

107. *The Structure of Semipermeable Membranes of Inorganic Salts.*

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LITTLE seems to be known of the ultimate structure of semipermeable membranes of insoluble inorganic salts, although Tinker (*Proc. Roy. Soc.*, 1915, *A*, **92**, 357), from a microscopic and ultramicroscopic study, concluded that such membranes were built up of particles between 0.1 and 0.8 μ in length; he held the view, which seems to be general to-day, that they were probably amorphous. Further, Manegold (*Kolloid-Z.*, 1932, **61**, 140) gives no information as to structure, although he postulates three possible divisions according to whether the membrane is (1) canalised by polydirectional capillaries, (2) granular, as in the sand filter, or (3) sieve-like, the precipitate fibres forming the meshes.

X-Ray examination does not appear to have been applied to the study of inorganic salt membranes, no doubt owing to their thinness. It is this very feature, however, which suggests that light might be thrown on their structure by means of the method of electron diffraction.

EXPERIMENTAL.

Precipitates formed from copper sulphate, ferric chloride, or lead acetate with potassium ferrocyanide, sodium silicate, sodium tannate, or sodium hydroxide were studied, and were prepared as follows: (i) The membrane was precipitated by mixing dilute aqueous solutions of the appropriate salts, washed in distilled water, and mounted on nickel or platinum gauze, either with or without a collodion supporting film. (ii) A drop of the aqueous solution containing the acid radical was placed on a collodion film floating on a solution of the metal salt, and a current was passed between platinum electrodes immersed in the two solutions. This method worked well in the case of the ferrocyanides but not with the silicates and tannates, the ions of which were too large to be driven through the collodion films; it has been found, however, to be well suited for the preparation of films of insoluble inorganic salts with small ions. The specimens were washed by floating on several changes of distilled water. (iii) A nickel gauze was dipped into an aqueous solution of gelatin containing the metal salt, immersed when dry in a solution of the other reagent, and finally washed as before with distilled water.

The films formed by direct precipitation (i) were of necessity semipermeable, because otherwise the precipitate would clearly have grown to a dense mass. In the other cases, it was

difficult to differentiate between the permeability of the support and that of the precipitate, especially in view of the fact that flaws unresolved by a microscope with a 4 mm. dry objective may have been present.

Results.—Copper ferrocyanide. Copper ferrocyanide films prepared by any of the three methods gave patterns of which Fig. 1 is characteristic. The rings showed no tendency to arc, even when the plane of the specimen was inclined steeply to the beam; thus the crystals had no common direction of orientation. The analysis is given below (I represents the ring intensity, and d/n , calc., is the spacing, d , calculated for the simple cubic lattice, $a = 4.98$ A., divided by the diffraction order, n), and the results agree well with a simple cubic structure; double shutter comparison (Finch and Quarrell, *Proc. Physical Soc.*, 1934, **46**, 148) with gold ($a_{\text{Au}} = 4.070$ A.) gave $a = 4.97_8$ A.

Copper ferrocyanide.

d/n , obs., A.	I .	Assigned indices.	d/n , calc.	d/n , obs., A.	I .	Assigned indices.	d/n , calc.	d/n , obs., A.	I .	Assigned indices.	d/n , calc.
4.99	s.	100	4.98	2.49	s.	200	2.49	1.76	v.f.	220	1.76
3.52	s.	110	3.53	2.24	f.m.	210	2.23	1.67	v.f.	300	1.66
2.88	m.	111	2.88	2.04	v.f.	211	2.04	1.57	v.f.	310	1.58

Diffraction intensities (here and in other tables): v.s. = very strong, s. = strong, m.s. = medium strong, m. = medium, f.m. = faint to medium, f. = faint, v.f. = very faint.

