

54. *Equilibria and Changes in Metal Hydroxide Sols.*

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Hydroxide sols of aluminium, chromium, iron (III), lanthanum, neodymium, and thorium have been studied from the point of view of the nature of the stabilising ion and of the changes which they undergo on ageing.

The sols of lanthanum and neodymium hydroxides are difficult to prepare in a pure condition and to investigate owing to their sensitiveness towards carbon dioxide.

Chemical methods for determining the free and bound kations in the positive sols have been developed and their trustworthiness discussed. The micellar charges appear, as a rule, to be due to adsorbed metal ions though, in some cases, both the free and the bound kations are probably present largely as basic ions. Hydrions play a part in the equilibria in hydroxide sols, and reasons are given for considering that in some of the less basic hydroxides part of the micellar charge may be due to bound hydrions.

The micelles may in exceptional cases have a crystalline character, but as a rule they appear to be liquid or glassy so that the sols are to be regarded as emulsions. The micelles then constitute a second liquid phase with a very high metal-hydroxide concentration, and into this medium penetrate many of the peptising metal ions which are first adsorbed on the surface of the liquid or glassy micelles. The invading kations are accompanied by balancing anions which thus become masked towards reactions external to the micelle, and in many cases the kations become co-ordinated to metal hydroxide and converted into highly basic ions. If a sufficient amount and concentration of the peptising kation is available, this process may continue until the original (liquid or glassy) hydroxide has become converted into what is essentially a liquid or glassy basic salt. The latter may persist in this condition as a sol for a long time, or it may pass into true solution as a soluble basic salt or separate out as crystalline basic salt, with disappearance of the sol condition.

The chief factors determining whether a crystalline basic salt is formed in any given case would seem to be the tendency for the metal hydroxide to co-ordinate with metal ions, and the solubility and crystallising capacity of the potential basic salt.

Ageing of metal hydroxide sols is attributed mainly to one of four causes : (i) coalescence of the liquid micelles to form larger droplets, (ii) dehydration of the hydroxide constituent of the liquid micelles, (iii) crystallisation of the hydroxide either before or after dehydration, and (iv) crystallisation of the basic liquid or glassy micelle as a definite basic salt, or its passage into true solution. Which of these factors is of most importance with any particular hydroxide will depend fundamentally upon the general characteristics of the metal. Ageing is normally slow, but in ferric hydroxide sols factor (ii) causes a marked ageing.

The operation of factors (iii) and (iv) is greatly facilitated by the atomic transference rendered possible by the equilibria between free and bound kations. Crystallisation is for this reason more likely to occur in sols where the micelles have a low value for the ratio, micellar hydroxide/bound kation. The basic chlorides do not crystallise readily, but a crystalline one did separate from a thorium hydroxide sol; further, it has been possible to identify some of the basic kations occurring in aluminium hydroxide sols by making use of the sparing solubility and good crystallising power of their sulphates.

In aqueous sols with liquid micelles the bound kations are of two types, (a) those in solution in the micelle—these are mostly basic and are accompanied by an equivalent number of anions—and (b) kations adsorbed on the surface of the micelles with equivalent anions in the electrical double layer. It is to these adsorbed kations, which appear to be mainly simple hydrated ions, that the ordinary charge of the micelles is due.

THE hydroxide sols investigated (see Summary) were all positive sols, with chlorion as negative or contra-ion. Our knowledge of such sols is incomplete in several particulars, for instance, (i) the nature of the stabilising ions, (ii) the mechanism by which they are attached to the micelles, (iii) the cause of the ageing of such sols. The experiments now described, the result of 10 years' work, throw some light on these matters. It is often supposed that the charge on the micelles of positive sols is due to adsorbed hydrions, but the alternative view that it originates from adsorbed kations of the metal of the hydroxide is held by many workers. On the latter view, the peptisation of a metal hydroxide by the corresponding chloride is due, in the main, to adsorption of metal ions, and there should be an equilibrium in the sol between the free and the bound metal ions. It is, however, quite likely that, in cases where the salt is appreciably hydrolysed, adsorption of hydrion would also play some part in the process.

