114. *Studies in the Growth of Metal Trees in Gels. Part I. The Morphology of the Lead Tree.*

By Alexander King and Norman Stuart.

The growth of lead trees by displacement of lead from solution by less noble metals has been studied in the presence of silica gel. Detailed experiments, tin being used as the reducing metal, indicate that the morphology of the lead tree produced is fundamentally dependent on the concentration of lead in the gel, a wide variety of growth types being obtained. One of these is a new, spiriform type of growth which is characteristic of lead concentrations of 0·02N.

Lead trees produced by metals far removed from lead in the electrochemical series are similar in form among themselves, but different from that of the lead trees grown from tin; no spiriform growths are produced in this case.

Colloidal materials in the gel have an inhibiting or modifying influence on the structure of the lead trees, which is unpredictable.

More than 100 years ago, Fischer (*Pogg. Ann.*, 1827, **10**, 603) observed that if a zinc rod was suspended in a solution containing 1 part of lead salt, 1½ parts of acetic acid, and 100 parts of water, a vegetable-like growth of metallic lead gradually sprouted from the zinc. This structure he termed the *arbor saturni*, and the corresponding tree of metallic tin was called the *arbor jovi*. Similar results were obtained by substituting iron, cadmium, or manganese for zinc in the above experiment. That magnesium would function in place of zinc was noticed by Roussin (*Chem. News*, 1866, **14**, 27) and Bryant (*ibid.*, 1899, **79**, 75), who reported the evolution of hydrogen during reduction by magnesium. Cossa (*Bull. Soc. chim.*, 1870, **14**, 199) studied the reduction of lead salts by aluminium.

Although it had previously been reported that tin would not displace lead from solutions of its salts, Sackur (*Z. Elektrochem.*, 1904, **10**, 523) made the important observation that lead is completely precipitated by tin from its solution in acetic acid, whereas tin is precipitated by lead from solutions of its salts in nitric acid. In hydrochloric and sulphuric acids an equilibrium is set up between tin, lead, and the salts of the two metals. The precipitation of lead by tin from lead perchlorate solution acidified by perchloric acid was studied by Noyes and Taube (*J. Amer. Chem. Soc.*, 1917, **39**, 1532) when measuring the electrode potential of lead.

Wöhler (*Annalen*, 1853, **85**, 253) discovered that if water is poured on a concentrated solution of lead nitrate or acetate so as to form a separate layer, and a piece of lead added so that it is dipping into both liquids, small crystals of lead were formed on that part of the metal immersed in the more concentrated solution. Senderens (*Bull. Soc. chim.*, 1894, **11**, 424) obtained similar results by the interaction of lead with neutral lead nitrate solution in the absence of air.

Lead may also be produced in an arboreal form by electrolysis of its salts. Lehmann (*Z. Krist.*, 1890, **17**, 277) considered that the electrolytic formation of metal crystals was very similar to normal crystallisation from solution. He noticed that although a low current density produced a uniform deposit of metal, a higher density resulted in the formation of a skeleton-like structure of metal, further increase in current strength altering only the mass of the crystals but not their form. Lead was rather exceptional in this connexion, for, with a weak current, leafy crystals apparently belonging to the monoclinic system and very similar in appearance to those of the chemically produced lead tree were formed, whereas with stronger currents crystals belonging to the cubic system, and under the best conditions, well-formed octahedra, were deposited. He assumed that these were due to the separation of a different molecular species of lead in solution, followed by subsequent crystallisation. Cohen and Inouye (*Chem. Weekblad*, 1910, **7**, 454) showed, by means of *E.M.F.* measurements that the supposed cubic and monoclinic forms were identical and thus not allotropic. Further work on the form of electrodeposited lead was carried out by Elbs and Rixon (*Z. Elektrochem.*, 1903, **9**, 267), who stated that lead separates sometimes as large shining plates and at other times as a sponge, the latter condition being due to the presence of plumbic salts in solution; and by Kohlschütter and Übersax (*ibid.*, 1924, **30**, 72), who measured the velocity of growth of deposited lead with varying current density. At low current densities, massive, leafy crystals were formed, at higher densities " crystal chains," the velocity of growth of which increased as the lead-ion concentration decreased.

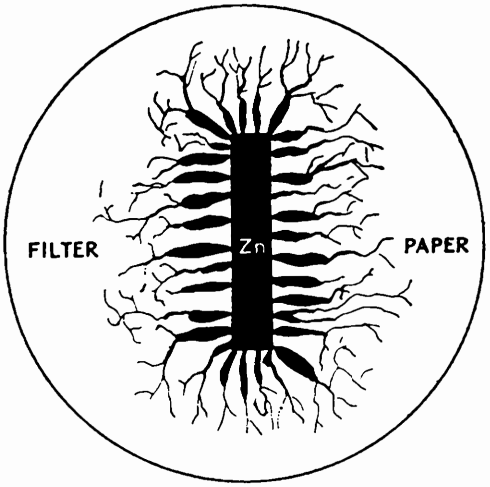
The fact that trees of similar form can be grown by chemical means or by electrolytic deposition makes it clear that the mechanism of formation of the lead tree is essentially electrochemical, and this is borne out by a study of lead equilibrium between metallic lead and lead nitrate solution which results in the growth of a tree. Von Hevesy (*Physikal. Z.*, 1915, **16**, 52) measured this equilibrium by the use of thorium-*B* as an indicator, and concluded that the rate of exchange of lead between the solid metal and the solution was too great to be due to thermodynamic equilibrium but was caused rather by the action of local electric currents, lead passing into solution at some points and being precipitated at others. The electrochemical nature of the process is also stressed by Kohlschütter (Festschr. Tschirch, Bern, 1926, p. 425), who formulates the reduction of lead salts by zinc thus: $Pb^{++} + Zn \rightleftharpoons Pb + Zn^{++}$. He ascribes the outward form of the tree to local concentration differences, as well as to the position of nuclei and to the crystal system to which the tree-forming metal belongs. The growth is also influenced by concentration cells set up owing to the formation of adsorbed, semipermeable films of basic salts of lead.

The characteristic feature of the ordinary lead tree, which becomes apparent to the eye when growth has been prolonged for a considerable time, is the extraordinary flatness of the leaflets, growth apparently taking place in two dimensions only and chiefly in one. A clue to the reason for this is given by Evans (*Chem. and Ind.*, 1925, **44**, 791, 812), who argues that the latent heat of crystallisation is dissipated by convection currents, etc., more easily at edges and at corners than in the centre of flat faces. This naturally causes growth to be quicker and more extensive at edges, and leads to the growth of platelets. Evans then gives directions for the formation of a two-dimensional lead tree. These are so important as to demand full description here. A filter-paper saturated with 10% lead acetate solution is placed on a sheet of glass, and a strip of zinc, the lower edge of which has been freshly cut, placed on top of the wet paper. In a few hours a two-dimensional tree grows out, having the form shown diagrammatically in Fig. 1. The obvious fact of metal dissolution at some points and deposition at others at once establishes the process as electrochemical, the current passing along the slender fronds of deposited metal and returning through the wet filter-paper—a fairly high resistance circuit. If the resistance of the circuit is reduced by the addition of sodium acetate to the lead acetate solution with which the filter-paper is impregnated, the velocity of growth becomes much faster owing to greater conductivity.