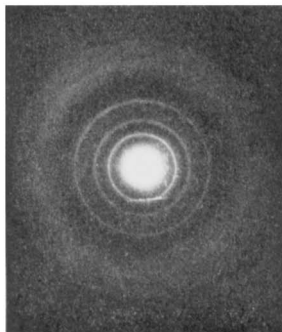
Unlike X -rays, electron-diffraction intensities cannot, for reasons pointed out by Finch and Sun (*Trans. Faraday Soc.*, 1935, **32**, 852), at present be utilised in carrying the analysis to the further stage of determining the position of the constituent ions. Keggin and Miles (*Nature*, 1936, **137**, 577), however, who studied by X -rays the structures of copper ferrocyanide, potassium ferrous ferrocyanide, Prussian-blue, and ferric ferricyanide, found in all cases a face-centred cubic structure of iron atoms with $a = 10.2$ A. It seems reasonable to suppose that the copper ions occupy the positions midway between the iron atoms, as do the ferrous ions in ferrous ferrocyanide; in this case, since copper and iron have approximately the same scattering power for electrons, the pattern obtained would fit a simple cubic structure with a side half that of the iron lattice, *i.e.*, 5 A. This accounts for only half of the copper ions if the copper ferrocyanide contains no alkali, as is almost certain to be the case with specimens prepared by the electrolytic method. It is not possible to suggest positions for the remaining copper ions, but they cannot lie at the centres of alternate cubes of side 5 A., as do the potassium ions in Prussian-blue, since this would have given rise to diffractions of an intensity too great to have been overlooked.

In all cases the average crystal size as determined by the breadths of the diffractions was between 100 and 150 A., and in no case was evidence obtained in the form of haloes to indicate the presence of amorphous material. Tinker found with the ultramicroscope only particles between 1000 and 4000 A. in length, which he thought to be approximately spherical, but since such crystals or accumulations of crystals are much too thick to be penetrated coherently by electrons, the electron-diffraction patterns must have been obtained from other portions of the specimens. In view of the mechanical strength of copper ferrocyanide membranes, it is reasonable to assume that the larger particles are held together by the smaller particles which diffract electrons, the structure being thus similar to that found in specimens prepared by the coagulation of zinc oxide aerosols, investigated by Whytlaw-Gray, Speakman, and Campbell (*Proc. Roy. Soc.*, 1923, *A*, **102**, 600), Finch and Wilman (*J.*, 1935, 751), and Finch and Fordham (*Proc. Physical Soc.*, 1936, **48**, 85). However this may be, there can be no doubt that copper ferrocyanide membranes are either wholly crystalline or contain only a negligible proportion of amorphous material.

Copper ferrocyanide membranes formed by mixing copper sulphate and potassium ferrocyanide solutions gave specimens the colour and texture of which were independent of the concentrations and the relative proportions of the solutions. On the other hand, it was found that contact with excess potassium ferrocyanide during removal from the solution, though apparently without effect on the membrane, resulted in an electron-diffraction pattern differing from that of Fig. 1, though a few of the more intense copper ferrocyanide rings were still present. It was found that this pattern was due to the copper hydroxide described below, together with copper ferrocyanide.

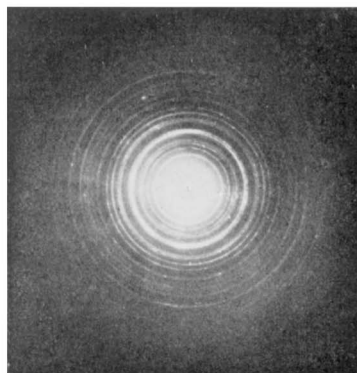
Copper ferrocyanide specimens contaminated with hydroxide (see Fig. 2) were also obtained on several occasions by the electrolytic method when a high voltage (220 volts) was used, but never with a low voltage (6—12 volts). With a high current density there was also a tendency

FIG. 1.



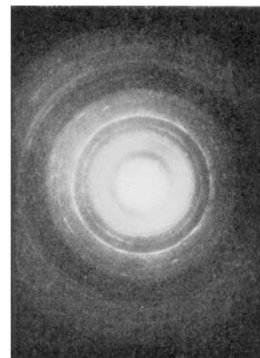
Copper ferrocyanide.

FIG. 2.