Study of any equilibria concerned requires therefore some method of determining the proportion of free and bound metal ion and hydrion. The electrochemical method of measuring the concentration of free ions in a sol has been widely used by Pauli and others (Pauli and Valkó, "Elektrochemie der Kolloide," 1929, p. 544) for the determination of chlorion and hydrion. It is generally considered to be the best method, as it can be applied directly to the sol itself, but, owing to the absence of suitable electrodes, it is only of restricted applicability. Analysis of the clear liquid obtained by coagulating the sols with suitably chosen electrolytes gives another method of attacking the problem which has also been used extensively by Pauli (*op. cit.*, pp. 519—531). It is this chemical method which we have chiefly used. The adsorptive capacity of the micelles present in a sol might differ from that of the coagulum obtained by the addition of electrolytes, so analysis of the liquid in contact with the curd does not necessarily give the composition of the intermicellar fluid, as has been pointed out by McClatchie (*J. Physical Chem.*, 1932, 36, 2087). It is difficult to foresee exactly how the two would differ, though it might be thought that curding would cause a diminution of surface and consequently reduced adsorption. The concentration of the free stabilising ion found by the analytical method would then be higher than that found by the electrical method. It is also possible that the electrolyte used for coagulation might disturb the adsorption equilibria by itself entering into some exchange reaction.

Our own results appear to show that little, if any, disturbance arises from these two causes if the coagulating electrolyte is properly chosen. We believe that the analytical method then gives results very close to the truth. It was possible to test this view for the case of hydrion with one of the thorium sols (see p. 300). Sodium metaphosphate curds thorium sols, precipitating any free thorium ions present. It does not liberate any acid when added to a solution of thorium chloride. Any acid found in the filtrate from the curd thrown down by sodium metaphosphate from a thorium hydroxide sol should therefore represent hydrion originally present in the sol. Very close agreement was obtained between the value obtained in this way and by the glass electrode on the sol itself.

No similar comparison is possible in the case of the metal ions, but it seems likely that the free ions found in the filtrate, after curding by an electrolyte which precipitates only the colloidal micelle, gives a correct value for the ionic concentration of the intermicellar fluid, apart from an uncertainty as to the precise nature of these ions (see below, also pp. 281, 282). This opinion is based on the fact that certain

of the sols on coagulation gave liquids in which no measurable amount of metal ion or hydrion could be detected. This showed that no metal ion was set free on coagulation in spite of the fact that much bound kation was present, and, as indicated previously, it is more likely that the coagulum would have a smaller adsorptive capacity than the micelles rather than *vice versa*. Ammonium sulphate was found the most suitable coagulant for determination of the free metal ions present in the sols. It precipitates the micelles of all the sols (except those of chromium) when added in small excess, and has no effect on the free metal ions. Considerable excess of this coagulant can generally be added without causing complications, though in some cases it must be used with discretion (see p. 286).

We at first thought that sodium metaphosphate was a suitable electrolyte for use when determining the hydrion concentration of the sols, since it is a good coagulant for the micelles and can also precipitate the free metal ions of most of the sols; but we found that some sols, more especially those of aluminium and ferric hydroxides, appeared to have a very high acidity when examined by this method, though direct glass-electrode measurements on them showed that very little hydrion was present.

The action of sodium metaphosphate (freshly prepared by heating ammonium sodium hydrogen phosphate) on fresh solutions of aluminium or ferric chloride or sulphate was therefore examined. An amorphous basic salt was precipitated owing to hydrolytic disturbance, so the filtrate was strongly acid, the same amount of acid being indicated by the glass electrode as by titration. Excess of metaphosphate will dissolve the precipitate or prevent its formation, and also protects the aluminium or ferric salt to some extent from the action of sodium hydroxide, but not completely.

It is because of this action on the free kations that acid is found in the filtrates from the metaphosphate curds of aluminium or ferric hydroxide sols. No precipitate is thrown down during the titration with alkali even although dissolved aluminium or iron is still present. This seems to be due to peptisation of the hydroxide by metaphosphate to form a negative sol, for, when a 0.1N-aluminium sulphate solution is stirred into an equivalent amount of sodium metaphosphate solution, no precipitate is obtained, although a thick curd is formed when the mixing is done in the reverse order. A complex alumina-metaphosphate anion is probably formed when larger amounts of metaphosphate are used.