The question as to why the lead is deposited so far from the zinc is answered by dipping the filter-paper containing the tree into dilute ammonium sulphide solution, whereupon a deep brown coloration indicates the presence and position of lead ions. This coloration is seen to occupy the whole paper except near the tree, a very faint colour being noticed between the fronds in the outer zone but none in the inner zone. Hence, after the process has been proceeding for some time, no deposition of lead can take place on the zinc, as there are no lead ions in the neighbourhood. The outgrowths, however, can still continue to extend, as they are in constant contact with the outer, unexhausted reservoir of lead ions.

The essential difference in appearance between the two-dimensional lead tree grown on a filter-paper and that normally prepared in solution is the development of structure and branching of the fine fronds in the former case. This is presumably due to the fact that an ordinary tree in solution is in close proximity to the zinc, this inner region of growth never becoming completely free from lead ions which are continually being replenished by convection currents, etc. It must be stated, however, that a definite two-dimensional platelet structure accompanied by branching often does become apparent in the tree as ordinarily grown, although to a minor degree.

Fig. 1.



From what has just been said it follows that the best means of studying the growth and morphology of metal trees is to produce them in a gel, where convection, mechanical disturbances, etc., are absent and electrolyte movement can only take place by diffusion or by electrolytic migration. It is to be expected that, under gel conditions, growth would extend for much longer distances from the reducing metal and produce a morphology characteristic of the conditions employed.

Simon (*Kolloid-Z.*, 1913, **12**, 171) carried out the reduction of lead salts by zinc in the presence of silica gel: to a 15% sodium silicate solution he added a slight excess of 50% acetic acid and about 10% of concentrated lead acetate solution, the mixture then being allowed to gel in test tubes. A piece of zinc was then inserted in the gel at the top of each tube, and in a few days trees had grown and extended throughout the length of the tube. The two photographic reproductions in Simon's paper show that the trees consisted of branched metal strips.

Just as it now appears that the Liesegang phenomenon in gels represents the normal course of precipitation when convection and mechanical disturbances are eliminated, the function of the gel being a secondary consideration, so will metal trees grown in gels probably represent perfect growth which is only suggested but never attained in ordinary solution.

In the present work many trees have been grown in silica gel, and the influence of lead-ion concentration, acidity, position of the reducing metal in the electrochemical series, gel rigidity, etc., on the morphology of growth determined.

EXPERIMENTAL

In all experiments, except those on the effect of gel rigidity, a standard gel was used, which was prepared by mixing a given volume of 2N-acetic acid with twice its volume of sodium silicate solution of *d* 1·06 and an equal volume of water in which the required quantity of lead salt was dissolved. The time of gelation varied widely according to the amount of electrolyte present, but was generally of the order of a few hours. If this order of mixing of the ingredients of the gel system was adhered to, precipitation of the lead was avoided, although those gels which contained a high concentration of lead salts were somewhat turbid.

In all the experiments described in this paper, the gel was contained in boiling tubes measuring 3·5 × 15 cm. A number of preliminary results have shown that the shape of the vessel has, as might be expected, a considerable influence on the form of the lead tree. This effect is being fully investigated.

Reduction was started by inserting a piece of metal into the gel at the top of each tube so that it was almost submerged. In a number of cases, especially those in which gelation did not take place till after a considerable time, the metal was suspended in the fluid mixture by means of a thread. Preliminary investigation seemed to indicate that different forms of growth were obtained according to whether the metal was suspended in the liquid system before gelation or inserted into the corresponding gel. A large number of mixtures of silicate, lead acetate, and acetic acid were therefore made in duplicate, the reducing metal being placed in the system (*a*) before and (*b*) after gelation. Although the conditions were chosen so as to produce a wide range of growth types, the differences between the (*a*) and (*b*) series were in no instance fundamental.

Most of the results to be described were obtained by the reduction of lead acetate in silica gel by metallic tin. The tin was usually inserted in the granulated form, although at times it was found more convenient to use thin sticks of cast tin, prepared by pouring the molten metal into a hard-glass tube and afterwards etching the surface. Comparative experiments showed that there was no difference in the type of growth produced in a given gel by the two types of metal.

Results.

(a) *The Influence of Lead Concentration.*—A series of gels were prepared, containing different amounts of lead acetate, with respect to which they varied from 0·1 to 0·001N. Reduction was effected in each case by means of tin, and the following results obtained.

Series I. (1) 0·1N-Gel. Very long, two-dimensional, sword-like growths of bright metal were obtained, which were characteristically straight and had little branching tendency. The width of the sword was of the order of 0·5 cm. Peculiar double growths appeared at the top of the tube [see Plate I (*a*)].

(2) 0·08N-Gel. Growth was very similar to the above. The sword-like growths, which were slightly and irregularly serrated, extended the whole length of the tube and there were more side branches [Plate I (*b*)].

(3) 0·06N-Gel. The tree, although still flat, was not so obviously uniplanar as those formed at higher lead concentrations. It was strikingly branched, all the branches being inclined at the same angle to the main " stem." Furthermore, secondary branches grew from the primary branches and were parallel to the main " stem," thus giving a peculiar lattice effect.

(4) 0·04N-Gel. The growths, although still fairly flat, were much less broad and less regularly branched. The existence of a main " stem " was less obvious, there being numerous " stems " of about the same magnitude growing from the tin inserted at the top of the gel. The plane of the growths had a tendency to twist slightly but regularly. The growth was more copious than at higher lead concentrations [see Plate I (*c*)].

(5) 0·025N-Gel. The whole structure of the metal was much finer, the growth being very copious, and the tendency of the flat ribbons of metal to twist more marked.

(6) 0·02N-Gel. The tree was still finer than with 0·025N-lead and was strikingly spiriform, somewhat resembling a very deeply cut screw having a minute barrel diameter and a very serrated edge to the pitch. The small branches, which were very frequent and regular, were all inclined at the same angle to the main " stems " and thus helped to emphasise the spiriform nature of the growth [Plate I (*d*)].