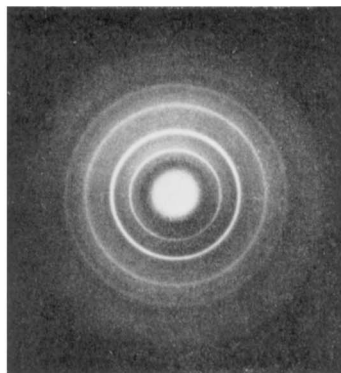
Copper hydroxide together with copper ferrocyanide.

FIG. 3.



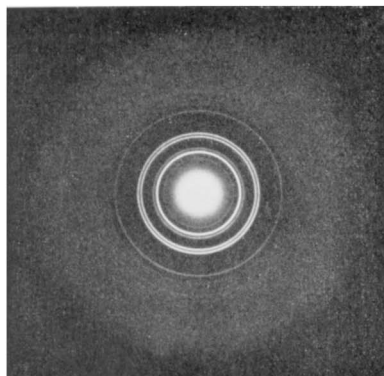
Lead ferrocyanide.

FIG. 4.



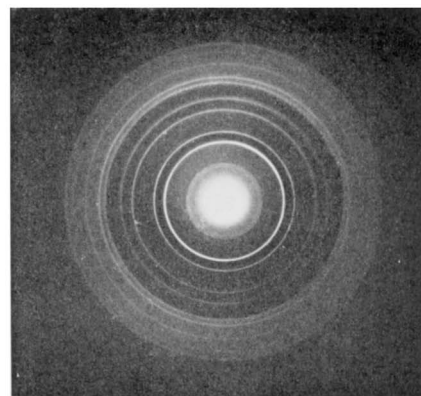
Lead silicate.

FIG. 5.



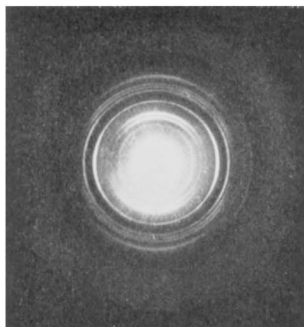
Copper hydroxide.

FIG. 6.



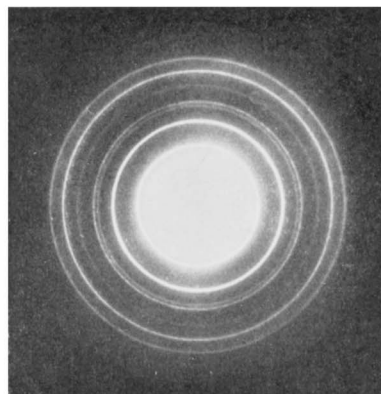
Lead hydroxide ; specimen normal to the beam.

FIG. 7.



Lead hydroxide ; specimen tilted.

FIG. 8.



Ferric hydroxide.

towards the formation of a blue precipitate on the upper surface of the collodion film; this was probably Prussian-blue, formed by the decomposition of the ferrocyanide ion.

Lead ferrocyanide. Lead ferrocyanide formed by the electrolytic method gave patterns similar to Fig. 3, the analysis of which is given below. The structure was simple cubic with $a = 8.28$ A., on which the values of d/n , calc., are based, and the crystals were greater than 200 A. in length, with no preferred direction of orientation.

Lead ferrocyanide.

d/n , obs., A.	<i>I.</i>	Assigned indices.	d/n , calc.	d/n , obs., A.	<i>I.</i>	Assigned indices.	d/n , calc.	d/n , obs., A.	<i>I.</i>	Assigned indices.	d/n , calc.
4.74	s.	111	4.78	2.50	s.	311	2.50	1.85	f.	420	1.85
4.17	s.	200	4.14	2.40	m.	222	2.39	1.60	f.	333	1.59
3.70	s.	210	3.70	2.08	m.	400	2.07	1.45	m.	440	1.46
3.39	m.	211	3.38	1.97	v.f.	330	1.95	1.41	m.s.	531	1.40
2.93	m.	220	2.93	1.90	v.f.	331	1.90	1.38	f.m.	600	1.38
2.82	v.f.	300	2.76								

As with copper ferrocyanide, a tendency was observed towards the formation of a hydroxide, described below, in specimens prepared both by precipitation and by electrolysis.