Chromium salts appeared to behave in a similar manner with metaphosphate, but there was no liberation of acid from thorium chloride.

Sodium metaphosphate can be satisfactorily used as a coagulant in determinations of the acidity of thorium sols and may give useful results for aluminium and ferric sols which contain only small amounts of free metal ions. In the last two cases, however, the values found are almost certain to be too high. Care should be taken to add only sufficient metaphosphate just to cause complete coagulation: an amount slightly less than that equivalent to the chlorine content of the sol will be required.

There is abundant evidence that some of the metals examined by us, and aluminium and chromium in particular, can form basic kations. It is probable, therefore, that, when a polyvalent kation such as Al^{+++} (presumably as $[Al(H_2O)_6]^{+++}$) is adsorbed by its hydroxide, some interaction might occur to produce basic kations. It is rather exceptional, however, for positive evidence of this to be obtained by direct analysis of the sols. The importance of these basic kations is illustrated by the results obtained with aluminium hydroxide sols No. 15 and 16. If, in the case of sol No. 15 all the free aluminium found in the filtrate from the curd obtained with ammonium sulphate is calculated as Al^{+++} it would account for all, or even a little more than, the total Cl^- ions. There would then be no kations left to stabilise the micelles. This is definite evidence that some, if not all, of the free aluminium is in the form of basic kations.

Sol No. 16 illustrates the same point still more clearly, and in that case the basic kations were actually isolated as a stable crystalline sulphate. The existence of basic kations in the micelles of aluminium hydroxide sol has been considered by Pauli (*Kolloid-Z.*, 1921, **28**, 49) and by Adolf, Pauli, and Jandraschitsch (*ibid.*, 1921, **29**, 281).

Isolation of the basic kations as crystalline sulphates enables differentiation between basic and other kations to be made to some extent in the case of aluminium, but we are not aware of any general method by which this can be done for other metals. We are, for this reason, not quite sure what we have estimated by our methods as "free kation." In the tables and discussions we refer to it as free Al^{+++} , Fe^{+++} , Th^{++++} , etc.; although it may not be only this and may in certain cases consist largely of basic ions.

Reasons are given later for considering that in many cases the free kations are actually present almost entirely as the simple (hydrated) ions and not as basic ions. The presence of basic kations would invalidate any electrode-potential method of measuring the kation concentration of the intermicellar fluid of hydroxide sols.

The mechanism by which free basic kations are produced must be considered. We have obtained much information on this matter from experiments with aluminium hydroxide sols and believe that the following explanation of the nature and reactions of metal hydroxide sols is consistent and satisfactory.

The majority of these sols appear to be emulsions. The second liquid phase which forms the micelles has a very high metal-hydroxide concentration and may be so viscous as to constitute a "glass". A crystalline core may be present in some cases. The peptising cations are adsorbed on the surface of the hydroxide "droplets," and the micellar charge is due almost entirely to cations which are so adsorbed and are balanced by an equivalent amount of anion in the electrical double layer. These adsorbed cations are probably hydrated and will be in equilibrium with similar ions which are free in the intermicellar fluid. Some of the adsorbed cations will, however, pass into solution in the liquid (or glass) of which the micelle is composed. The cations which do this will of necessity be accompanied by an equivalent number of anions. Although the latter remain in the ionic condition, they have been withdrawn from the intermicellar solution and have become inert towards tests carried out on this. This appears to be a reasonable cause of the masking of much of the chlorion in old ferric hydroxide sols when the chlorion was determined by the calomel electrode (Pauli and Valkó, *op. cit.*, p. 520).

If the cations which thus invade the micelles are those of the metal forming the hydroxide, there will be some tendency, varying from metal to metal, for co-ordinated water to be replaced by co-ordinated metal hydroxide. Very basic cations then result. General similarity of composition between these and the fluid constituting the micelles will lead to the basic ions or salt being much more soluble in the micellar than in the intermicellar fluid, so that, with most sols, few of these basic ions will escape from the micelles and become free. It seems likely for this reason that the free cation will usually come from the adsorbed cations and consist almost entirely of the simple hydrated ions in most of the cases with which we are concerned.