(7) 0·015N-Gel. The growth was again finer; the filaments were less straight and seemed to twist irregularly. Spiriform structure was still observed but was much less obvious for two reasons, *viz.*, because the pitch was much greater and because the side branches grew off the main filaments at different angles. The total amount of growth was noticeably less in this specimen than in those at higher lead concentrations, and its rate slower.

(8) 0·0125N-Gel. The growth was finer than that of (7) but very similar in structure [see Plate I (*e*)].

(9) 0·01N-Gel. The filaments were now very fine and branched. They appeared on close

examination to be spiriform, but the thinness of the filaments made this very difficult to see. The total amount of growth was small.

(10) 0·0075N-Gel. A very few, hair-like filaments grew slowly from the tin but only penetrated a few cm. into the gel [see Plate I (*f*)].

(11) 0·001N-Gel. No growth.

The above series of experiments was several times repeated, the reproducibility of the forms described being established. It thus appears that the form of the lead tree is fundamentally dependent on the concentration of lead in the solution. Abundant additional evidence of this fact is presented below, it being found that, even when the other conditions are varied considerably, the form of growth produced by reduction is invariably that characteristic of the lead concentration.

Three main types of lead tree appear to be formed : at high lead concentrations, flat, straight, sword-like growths; at concentrations in the neighbourhood of 0·02N-lead acetate, strikingly spiriform growths; and at still lower concentrations, fine, irregular, branched filaments. Of these three types, the spiral growth is the most noteworthy, and it had not been described until one of us published a preliminary note on this structure (Stuart, *Nature*, 1937, **140**, 589). Arising electrochemically, these spiriform crystals are entirely different from those helical and spiral precipitates of lead iodide, lead chromate, and calcium phosphate described by Hatschek and his collaborators (*Kolloid-Z.*, 1920, **27**, 225; *Biochem. J.*, 1920, **14**, 418), nor do they resemble the spiral crystals of Copisarow (*Kolloid-Z.*, 1929, **47**, 60).

In the above series of experiments it was found that growth was most easily induced in gels with low lead concentration; indeed, in the higher lead content gels, it was frequently necessary to wash the tin in dilute hydrochloric acid before inserting it in the gel, in order to induce growth. The total amount of growth, as well as its rate, appeared to be maximum at medium lead concentrations (0·06—0·04N) and to decrease gradually to zero in either direction.

(b) *The Influence of Acid Concentration in the Gel.*—A series of gels were now prepared in which only the quantity of acetic acid was varied. The results are collected in Table I, the normality of the acid representing the total quantity added and not the amount of free acid remaining after neutralisation of the silicate. The normality of the gel with respect to lead acetate was 0·02 in each case, *i.e.*, corresponding to the system producing the spiral growth. Reduction was affected by means of tin.

TABLE I.

Series II.

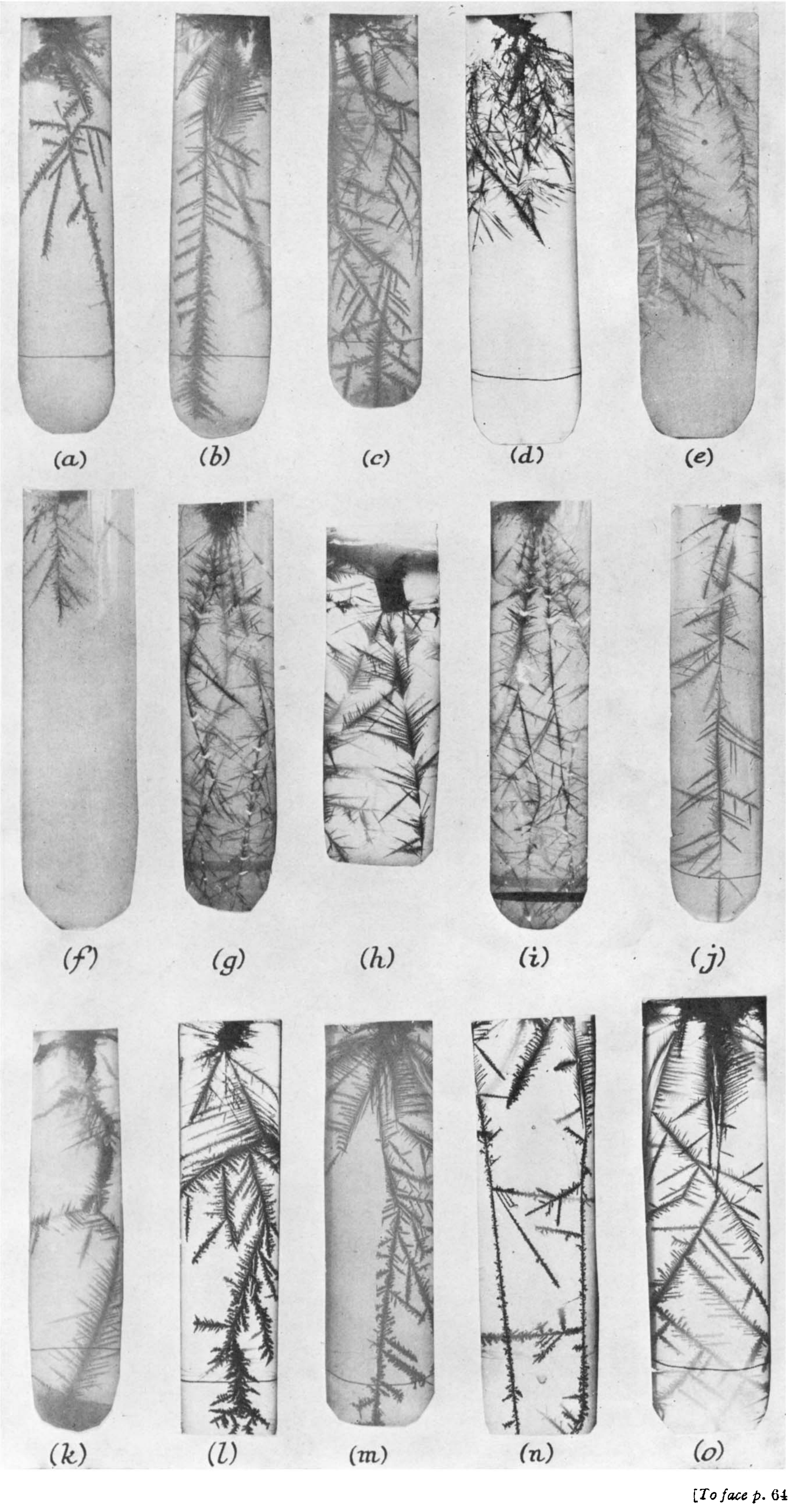
No.	Acid concn., N.	Time of gelation.	Description of tree.
1	0·25	20 mins.	No growth.
2	0·3125	5 mins.	No growth but a greyish membrane on the tin surface.
3	0·375	15 mins.	Short growth of rather flat, branched type.
4	0·4375	1 hr.	Rather irregular fine growths; much branched; spirals of large pitch.
5	0·5 *	3 hrs.	Distinct spirals of rather large pitch which opens out lower in the tube.
6	0·55	3 hrs.	Larger spirals, but of smaller pitch than those of (5). The pitch opens out lower in the tube and finally gives place to a fine, irregular, branched growth.
7	0·6	6 hrs.	Spirals still larger and more developed than in (6) : see Plate I (*g*).
8	0·7	12 hrs.	Very similar to 7 : see Plate I (*h*).
9	0·8	18 hrs.	Pitch of spirals is much smaller and opens out lower down in the tube; see Plate I (*i*).
10	0·9	24 hrs.	Very similar to 9.
11	1·0	24 hrs.	Spiral of different type, resembling a thin ribbon of lead twisted into a spiriform strip. The edge of the ribbon was unserrated and there were practically no small branches. The few branches which were formed were long and of similar form to the main stem. See Plate I (*j*).