Ferric ferrocyanide. Ferric ferrocyanide prepared by the electrolytic method had a green colour rather than that characteristic of Prussian-blue. The patterns obtained agreed with the simple cubic structure found by Keggin and Miles to be common to several complex iron cyanides. The crystals were 150 A. in length and had no common direction of orientation.

Silicate membranes. The well-known "chemical gardens," obtained by placing a crystal of a metal salt in "water-glass" solution and commonly ascribed to the formation of membranes of metal silicates, gave in all cases patterns corresponding exactly to the hydroxide patterns described below; similar patterns were obtained from specimens prepared by precipitation from solution. It would seem that the sodium silicate in water-glass is largely decomposed into silicic acid sol and sodium hydroxide, so that the addition of a metal salt resulted in the formation of a mixed gel of the crystalline hydroxide, yielding sharp rings, and amorphous silicic acid, yielding haloes approximately coincident with those of the necessary collodion support.

The electrolytic method, in general, gave specimens consisting of the metal hydroxide, but in one case, with lead acetate, a precipitate formed on the upper surface of the collodion film and gave the pattern (Fig. 4) due to a silicate, or possibly to a different hydroxide, of lead. The plane spacings are recorded below, but no simple structure could be assigned with any certainty. The crystals were approximately 100 A. in length and had no common direction of orientation.

Lead silicate.

d/n , obs., A.	<i>I.</i>	d/n , obs., A.	<i>I.</i>	d/n , obs., A.	<i>I.</i>	d/n , obs., A.	<i>I.</i>
4.72	f.	2.19	f.	1.55	m.	1.19	v.f.
3.77	s.	1.88	m.	1.35	f.	1.10	v.v.f.
2.68	v.s.	1.75	v.v.f.	1.25	v.f.	1.02	v.f.
2.34	f.	1.67	v.v.f.				

Tannate membranes. Diffraction patterns obtained from precipitated tannate membranes consisted in all cases of three haloes somewhat similar to those afforded by amorphous substances, and almost identical with those obtained from the sodium tannate itself. Attempts to prepare tannate membranes by the electrolytic method in all cases resulted in the formation of the corresponding hydroxide.

Metal hydroxides. All the metal hydroxide specimens were prepared by the electrolytic method; dehydration might have been expected in the high vacuum of the electron-diffraction camera, but in no case was a pattern obtained which corresponded to a known oxide.

Copper hydroxide gave the pattern (Fig. 5) recorded in the table, but no simple structure could be assigned to it, nor has any X-ray work been published with which comparison could be made. The crystals were 150 A. in length and had no preferred direction of orientation.

Copper hydroxide.

d/n , obs., A.	<i>I.</i>	d/n , obs., A.	<i>I.</i>	d/n , obs., A.	<i>I.</i>	d/n , obs., A.	<i>I.</i>
5.00	f.	2.81	s.	1.75	f.	1.50	v.f.
4.10	v.s.	2.06	m.s.	1.66	f.	1.41	v.f.
3.72	m.	1.87	f.m.	1.57	v.f.	1.34	v.f.
2.99	s.						

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Lead hydroxide specimens gave the pattern, Fig. 6, when normal to the beam; on tilting to 45° arcing occurred and a pattern, Fig. 7, was obtained, the analysis of which is given below. The structure was close-packed hexagonal with $a = 5.26$ A., $c = 14.7$ A., and $c/a = 2.80$, on which the values of d/n , calc., are based, the c axes of the crystal being normal to the plane of the specimen. The breadths of the arcs showed that the crystals were over 200 A. in length along the a and the b axis, but probably less than 100 A. along the c axis. Lead hydroxide does not seem to have been studied by X -rays.