Only when the micellar fluid has attained nearly to the composition of a definite basic salt will the concentration of basic cations be such that any considerable number of these can escape into the intermicellar solution. These conditions are most likely to arise when the sol has a high concentration of free cations in the intermicellar fluid and a low value for the ratio, micellar hydroxide/bound cation.

When the micelle has reached this condition it can be considered to be a liquid or glassy basic salt. This may either persist as a very clear transparent sol for a long time, or it may break up and pass into true solution, or it may actually crystallise. Such crystalline basic salts will only be easily attainable if they are sparingly soluble and have good crystallising powers, and if the tendency for the metal hydroxide to co-ordinate to the cation is high.

The only certain case in which a definite crystalline basic chloride has been observed to crystallise directly from a metal hydroxide sol is that of thorium hydroxide sol No. 10 which, after 6 years, had deposited a small amount of the compound $3\text{Th}(\text{OH})_4, \text{ThCl}_4, 10\text{H}_2\text{O}$, probably $[\text{Th}\{\text{Th}(\text{OH})_4\}_3]\text{Cl}_4, 10\text{H}_2\text{O}$. No such basic thorium chloride is recorded in the literature, though Rosenheim and Schilling (*Ber.*, 1900, 33, 978), Rosenheim, Samter, and Davidsohn (*Z. anorg. Chem.*, 1903, 35, 425), and Matignon and Delépine (*Ann. Chim. Phys.*, 1907, 10, 133) have prepared $\text{Th}(\text{OH})_4, \text{ThCl}_4, x\text{H}_2\text{O}$ and $\text{Th}(\text{OH})_4, 3\text{ThCl}_4, x\text{H}_2\text{O}$ with various values of x , in a crystalline state. There are also indications that crystalline basic chlorides can separate from sols of lanthanum and neodymium hydroxides (see pp. 299, 300).

When hydron becomes bound to the hydroxide micelle some of it will also dissolve in the micellar fluid. There it may react at once with the hydroxide to form cations of the metal, which will then react as outlined above. In such cases, sols prepared by peptisation with hydrochloric acid will be indistinguishable from those of similar concentration peptised by metal chloride. This is true of sols prepared from translucent aluminium hydroxide precipitated and washed at room temperature.

If, for any reason, the hydroxide does not react easily with hydron, the latter may persist for a considerable time and the hydron dissolved in the two liquid phases will be in equilibrium *via* the hydron adsorbed on the outside of the micellar "droplets." In such a case the sols prepared by peptisation with hydrochloric acid will differ from those peptised by the metal chloride, though in time they should become identical. Sols derived from translucent aluminium hydroxide prepared at 100° behaved in this manner (see p. 289). This hydroxide may be regarded as based on $\text{Al}_2\text{O}_3, \text{H}_2\text{O}$ (cf. Böhm, *Z. anorg. Chem.*, 1925, 149, 203).

Crystalline basic aluminium sulphates isolated *via* the sols as indicated above appear to contain ions in which the aluminium ion is co-ordinated to hydroxide. (Confirmation of this by X-ray examination of the crystals is still required.) It is probably basic ions of this type which will be chiefly formed from hydroxides of trivalent metals under sol conditions where the hydroxide is always in relative excess. Under other conditions, as we know from work not yet published, simple hydroxylated ions such as $[\text{AlOH}(\text{H}_2\text{O})_5]^{+}$ may occur. We have observed no indication that simple basic cations of this type play any important part in metal hydroxide sols such as we have studied. Such evidence as

we have is rather against it, for a large proportion of the total aluminium which was not obtained as crystalline compounds containing the very basic kations described above has been isolated as ammonium alum.

Additional evidence for our emulsoid theory is furnished by the chromium hydroxide sols where, in several cases, curious glassy products were obtained during the preparation of the sols which were very insoluble in water and approximated in composition to a basic salt, $[\text{Cr}\{\text{Cr}(\text{OH})_3\}_6]\text{Cl}_3 \cdot x\text{H}_2\text{O}$.