* Identical in conditions and form with Series I, No. 6.

In view of the fact that variation in the amount of acid had only a secondary effect on the spiriform growths characteristic of 0·02N-lead acetate, similar experiments were carried out with 0·08N- and 0·0125N-lead gels, the results being recorded in Table II, (*a*) and (*b*), respectively.

Several general tendencies emerge from these results; first, and most important, acid concentration has, except at the extreme ends of the scale, little effect on the form of growth, which is essentially conditioned by the lead concentration. Thus the trees of Series II are essentially spiriform, the acid concentration producing only secondary variations. Series III and IV are typical of 0·08N- and 0·0125N-lead concentrations respectively.

PLATE I.



(a) (b) (c) (d) (e)

(f) (g) (h) (i) (j)

(k) (l) (m) (n) (o)

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PLATE II.

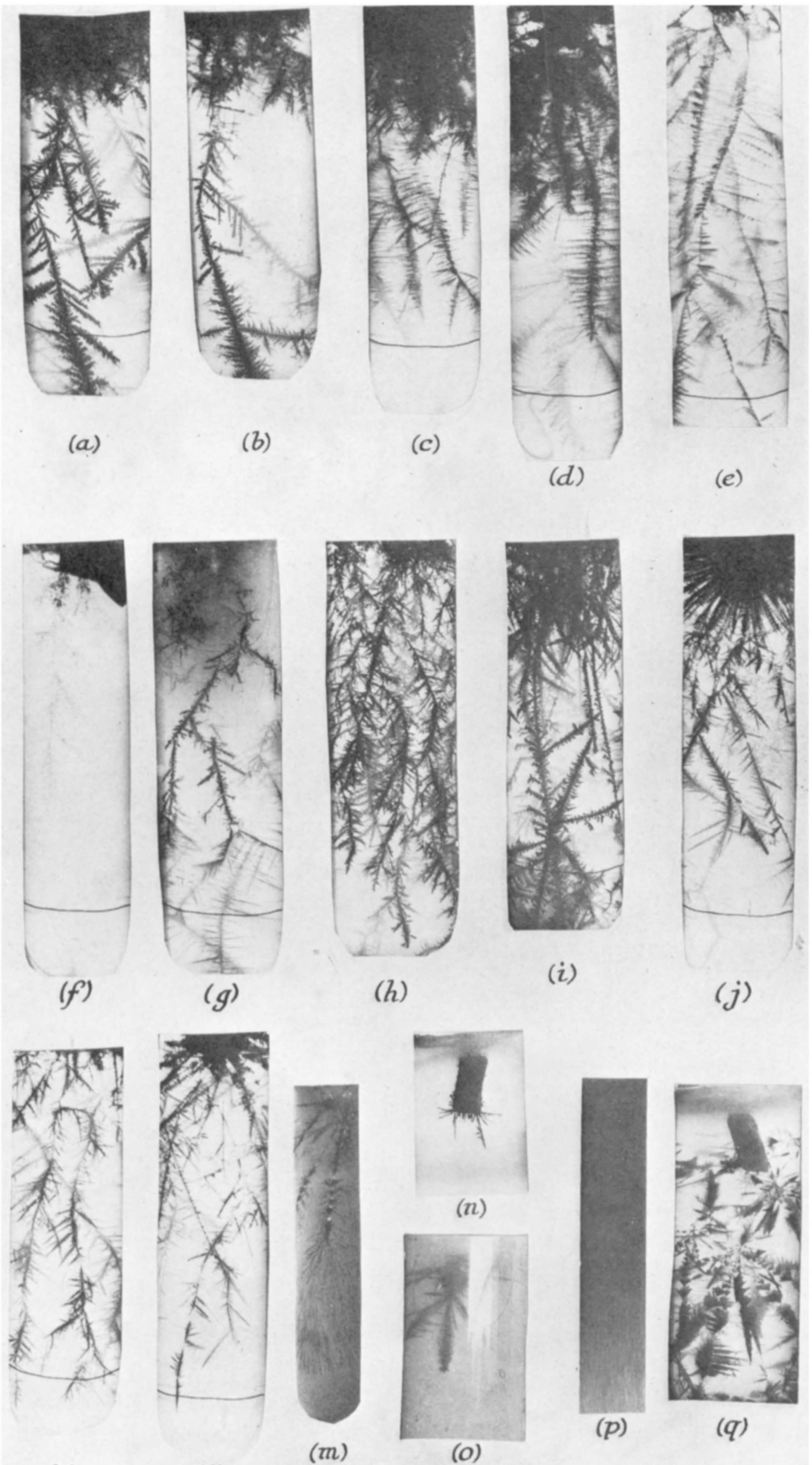


TABLE II.

(*a*) *Series III. Lead acetate* = 0·08N. *Acetic acid concentration varied.*

No.	Acid concn., N.	Description of tree.
1	0·375	A grey skin formed on the tin within a few days and, in the course of months, very broad two-dimensional platelets of length *ca.* 1 cm. grew.
2 *	0·5	Long, flat, sword-like growths.
3	0·625	Very flat, jagged, sword-like growths with a few side branches all emerging at the same angle to the main stem.
4	0·75	Long, flat growths similar to the above but even wider.
5	1·0	Much less growth than at lower concentrations but still strikingly flat.
6	1·5	Grey membrane of lead on the tin.

* Identical in conditions and form with Series I, No. 2.