Lead hydroxide.

d/n , obs., A.	I .	Assigned indices.	d/n , calc.	d/n , obs., A.	I .	Assigned indices.	d/n , calc.	d/n , obs., A.	I .	Assigned indices.	d/n , calc.
4.51	f.	100	4.55	2.27	s.	200	2.28	1.73	f.m.	210	1.72
4.29	f.	101	4.35	2.16	f.m.	202	2.17	1.53	f.	300	1.52
3.68	m.s.	004	3.68	2.09	f.m.	203	2.07	1.33	f.	220	1.32
3.33	m.s.	103	3.34	1.91	m.	204	1.93	1.28	f.	310	1.27
2.65	s.	110	2.63								

Ferric hydroxide gave the pattern, Fig. 8, analysed below, the structure being face-centred cubic with $a = 5.70$ A. The crystals were greater than 200 A. in length and had no common direction of orientation. This substance cannot be the hydroxide, goethite, $Fe_2O_3 \cdot H_2O$, investigated by de Jong (*Natuurwetensch. Tijds.*, 1930, 12, 69).

Ferric hydroxide.

d/n , obs., A.	I .	Assigned indices.	d/n , calc.	d/n , obs., A.	I .	Assigned indices.	d/n , calc.	d/n , obs., A.	I .	Assigned indices.	d/n , calc.
3.26	f.	111	3.29	1.43	m.	400	1.43	0.945	f.m.	600	0.95
2.83	v.s.	200	2.85	1.31	v.f.	331	1.31	0.90	f.	620	0.90
2.00	v.s.	220	2.01	1.27	s.	420	1.27	0.86	v.f.	622	0.86
1.72	m.s.	311	1.72	1.17	m.s.	422	1.16	0.79	v.f.	640	0.79
1.64	m.s.	222	1.64	1.01	v.f.	440	1.01	0.76	v.f.	642	0.76

DISCUSSION OF RESULTS.

The experimental results described above indicate that semipermeable membranes of different substances possess a wide variety of structures with only one feature in common, namely, that they all consist of films of gels, whether the final unit is amorphous or crystalline. The current view that semipermeable membranes are of necessity amorphous is seen to be unfounded, since all the ferrocyanide membranes examined were built up of crystals more than 100 A. in length; on the other hand, the tannate membranes were in all cases amorphous. All these membranes were normally chemically homogeneous, whereas it seems probable that silicate membranes consist of mixtures of the metal hydroxide and silicic acid gels, the former being crystalline and the latter amorphous. It seems probable that all insoluble inorganic salts would be capable of forming membranes if suitably supported, the distinguishing feature of the membranes usually employed being their mechanical strength.

The conclusions to be drawn from these results with regard to the theory of semipermeable membranes may best be discussed in the case of copper ferrocyanide. The theory put forward by Tinker depended upon a calculation of the pore size for a granular structure with particles 1000—4000 A. in diameter. The facts and considerations set forth above would seem to indicate rather a net structure, in which case no calculation of the pore size is possible. Hence, it would seem that previous evidence of a correlation between pore size and permeability is inconclusive, inasmuch as the microscope is unable to detect the presence of crystals about 150 A. in length, the presence of which in profusion must considerably modify the size of the pores. In view of the absence of other evidence in favour of a simple sieve theory of membrane action, it must be concluded that the experimental results so far published favour rather an adsorption theory as being the most likely explanation of the different permeabilities of membranes obtained from different substances by various methods of preparation.

SUMMARY.

The structures of semipermeable membranes of the ferrocyanides, hydroxides, "silicates," and tannates of copper, lead, and trivalent iron have been examined by

electron diffraction. The ferrocyanide membranes were found to be crystalline, and whilst all the crystals exceeded 100 A. in length, many were less than 200 A.; the hydroxides were likewise crystalline. The tannates, on the other hand, were amorphous. It was found, further, that the "silicate" membranes consisted in general of mixtures of gels of crystalline metal hydroxides and amorphous silicic acid. Crystal structures are suggested for copper and lead ferrocyanides and for lead and ferric hydroxides. The results obtained show that the correlation between permeability and pore size as obtained by microscopic methods is fortuitous.

The authors thank Professor G. I. Finch for his encouragement and assistance, and the Department of Scientific and Industrial Research and Imperial Chemical Industries Ltd. (Dyestuffs Group) for grants.

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[Received, January 30th, 1937.]