The tendency for the aluminium basic micelles to pass into true solution seems to be much greater than that of the corresponding micelles of the other hydroxides, which tend therefore to remain in the emulsoid or glassy condition. If sufficiently favourable conditions for crystallisation could be found, it should be possible to prepare crystalline basic salts from all the sols examined by us.

The emulsoid theory also gives a satisfactory explanation of the limiting value of the ratio, metal hydroxide/bound kations (called " n " in the tables), which is strongly indicated in the case of ferric and chromium sols. It is evidently due to the formation of ions similar to those found with aluminium. An n value of 4 or 6 for chromium would correspond to the ions $[\text{Cr}\{\text{Cr}(\text{OH})_3\}_4]^{+++}$ and $[\text{Cr}\{\text{Cr}(\text{OH})_3\}_6]^{+++}$. If such low n values were determined entirely by adsorption on the surface of solid particles, these would have to be so small that they would be of "molecular" dimensions, and micelles of this character might be expected to give rise to crystalloidal rather than colloidal solutions. This applies with still greater force to thorium and other hydroxide sols with an n value as low as 2. With aluminium, lanthanum, and thorium hydroxide sols the analytical figures appear to show that n values even lower than 2 may occur. The same is true of the ferric sols prepared by the action of boiling water on ferric chloride. It is possible that in certain cases very low n values may arise because so many hydrated kations (*e.g.*, $[\text{Al}(\text{H}_2\text{O})_6]^{+++}$) have penetrated into the micellar "fluid" that some have to remain in the hydrated condition, as there is insufficient hydroxide to convert all into basic kations.

All these hydroxide sols give glassy residues on evaporation at room temperature, and the curds obtained by the action of ammonium sulphate break up into angular glassy fragments even in presence of water. Sometimes these fragments are under such strain that they show double refraction.

Work in the basic region of the system $\text{Al}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$, not yet published, has, moreover, shown that over a considerable part of the system, two liquid phases coexist. These separate from clear solutions which there is no reason to regard as colloidal, and whereas the one is an ordinary aqueous solution, the other forms transparent spheres and discs of glass which may be relatively large when seen in a microscope. The range of composition of these glasses covers that of the sol micelles under discussion, and like the micelles, they are metastable towards several crystalline basic sulphates, including those described in the present paper.

There is thus much evidence to justify the view that the micelles of hydroxide sols and the curds obtained from them by the action of appropriate anions are of a liquid or glassy nature.

The view that aluminium and other metal hydroxide precipitates are curded emulsions gives a reasonable explanation of the obstinate retention of anions by such precipitates. Retention of anions by microcrystalline hydroxides such as that of aluminium precipitated in the opaque form by means of ammonia in excess is not to be expected and does not in fact occur (see p. 288). Aluminium hydroxide sols can be prepared from the microcrystalline hydroxide formed at room temperature (see p. 287), but we believe that this is impossible unless a proportion of the amorphous hydroxide is present or is formed during peptisation. In the milky sols so obtained, the micelles probably consist of a core of crystalline material protected by an emulsoid sheath of amorphous hydroxide.

We have found that with freshly prepared metal hydroxide sols practically the whole of the chloride is in the filtrate separated from the hydroxide curd after precipitation and washing with ammonia. As some of the sols age, a proportion of the chloride becomes held in the micelle in such a way that it escapes the action of ammonia, and in some cases the amount thus hidden is considerable. Pauli and Valkó (*op. cit.*, p. 520) found that a large proportion of the total chlorion might fail to respond to the calomel electrode, and considered it to be present in some sort of Werner complex. This is quite likely with some of the hydroxides. We consider that these facts are quite consistent with the emulsoid theory.

The ion $[\text{CrCl}(\text{H}_2\text{O})_5]^{+++}$ is well known, and it is possible that a similar aluminium ion may be capable of existence, but, just as there seems no evidence that the simple hydroxylated ion $[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{+++}$ is of importance in sols under ordinary conditions, so there is no evidence for the presence of $[\text{AlCl}(\text{H}_2\text{O})_5]^{+++}$ or any other chlorinated ion: there is, in fact, strong evidence to the contrary. It was found that one of the crystalline basic salts would dissolve in 0.1N-hydrochloric acid, and if the solution was then diluted $2\frac{1}{2}$ times a considerable fraction of the solute crystallised out again unchanged, containing no trace of chlorine (see p. 291). This unexpected behaviour indicates a high degree of stability of the basic aluminium ions and is strongly opposed to the view that any replacement of their hydroxyl by

chlorine is likely to occur. It is evident that simple hydroxylated or chlorinated kations of aluminium, chromium, or other metals could take part in the adsorption equilibria like any other kation if they were prepared by suitable methods and added to the hydroxide sols. That does not mean, however, that they are normally present in appreciable amount in such sols prepared by peptisation in the usual way.