(*b*) *Series IV. Lead acetate* = 0·0125N. *Acid concentration varied.*

No.	Acid concn., N.	Description of tree.
1	0·375	Very small, very fine, branched tree.
2	0·5 †	Irregular, twisted, fine growth; much twisting; some spiral tendency.
3	0·625	Similar to (2) but much coarser and with the spiral tendency more evident. Total amount of growth is maximum for the series. The filaments become noticeably coarser at the bottom of the tube.
4	0·75	Very similar to (3) but considerably less growth. Spiriform tendency is still slight.
5	1·0	Very slow and small growth which finally produces a single straight filament with numerous parallel side branches at right angles to it.
6	1·5	No growth or deposit on the tin.

† Identical in conditions and form with Series I, No. 8.

It also appears that there is an upper limit of acid concentration above which growth will not take place (*ca.* 1·5N) and a lower one below which it is negligibly slow. In the middle range of acid concentration, growth reaches its maximum in both rate and amount.

Further general tendencies are observed in the spiriform growths of Series II (that of the optimum concentration of this growth type). The spirals are of small pitch at the top of the tube and consist of spiriform strips whose small, regular, side branches all emerge at the same angle and make the spiriform nature of the structure strikingly obvious. As the growth descends in the tube, the spiral pitch increases gradually and at the same time branching becomes more irregular, the side branches emerging at different angles to the main stem. The spiriform feature thus becomes much less prominent and resembles the type of structure normally produced at slightly lower lead concentrations. The growth at the lowest part of the tube is very irregular and, consisting as it does, of fine branched filaments, resembles the growth at *ca.* 0·0125N-lead.

The silica gel prepared by the neutralisation of sodium silicate by acetic acid contains a high concentration of sodium acetate which should probably form an efficient buffer for acetic acid. As this seemed a possible explanation of the unexpected lack of influence of the action of acid on the morphology of the lead trees, a series of p_H determinations was carried out with gels prepared from various amounts of acid. The results are collected below :

The p_H *values of gels of various acid contents.*

Normality of gel with respect to total vol. of added acid	0	0·125	0·25	0·3	0·35	0·4
p_H	10·0 *	10·0	10·0	10·0	9·5	4·3
Normality of gel with respect to total vol. of added acid	0·5	0·6	0·7	0·8	0·9	1·0
p_H	4·0	4·0	4·0	4·0	4·0	4·0

* Precipitate of lead hydroxide.

They show that, between concentrations of 0·4 and 1·0N, the acid is effectively buffered. This was the concentration range at which growth was found to take place, only the 0·35N-specimens being of abnormal form. The secondary modifications in growth form as well as of rate and magnitude of growth are thus to be ascribed to the acetate-ion concentration.

In view of the failure of the above experiments to produce systems of varying hydrogen-ion concentration, a series of gels was prepared from sodium silicate and nitric acid to which lead nitrate had been added. The acidity was adjusted so that 8 gels of constant lead nitrate concentration but with different p_H values between 3·5 and 8·5 were formed. On the addition of tin, reduction did not take place, nor was the metal in the least corroded. It is thus established that although tin will displace lead from solutions of some of its salts (in gels) it will not do so from other salts. Further work on this point is in progress. (See also Table X.)

(c) *Trees produced at Higher Lead Concentrations.*—In Series I it was found impossible to work at higher than 0·1N-lead acetate concentrations owing to precipitation. The effect of acid concentration having been investigated, a series of gels was prepared in which the acetic acid was increased from 0·5 to 1·25N, and the lead acetate concentration varied. The results, collected in Table III, are observations of the trees after 3 months' growth.

TABLE III.

Series V. Acetic acid concentration 1·25N. *Lead acetate concentration varied.*

No.	Pb, N.	Description of tree.
1	0·25	No growth.
2	0·2	Minute growths on some parts of the metal.
3	0·17	Granular membrane covering the tin.
4	0·135	Very coarse growth; not flat: see Plate I (*k*).
5	0·10	Copious growth of the lattice type (cf. Series I, No. 3). The structure is very fine at the top of the tube, but coarser below.
6	0·085	The most copious growth observed in the course of the present work; very flat, coarse, and extremely irregular tree of the lattice type: see Plate I (*l*).

(d) *The Influence of Gel Rigidity.*—Although it appears from the study of periodic precipitation in gels that the phenomenon is essentially due to the elimination of mechanical and convectional disturbances, yet it is true that the gel may exert a fundamental and often specific effect. For instance, although it is possible to prepare Liesegang rings of silver chromate in gelatin, lead chromate rings cannot be formed, although just the opposite holds good in agar gels. All the present work has been carried out in silica gel which, because of its lack of protective properties, would be expected to have less influence than any other gel on the crystal form and rate of growth. It is hoped soon to extend the work to other gels. The present series of experiments concerns the effect of gel rigidity on the form of the lead trees. As the concentration of acetate has been shown to have a secondary modifying effect (see above), an excess of sodium acetate was added in the case of the more dilute gels so that the acetate concentration should be constant throughout the series. The figures in col. 2 of Table IV represent the fraction or multiple of the silica concentration of the standard gel (see p. 644) in the specimen under investigation. The excess of free acid present after neutralisation of the silicate was adjusted in each case to 6·5 c.c. of 2N-solution per 80 c.c. of gel, this being the same as in the standard gel.

The physical effect of gelation appears to have considerable effect on the electrochemical behaviour of the system, because, in the sol, reduction of lead acetate by the tin cannot take place whereas immediately after gelation (without any chemical change) reduction commences. In all but the most liquid gels (which appear to produce trees of irregular morphology) the lead tree is once again typical of the lead concentration employed, *e.g.*, those of Series VI were of the spiriform type, those of Series VII of the sword type. In the former instance, increasing rigidity of the gel had the effect of compressing the spirals, thus decreasing the pitch and at the same time producing narrower strips of metal. In practically every case it is noticed that the main direction of growth of the lead tree is parallel to the axis of the tube, even when the tube is allowed to rest in a horizontal position during growth. In Series VI, No. 3, growth was made to take place simultaneously from both ends of the gel and was of the same type and magnitude in each case, gravity obviously having little effect.

(e) *Rate of Growth.*—In order to give some idea of the rate of growth of the lead tree, a large test tube (36 × 4·5 cm.) was filled with a silica gel made 0·08N with respect to lead acetate, and growth induced, as usual, by tin. The tree produced was of the sword type characteristic of this lead concentration, and grew at the rate of 1·5 cm. per diem for the first 6 days, after which it grew much less rapidly and was 15·2 cm. long at the end of 3 weeks; the rate of growth was then 0·25 cm. per diem. By the end of 2 months the tree was 24·8 cm. long, and a further 5·1 cm. were added during the third month. It should be noted that growth is much faster at slightly lower lead concentrations but, being less straight, is difficult to measure.

The marked diminution of growth as the tree extends well down into the tube is due, not only to the decrease in the concentration of lead ions, but also to the extended length of the electrochemical circuit between the growing tip of lead and the tin.

