Becquerels—published in 1906 in the *Zeitschrift für physikalische Chemie*. He allowed two solutions to react through a crack in glass, and, *e.g.*, with sodium sulphide and copper sulphate, obtained fine crystals of copper sulphide. He himself had never had any success with metallic sulphides in gels, although he had tried a good many. He would suggest that Mr. Dreaper should experiment in that direction. The sulphides were a very attractive problem, as they were strikingly crystalline in nature, whereas it had not been possible so far to obtain crystals by laboratory methods.

Prof. E. J. MILLS referred to some experiments he had performed many years ago between glass plates, without gels. Of two glass plates, the upper had a small hole through which a reagent (such as sulphuric acid) could be introduced; the pair, which lay very close together, contained a precipitant (such as a solution of barium chloride). Other pairs, *e.g.*, ferric chloride and potassium ferrocyanide, were tried. Stratifications were then obtained in ribbon-section, the circular sections being

traversed by radial lines. It was one of the most beautiful sights in chemistry to see ribbon after ribbon forming in this way—the process depending partly on diffusion, partly on flow. The process could be carried out on almost any scale, and showed detail better than when performed in a tube. He would venture to suggest trying the gel experiments in this manner. But the plates must be truly plane.

The Ayrton, in reply, said it was interesting to know that Mr. Hatschek considered that the rigid structure of gels might be the cause of the formation of true spherulites, and that this might account for their non-formation in aqueous solutions. He quite agreed with him that at a higher magnification the barium sulphate might appear crystalline. That led to the larger question whether colloids were not generally crystalline in their ultimate structure. In the case of lead chloride and in all other cases he had used distilled water. Without actually knowing anything of Dr. Mills' work he had previously worked between glass plates under a microscope, but had found it almost impossible to obtain results of a definite order. When working with capillary tubes, one could be certain of measurements, etc.

Manchester Section.

Meeting held at the Manchester University on Friday,
February 7th, 1913.

DR. G. J. FOWLER IN THE CHAIR.

THE EFFECT OF INCOMBUSTIBLE DUSTS ON THE EXPLOSION OF GASES.

BY PROF. H. B. DIXON, M.A., PH.D., F.R.S., AND COLIN
CAMPBELL, M.SC.

The effect of incombustible dusts on the explosion of gases is of special interest at the present time by reason of the method now being extensively tried in mines for rendering coal-dust non-explosive by mixing it with incombustible dusts.

On the one hand, the opinion is held that such inert dusts as powdered shale, Fuller's earth and flue-dust, act the same part, when mixed with coal-dust, as inert gases do when mixed with explosive gas mixtures: on the one hand it has been contended that the introduction of a finely divided solid into a coalmine might be dangerous owing to its action in promoting the combustion of fire-damp upon its surface, and in particular the experiments of the late Sir F. Abel have been quoted as proving that danger from such catalytic action is by no means remote.

The Committee appointed by the Home Office to carry out experiments on the prevention of explosions in mines have examined this problem at their experimental station at Eskmeals both by trials in a gallery similar to that used by Abel, and also by exploding gases in tubes and bombs with and without the addition of dusts. Meanwhile we have made many laboratory experiments here to test the question whether the presence of a "catalyst," such as platinum, can induce an explosion in an otherwise non-explosive mixture of gases, and whether finely divided magnesia or shale-dust acts catalytically in propagating flame, or merely behaves as an inert substance.

According to the kinetic theory, the molecules of a gas are in a constant state of motion, coming into collision one with another and with the walls of the containing vessel. The temperature of the gas depends upon the "mean velocity" of the moving molecules. But these motions are not uniform. At any moment some molecules are moving faster and others slower than the average. Clerk Maxwell has calculated that about 2 per cent. of the molecules of any gas are moving with a velocity more than twice that of the mean velocity. In an inflammable mixture of gases such as electrolytic gas there is a similar distribution

of velocities, so that there are some hydrogen molecules moving more quickly than the other hydrogen molecules, and some molecules of oxygen moving more quickly than the other oxygen molecules. If chemical combination begins as a result of the collisions between two of these more rapidly moving molecules of opposite kind which are comparatively so few in number, this combination would take place here and there at infrequent intervals, and the heat generated would be dissipated among the mass of the surrounding molecules.

When such a mixture is heated up artificially more and more of the molecules will move rapidly enough to produce chemical combination on collision; and finally a state will be reached at which these collisions are sufficiently numerous to overcome the loss of heat by conduction. At this stage the mass of gas as a whole begins to self-heat, i.e., to rise in temperature owing to the chemical action independently of the external source of heat. This is the "Temperature of Ignition." If nothing interferes with the free motion of the molecules, the number of chemically effective collisions increases at an ever-increasing rate until a flame appears and spreads through the mixture. Below the "Ignition temperature" chemical combination is quite slow; above the ignition-temperature combination increases in rapidity until inflammation occurs: in the flame, combination is very rapid. In flame the rapidity of chemical combination may vary greatly: in the most intense form of flame—that of the explosion-wave—the combination is almost instantaneous.

In the explosion-wave the physical pressure-wave generated by the movement of the molecules in the burning layer, is transmitted (by collisions) into the unburnt gases beyond and is continually renovated by the chemical action there set up. The average rapidity of the molecules taking part in the wave is so great that it is probable that a large percentage of the collisions between molecules of an opposite kind result in chemical combination, and the flame travels forward with the forward velocity of the molecules themselves.

In the transmission of flame through a gas mixture the most usual case is for a portion only of the gas to be ignited and for the heat so produced to raise the temperature of the contiguous portion to the ignition point, and so on layer by layer through the mixture.

But in a mixture of gases, such as methane and air, the quantity of inflammable gas present may be insufficient to allow the flame to propagate itself throughout the mixture when a portion of the gas is so raised in temperature by the introduction of a flame or spark. In the portion of gas directly heated by contact with the flame chemical union between the methane and oxygen molecules is set up, and this region of combustion is visible as a halo or "cap" round the source of heat. When a safety-lamp with lowered flame is introduced into an atmosphere in which methane or coal-gas is gradually introduced, a delicate cap shows in a cone above the flame which increases in height and intensity until it reaches the top of the lamp. As the mixture in the lamp becomes explosive the flame expands at the top and creeps down inside the lamp until the whole of the gauze is covered with flame, and the original flame over the wick goes out for lack of air. The phenomena described are well seen in the apparatus constructed by Messrs. Oldham for lamp-testing. In the same apparatus, filled with a mixture below the explosive limit, the naked flame of a taper shows a blue cap, which may be easily detached by a rapid movement of the taper. Detached caps or "flares" of flame may thus be formed which move upwards and die out after a time. Similarly, when a rapid current of air containing inflammable gas is drawn past a flame in a gallery portions of the cap on the lee-ward side of the flame may be detached and float away as "flares." In these caps and flares visible combustion is set up, but it dies down when separated from the original source of heat because the rate of chemical union in the dilute mixture is not rapid enough *per se* to maintain the temperature above the ignition-point.

Since the chemical combination depends upon the collisions between molecules of methane and molecules of oxygen, it will be evident that, just as there is a lower-limit of methane necessary for the propagation of flame, so there must be a lower limit of oxygen also. In mixtures of