Masking of chlorion owing to retention in the liquid or glassy micelle must not be confused with another effect. All negative ions present in the system take some part in the precipitation whenever a positive sol is curded by sufficient addition of suitable electrolytes. All the curds obtained from our sols by the action of ammonia would be expected to carry down a little chloride for this reason, but it would be removed relatively easily by washing with ammonia, though not by water. Action of this sort is not likely to be very important in the case of chlorion, since the efficacy of anions as coagulants is mainly determined by their valency and tendency to form sparingly soluble salts.

It is evident that, for all the reasons discussed, there must be considerable uncertainty about the micellar charge. This is likely to be greatest in old sols. Sol analyses in which chlorion concentrations have been determined by means of the calomel electrode are not necessarily any more correct than those obtained by our chemical methods. A knowledge of the free kations present is essential—it cannot be assumed that only free negative ions are present in a positive sol in addition to the positive micelles.

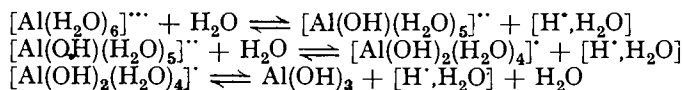
Nearly all the sols with which we have worked were prepared by peptisation of the metal hydroxide in a solution of the corresponding chloride or by hydrochloric acid. The former peptising agent may be the more effective, and sols prepared by the two methods are not always identical (see p. 280). They were fairly concentrated and were not subjected to dialysis, which would have rendered them less suitable for our purpose. The free metal ion was estimated in the filtrates from gels obtained with ammonium sulphate in the case of all the sols except those of chromium hydroxide, which were coagulated by potassium ferrocyanide. Total chloride was determined in the filtrate from the curd obtained with excess of ammonia, the curd being well washed with ammonia. Alternatively, the sol was digested under reflux well below 100° with 2*N*-nitric acid until the colloidal condition was broken down, and chloride was then determined in the solution by means of silver nitrate. Results obtained by these two methods usually agreed closely. Hydrion present in the sols could only be determined with certainty by means of the glass electrode in the case of aluminium, ferric, and chromium sols, although the chemical method was satisfactory for thorium sols (see pp. 278, 300). "Total chloride" less "free metal ion and hydrion" gave "bound metal ion."

The analytical difficulties are considerable and the differences sought are often small, but the following conclusions seem to be justified by the results obtained.

Period required for Peptisation at Room Temperature.—The rate of sol formation increases with the concentration and the excess of peptising agent employed, provided that the amount of hydroxide present be not enough to act as a mechanical barrier to liquid motion; for instance, compressed cakes of ferric or chromium hydroxide are difficult to disperse by limited volumes of liquid. This effect is of importance when preparing very concentrated sols. The actual time before peptisation is complete varies widely from case to case—many days may be needed. The curding effect of a high concentration of peptising agent may interfere with sol formation.

The *rate of ageing* of the sols as indicated by the setting free of previously bound kations is always slow. It appears to be more rapid in the aluminium and ferric sols than in the others examined by us.