(f) *Reduction by Other Metals.*—Many of the features of the morphology of lead trees produced by reduction of lead salts by tin may be due to the fact that these two metals are adjacent in the electrochemical series and have normal electrode potentials which are exceptionally close.

TABLE IV.

(*a*) *Series VI. Lead acetate* 0·2N. *Silicate concentration varied.*

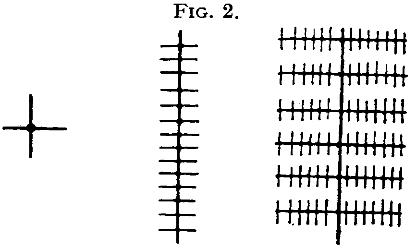
No.	Gel rigidity.	Time of gelation.	Description of tree.
1	0·125	6 days	The tin was suspended in the liquid 1 day after mixing. During the next 5 days no growth or change in appearance of the tin took place. Immediately after gelation to a very liquid gel, growth began, and after 28 days reached 1/3 of the length of the tube. Thereafter no further growth. The tree was rather coarse at the top and very irregular, there being no sign of spiriform structure; the lower part of the growth was very irregular and angular.
2	0·25	2 days	The tin was again suspended in the sol but did not effect reduction. Immediately on gelation, growth of the lead tree commenced and proceeded until the bottom of the tube was reached. The upper part of the growth consisted of very bright and broad spiriform strips, the pitch opening lower down, as in Series II. At the bottom of the tube were fine, irregular annular strips as in (1).
3	0·5	24 hrs.	Tin was inserted at the bottom of the tube before gelation and at the top afterwards. The growths from both ends were identical and strikingly spiriform, the pitch opening progressively from the metal. The two trees met in the middle of the tube without overlapping, both being fine and much branched in this region.
4	0·75	24 hrs.	Spiriform growth, much finer than (2) or (3), with opening pitch and increased branching lower in the tube.
5	1·0	4 hrs.	Fine, spiriform tree, smilar to (4) but with smaller total amount of growth.
6	1·25	0·5 hr.	Spiriform structure, noticeably finer and tighter than (5). Pitch of spiral *ca.* 2·5 mm. After 28 days, growth had reached only half-way down the tube, and after a further month had not increased.
7	1·375	15 mins.	Spiriform growth even finer than (6), so that the spirals are difficult to see with the naked eye. Considerable amount of branching, but as in (6) the branches are unserrated metal strips.

(*b*) *Series VII. Lead acetate* 0·08N. *Silicate concentration varied.*

1	0·125	Does not gel: no growth even after 2 months.
2	0·25	Very liquid gel in which spongy mass of metal, *ca.* 3 cm. long, is formed.
3	0·5	Very transparent gel: very thin, two-dimensional branched sword-like growths very similar to those of Series I, No. 1, appear. Total length of growth 7·5 cm. Granular spots noticeable on the shiny metal surface.
4	0·75	Very copious tree of the Series I, No. 1, type; near the top are large serrated fan-like structures: see Plate I (*m*).
5	1·0	Tree growth not so copious, but the " swords " are longer and straighter than in (3) or (4): see Plate I (*n*).
6	1·25	Very copious growth with huge fan-like structures above, and heavy branched swords below: see Plate I (*o*).

For this reason it is to be expected that external conditions might have a relatively large effect on electrochemical behaviour and hence tree growth than for any other two metals in the series. That being so, reduction by other less noble metals should produce a morphology different from those already described and be less susceptible to changes in concentration, etc. A series of lead trees were therefore grown by reduction by means of zinc in gels containing different concentrations of lead acetate. These experiments are described in Table V, which corresponds exactly to the tin reductions of Series I. A new type of growth is observed in this series, *viz.*, the cross type depicted diagrammatically in Fig. 2.

FIG. 2.



(*a*) *End on* (*b*) *Side view* (*c*) *Branched type*

The trees produced by zinc reduction are essentially different from those by tin, in the initial, almost instantaneous production of a black spongy mass of metal from which flat, irregular growths of the sword type slowly develop, and in the cross type of growth which is characteristic of medium and low lead concentrations. Once again the effect of lead concentration is all important, and it is significant that the sword type of growth found to be characteristic of high-lead-concentration, tin-induced trees is also produced by zinc reduction at the same concentration. Once again, rate and magnitude of growth are maximum in the region of 0·06N-lead acetate gels. Spiriform growth was not observed.

TABLE V.

Series VIII. Acid concentration 0·5N. *Lead concentration varied. Reducing metal, zinc.*

No.	[Pb].	Description of tree.
1	0·125	Within 10 seconds the zinc is covered with a black velvet skin of lead which grows outwards to form a spongy mass of thickness *ca.* 1 cm. By the end of 24 hrs., coarse, flat, serrated fronds of bright silver colour have begun to grow from the sponge and these slowly increase in size for a few weeks, by which time they are very similar to the sword type of Series I, No. 1, but more irregular : see Plate II (*a*).
2	0·1	Very similar to (1) but growth less coarse. The main growth is essentially of the latticed sword type, but after one month, fine filaments of the cross type appear at the bottom of the tube.
3	0·05	The sponge-like growth at the top of the tube is now clearly seen to be composed of fine, entangled filaments of the cross type. The later, slower growth is still of the sword type but is less obviously flat and more branched. Cross filaments grow from the sword tips in later stages : see Plate II (*b*).
4	0·04	The sponge-like growth is now much less black and the slower growth from it now consists of parallel filaments the branches of which are short (Fig. 2, *a*, *b*). One flat sword growth appears in the midst of the latter.
5	0·02	Much less growth than above. The metal is now of a pale grey colour : see Plate II (*c*).
6	0·015	Pale grey cross filaments with much branching of the type of Fig. 2, *c*.
7	0·01	There was now no spongy growth round the zinc, the cross fronds growing directly from the metal. These are fewer and finer than before but with longer primary and secondary branches : see Plate II (*d*).
8	0·0075	A few pale grey filaments of extremely fine structure and with long branches reach to the bottom of the tube : see Plate II (*e*).
9	0·002	Almost invisibly fine, hair-like growth from the metal, extending only a few cm. into the gel : see Plate II (*f*).
10	0·001	No visible growth.

TABLE VI.

Series IX. Acid concentration 0·5N. *Lead acetate concentration varied. Reducing metal, aluminium.*

No.	[Pb].	Description of tree.
1	0·125	Very flat, branched growths similar to the sword type of tin but more irregular.
2	0·1	Much as (1), but more copious growth and rather more regular. At the bottom of the tube the fronds become very fine.
3	0·08	Coarse, flat growths with much irregular branching.
4	0·04	Less growth than (3) and finer. A few filaments of the cross type appear below.
5	0·03	The cross type of growth now predominates in the upper part of the tube but there are still numerous unbranched, flat fronds.
6	0·02	Very similar to (5), but the fronds are now very fine and less obviously flat : see Plate II (*g*).
7	0·01	Fewer, longer, finer cross growths similar to the zinc-induced tree of Series VIII, No. 7, but ending in fine, irregular branched growths very similar to those of the tin tree of this concentration.
8	0·0075	Exceedingly fine, pale grey tree of the cross type, very similar in form to, but smaller than, the zinc-reduced tree at the same lead concentration.

The aluminium used for reduction had to be washed in acid before introduction into the gel. Growth of the lead tree started immediately, producing a spongy growth which appeared to be complete within a few hours. The later structures grew slowly down from this and appeared to be stationary after about 4 weeks. In general the lead trees reduced by aluminium resembled those by zinc, but the flat growths at high lead concentrations were rather more irregular and less like those of the tin-reduced trees. At medium lead concentrations the cross type of structure predominated, and at still lower concentrations tended to end in fine, branched growths. The results are recorded in Table VI.

The formation of the trees with magnesium (Table VII) was somewhat different from the others. Immediately on introduction of the metal an evolution of hydrogen commenced; this produced large lenticular bubbles in the gel, which somewhat obscured the growth. In some cases these appeared several inches below the growing tip of the tree. At higher lead concentrations a black lead sponge grew quickly from the magnesium. The lead trees were very small in this series and growth was complete in about a day. The structure was of the cross filament type throughout, there being no trace of the " sword " and other types produced by reduction with other metals. Oxidation of the magnesium produced a white precipitate in

TABLE VII.

Series X. Acid concentration 0·5N. *Lead acetate concentration varied. Reducing metal, magnesium.*

No.	[Pb].	Description of tree.
1	0·125	Immediate production of a lead sponge round the magnesium; from this a few irregular platelets appeared within a day and had grown no more by the end of 2 months.
2	0·08	More growth than in (1) and rather less irregular. A few cross filaments appeared. Growth complete in one day.
3	0·06	Rather irregular tree of the cross filament type was complete in 1 day. Total amount of growth small.
4	0·03	Similar to (3) but cross filaments very distinct.
5	0·01	Very fine, branched cross growth similar to the corresponding trees reduced by zinc or aluminium.
6	0·0075	Growth almost obscured by bubbles; very fine and of pale colour.

the upper part of the tube, which tended to spread downward, especially along the strands of metal, which became coated with small white crystals eventually giving the structure the appearance of snow-covered trees.

The metals zinc, aluminium, and magnesium are somewhat removed from lead in the electrochemical series and produce trees of a morphology resembling one another, but lacking in the structural detail and regularity of the trees produced by tin. In no case could any trace of spiral structure be observed. The more noble metals adjacent in the series to tin are cobalt and nickel, but even when etched with acid or used in the form of a fine powder, they would not replace lead from lead acetate solution in silica gel. A series of reductions was carried out by means of iron and cadmium, the next metals in the series. The results of these experiments are collected in Table VIII.

TABLE VIII.

(*a*) *Series XI. Acid concentration* 0·5N. *Lead acetate concentration varied. Reducing metal, iron.*

No.	[Pb].	Description of tree.
1	0·125	Long, straight, unbranched sword-like growth, irregularly serrated.
2	0·08	Long, irregular branched swords, the whole structure becoming progressively coarser with distance from the iron.
3	0·04	Much finer than (2) and more branched.
4	0·03	Still finer than (3); long, twisting fronds with many branches extend to the bottom of the tube. In the upper part of the tube are many spiriform growths which are extremely fine and of very small pitch: see Plate II (*h*).
5	0·02	Much less growth than in (4), and tree obscured by bubbles and iron oxidation products.
6	0·015	Structure is predominantly of the cross type, but a few minute, tight spirals can be seen.
7	0·01	Rather fine tree of the cross type.
8	0·0075	As (7) but finer.

(*b*) *Series XII. Acid concentration* 0·5N. *Lead concentration varied. Reducing metal, cadmium.*

1	0·125	A close mass of grey, unbranched spines *ca.* 3 cm. long grows out from the metal. Below this, long, irregularly branched swords extend to the bottom of the tube: see Plate II (*i*).
2	0·08	The spines surrounding the metal have now small, regular branches; the main, sword-like growth is straight and more branched.
3	0·06	The spines surrounding the cadmium are now clearly of the cross filament type, rather coarse and very straight. Growth in the lower part of the tube is finer than before.
4	0·04	Still less and finer growth than in (3). The cross filaments radiating from the cadmium are fewer and quite straight.
5	0·03	Growth now extends only half-way down the tube and is less regular and flat. The cross filaments surrounding the cadmium are fewer and larger. One or two minute spirals of small pitch were noted: see Plate II (*j*).
6	0·02	The structure is now mostly of the cross type and extends almost to the bottom of the tube, changing to the fine branched type in the lowest part. Spiriform growth is more obvious than in (5): see Plate II (*k*).
7	0·015	Fewer and finer but longer cross growths, some of which become branched below. Spiriform tendency is still noticeable: see Plate II (*l*).
8	0·0075	Long, branched cross filaments of a pale grey colour; no spirals.

The trees produced by reduction with iron and cadmium are transitional between those with tin and with the less noble metals zinc, aluminium, and magnesium. As with tin, there was no immediate growth of a lead sponge, although a tendency in this direction was manifest in the cadmium growths which formed a close mass of straight spines round the reducing metal. At high lead concentrations sword-like growths were produced, which were similar to those from tin but less regular. In the region of 0·03—0·015N-lead concentration, spiriform structures were observed as with tin, although these were much less prominent and more difficult to see than with the latter metal.

The growths from iron, like those from magnesium, were obscured by oxidation products, a rust coloration gradually diffusing throughout the tube. In this series, the cross filament type of structure, which is predominant in trees produced by less noble metals and entirely absent in tin-reduced trees, first makes its appearance, but only at the lowest concentrations. Iron wire would not effect displacement of lead from lead acetate, even after etching with acid; iron powders, especially those produced by low-temperature reduction, were active in this connection.

The results of a few miscellaneous reductions are described in Table IX.

TABLE IX.

Series XIII. Acid concentration 0·5N.

No.	Reducing metal.	[Pb].	Description of tree.
1	Mn	0·02	Pale grey cross type of growth very similar to that produced by zinc at the same concentration.
2	Cr	0·02	Do.
3	Amalgamated Sn	0·06	No growth.
4	Pb	0·04 *	A grey skin of metal formed round the lead.
5	Cu	0·02	A coherent black coating covered the etched copper wire, and the blue colour of the cupric ion appeared in the gel, gradually diffusing throughout. A fine, black veil-like deposit of lead grew out about 1 cm. from the copper in all directions.