Hydrolysis of Sols and the Part played by Hydrions.—No hydrolysis was apparent in any hydroxide sol of lanthanum or neodymium. The glass electrode showed that the p_H was about 7.5. Very little acid was present in the chromium and the thorium sols, but the aluminium and ferric sols contained an appreciable amount. These differences are connected with the different degrees of hydrolysis of the several metal chlorides. Pauli and Valkó (*op. cit.*, p. 100) suggested that, on adsorption by a metal hydroxide, hydrions would probably react with hydroxyl to form water and so liberate an equivalent amount of metal ion. The nature of the metal and other circumstances will, however, determine whether this happens. It is quite possible for a hydrion to remain in close proximity with a hydroxyl group covalently attached to a metal atom (which is not the same as a hydroxyl ion), just as it can remain associated with a water molecule: the less electropositive the metal the more readily this will happen. It seems clear that hydrolytic equilibria of the types



must occur in the solution. All the ions so formed will be adsorbed on and dissolve in the micelles of the sol to some extent. In so far as their adsorption is determined by dipole effects, it will depend

upon the charge and volume of the adsorbed ion and might be expected to diminish in the order $[H^+ \cdot H_2O] > [Al(H_2O)_6]^{+++} > [Al(OH)(H_2O)_5]^{++} > [Al(OH)_2(H_2O)_4]^+$.

It is important to recognise that the whole series of ions consisting of $[Al(H_2O)_6]^{+++}$ at one end and $[H^+ \cdot H_2O]$ and neutral $[Al(OH)_3]$ at the other, with all possible basic ions as intermediate stages, must co-exist in approximate hydrolytic equilibrium in the intermicellar and micellar liquids and in the adsorption film. It is convenient to consider aluminium sols as an example, for the various possible ions are better known to us than those of other metals.

The proportions of the various members of this series which are present in different sols will depend upon several factors of which the chief will be (a) the specific peculiarities of the metal, (b) the concentration of the sol and in particular that of the "free" kation, and (c) the n value of the sol. The lower the value of n , the more will basic ions of the highest basicity be favoured, whereas a high concentration of total free kations in a sol will tend to favour the simpler kations rather than the basic ions.

The equilibria concerned will not be absolute, for the sol condition is a metastable one and, in the sols under consideration, represents a transition stage leading from amorphous hydroxide to crystalline hydroxide or crystalline basic salt.

The precise ionic state of a sol is hard to define and depends upon its past history—whether it has been freshly prepared and by what method, whether it has been dialysed, and so forth.

The two chief causes of the increase of free kations when emulsoid sols age would seem to be: (1) diminution of surface owing to coalescence of emulsoid droplets and consequent liberation of some of the adsorbed kations, (2) adjustment of the hydrolytic equilibria owing to increased formation of basic ions. This does not necessarily increase the number of positive equivalent ions in solution, but does increase the total amount of metal in the "free" state in solution.

It would appear that a peculiar situation might arise when the micelles of a sol, having become saturated with kations, break up and pass into true solution as very basic kations. Before this occurrence, the various kations present in the intermicellar fluid would be in approximate hydrolytic equilibrium. This would be upset by the sudden influx of very basic kations, and one of two things would probably happen: either the very basic kations would separate out as crystalline basic salts or, if solubility conditions were not suitable for this, fresh readjustments of the hydrolytic equilibria would occur. These might lead either to an increase of simpler basic kations at the expense of non-basic kations or to an actual separation of metal hydroxide, and as this would probably be slow, the conditions should be very suitable for formation of crystalline hydroxide or oxide.

A change in the proportions of hydrion and metal ions in the intermicellar fluid may arise owing to a change in the nature of the micelle due to dehydration, or to some other cause accompanied by a change in the relative adsorptive capacity of its surface for these ions. This seems to apply to ferric sols. Owing to their positions in the adsorption scale it would seem that with most hydroxide sols the simple hydrated metal ions are probably the principal stabilising ions, with the various basic ions playing minor parts. Hydrion may become important as a stabilising ion with the more acidic or less reactive hydroxides (see p. 300 for a case with thorium hydroxide, and p. 289 for two examples with aluminium hydroxide).

The series of hydrolytic equilibria mentioned above may come into action in a solution prepared from a simple metallic salt. This happens with ferric chloride. A freshly prepared, dilute (0.5N) solution of this salt in cold water rapidly reaches a condition of apparent hydrolytic equilibrium with a low hydrion concentration. A slow hydrolysis continues, however, and after several years practically the whole iron content of the original solution may have separated as a yellow precipitate below a colourless solution of hydrochloric acid. The hydrolytic changes seem to be accentuated in this case by the formation of the less basic or less reactive $Fe_2O_3 \cdot H_2O$, which forms in ageing sols.