* Stannous acetate.

Chromium and manganese produced trees identical with one another and with those grown from zinc and aluminium at the same concentration of lead. Most surprising was the observation that the more noble metal copper displaced lead from lead acetate solution in the gel.

(g) *The Influence of Non-electrolytes and Protective Colloids on the Lead Tree.*—It has long been known that the addition of gelatin or glue to the electrolyte may modify the form of metals produced by electrodeposition in the case of lead. Freundlich and Fischer (*Z. Elektrochem.*, 1912, **18**, 885) investigated the effect of gelatin on the form of lead deposited from its acid solution by zinc, and found that smaller crystals were produced. Gray (J., 1925, **127**, 776) found that the presence of colloids tended to diminish the size of deposited lead crystals and increase their cohesive power, presumably owing to an adsorbed film of the colloid.

In some preliminary experiments, a few drops of B.D.H. universal indicator were added to the gel, with the result that the form of growth of the lead tree was considerably modified and, when larger amounts of indicator were used, completely inhibited. Several reductions were therefore carried out under various conditions, in the presence of different organic materials. These experiments, some of which have been repeated and found to be reproducible, are described in Table X.

It thus appears that colloidal materials invariably change the form of the lead tree, the results being unpredictable. The total amount of growth is usually reduced by the colloid and the branches or filaments become finer in texture and less regular. The inhibition of growth, or diminution in its rate, is presumably due to adsorption of the colloid on the growing surface of the metal and " sealing " of active centres.

DISCUSSION.

The foregoing results, which relate the morphology of the lead tree to external conditions, are chiefly remarkable for their reproducibility and for the fact that the growth type is so sensitive to small changes in the lead concentration of the gel.

The mechanism of formation of the trees is obviously electrochemical, and many of the observations indicate that the electrochemical equilibrium must be profoundly modified by some of the changes in condition employed here. Especially unexpected was the effect of gelation on the system (Series VI, No. 1; VII, Nos. 1, 2); before gelation, tin would not

TABLE X.

Lead acetate 0·02N. *Different organic materials added to the gel before setting.*

No.	Acid concn., N.	Reducing metal.	Substance added.	Description of tree.
1	0·5	Sn	Universal indicator	Normal spiriform growth but with hair-like side branches. At the bottom of the tube the spirals change to a wisp of hair-like filaments : see Plate II (*m*).
2	0·65	Sn	Do.	A serrated ribbon of bright metal, about 8 mm. wide, twisted into a spiriform strip.
3	0·9	Sn	Do.	Lead-coloured membrane forms round the tin and a few short, branched needles grow in the course of 3 months : see Plate II (*n*).
4	0·65	Zn	Do.	Instead of the normal cross filament type, grey threads of metal, so fine as to be almost invisible, spread parallel throughout the length of the tube : see Plate II (*p*).
5	0·9	Zn	Do.	Do.
6	0·65	Sn	2·0% Alcohol	Normal growth.
7	0·65	Sn	2·0% Acetone	Do.
8	0·65	Sn	1% Sucrose	Spiriform growth, much coarser than normal.
9	0·65	Sn	0·1% Gelatin	Spiral tree broader than usual but with a small total amount of growth.
10	0·65	Sn	0·1% Soluble starch	A few sharp, straight spines grow to the length of 2 cm. in the course of 3 months : see Plate II (*o*).
11	0·5	Sn	0·2% Gum arabic	No growth
12	0·5	Sn	0·1% Agar	Do.
13	0·8	Sn	Universal indicator (3 drops)	Numerous spirals of close pitch : see Plate II (*q*).

replace lead from solution; immediately after setting of the gel, reduction commenced. This, and the extraordinary effect of colloidal materials on the rate and amount of growth, suggest that the gel may, after all, have a specific effect on the morphology of the growth.

Generally there is a change in structure type as the tree grows down into the tube; regular spiriform growths, for example (characteristic of 0·02N-gels), generally descend with increasing pitch, develop irregular side branches, and finally end in thin, branched filaments. The later lead growths are, in fact, characteristic of progressively more dilute lead gels, and are presumably due to impoverishment of the lower portion of the gel with respect to lead. This effect is again apparent in trees prepared by reduction with zinc, in which the flat, sword-like growths of high lead concentrations degenerate at the bottom of the tube into the fine, cross filament type which appears as the initial growth only at low lead concentrations. Experiment No. 3, Series VI, is of special interest in this connexion. In this example, growth was initiated from both ends of the gel and took place to an equal extent in each case, gravity thus having no effect. The two trees changed in type quickly from the striking, tight spiral structure to the fine, irregular, branched type—a transition which usually takes place gradually over the whole length of a tube—within a distance of a few inches. Presumably this is due to the double growth which uses up the lead acetate more quickly than a single tree and removes it by osmotic means from the middle of the tube, in both directions. Thus, although the fine branches of the later growth met in the middle of the tube, there was no overlapping of the two structures. It appears, therefore, that although the initial growth of the lead tree depends essentially on the lead concentration of the gel in which it is grown, the modifications of structure which take place after the first growth period are caused by the *change* in concentration of the lead from the lower part of the gel to the lead-impoverished region in the neighbourhood of the growing tip. The upper part of the gel in which the primary stages of growth took place probably becomes entirely free from dissolved lead, as the initial structure does not increase or modify during the later stages of growth.

SUMMARY OF RESULTS.

(1) The work of previous investigators on metal trees is summarised.

(2) It is found that tin displaces lead from lead acetate in silica gels but not from lead nitrate in gels under the same conditions.

(3) The morphology of lead trees grown by tin reduction is fundamentally dependent on the concentration of lead in the gel, widely different growth types being produced.

(4) A new spiriform type of growth is described.

(5) The effect of the quantity of acetic acid in the gel mixture is unimportant in modifying the morphology, as the system is efficiently buffered.

(6) The formation of a lead tree by means of the action of tin in the silica–acetate system does not take place in the sol.

(7) Visible tree formation commences immediately on gelation.

(8) The rate of growth of the lead tree is initially rapid, but slows down owing to impoverishment of the gel with respect to lead and to increase in the size of the electrochemical circuit.

(9) The growth of lead trees in lead acetate impregnated silica gel can be induced by reduction with zinc, aluminium, magnesium, manganese, chromium, cadmium, iron, and copper, but not with nickel or cobalt.

(10) The morphology of the lead trees produced by metals far removed from lead in the electrochemical series is somewhat similar, and spiriform growths are not produced.

(11) Colloidal materials in the gel have an unpredictable inhibiting or modifying influence on the structure of the lead trees.

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[*Received, February 28th,* 1938.]