Freshly prepared ferric hydroxide sols, if sufficiently concentrated, can give a precipitate with hydrochloric acid. The less concentrated sols give none in the fresh condition but, as they age, they give a yellow precipitate with hydrochloric (or nitric) acid in increasing amount, until when they are a year old, over 80% of the iron content may be precipitated. These yellow precipitates are again dispersed by addition of water. Analysis of such a precipitate, thrown down by 2N-hydrochloric acid from a four-year old ferric hydroxide sol, washed with alcohol, and dried in air, gave figures corresponding to $(FeO,OH)_{10.7} \cdot [Fe(OH)_3]_3 \cdot FeCl_3$, whereas ferric hydroxide, precipitated cold and similarly washed and dried, was $Fe(OH)_3 \cdot 0.74H_2O$. The alcohol washing of the curd had removed some ferric chloride,* so the precise formula is uncertain, but the result suggests that the ageing process producing the less soluble curd is a partial dehydration of the original micelle which, in the fully aged sol, would presumably be based upon $FeO \cdot OH$ instead of $Fe(OH)_3$ (cf. Böhm, *loc. cit.*). These changes

* Much more than could have been present in the small amount of adhering mother-liquor. This supports the view that bound ferric ions, or other kations which could readily react to give ferric ions, were present on the curd.

are accompanied by a small but distinct increase in the acidity of the sol, and after several years a considerable amount of the iron content may have separated out as a yellow curd.

A small increase with age in the n value of the sol may be a contributory cause of the decreasing solubility of the curd, but seems insufficient by itself to account for the observed behaviour. The different behaviour of thorium hydroxide sols prepared by the hot and the cold processes may also be due to a difference in the degree of hydration of the micelles.

A considerable orange-brown deposit had settled out of ferric hydroxide sol No. 25 (see p. 297) by the time this was $3\frac{3}{4}$ years old. This was still colloidal and easily dispersed by water, but its X-ray powder photograph appeared to be identical with that given by Böhm (*loc. cit.*) for the mineral rubinglimmer (ruby mica, γ -goethite), the form of $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ corresponding to bauxite, $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. (Böhm showed that bauxite is not $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, as commonly stated.) It seems evident, therefore, that the majority of ferric hydroxide sols prepared by the cold process will eventually deposit crystalline $\gamma\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ on ageing. Sols prepared by the hot process will ultimately behave in the same way and so even will solutions of ferric chloride. The reversal of the hydrolysis which the hot-process sols appear to show on ageing at room temperature (see p. 295) is to be regarded as a metastable interlude only possible so long as crystalline nuclei of the very insoluble $\gamma\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ have not formed to an extent sufficient to switch over the hydrolysis in the other direction.

The equilibria in the adsorption film on the micelles and the ionic interchange between the adsorption film and the body of the intermicellar and micellar solutions would seem to be chiefly responsible for the ageing of sols. Colloidal solutions must be regarded as metastable systems. The adsorbed ions, although essential to the very existence of the colloidal state, also provide the mechanism by which this is finally broken down. This matter was discussed in connection with colloidal sulphur by Bassett and Durrant (J., 1931, 2924). The metastability of colloidal systems arises from several causes which will be briefly considered.

(i) The free ions functioning in a sol may be, and generally are, of the wrong kind at first; for instance, hydron or $[\text{Al}(\text{H}_2\text{O})_6]^{+++}$ in the peptising solution may have to be converted mainly into some basic ion. If such an adjustment occurs slowly, there may well be an initial peptisation and sol formation conditioned by adsorption of ions which slowly undergo adjustment to others more truly characteristic of the particular sol in its more or less stable form. If the adjustment is rapid, it will not be possible to distinguish this from the peptisation stage itself. Slowness in the rate at which the minimum concentration of free kations was reached in some of our experiments may be due to some such cause.

(ii) If a sol is an emulsoid, there will usually be an instability due to a tendency towards diminution of micellar surface by formation of larger "droplets" and ultimately of an uncharged, second, liquid phase. This is probably one of the causes of the normal slow separation of kations from these sols on ageing, for diminished surface means diminished adsorption.

(iii) In metal hydroxide sols, instability may arise owing to a tendency for the hydroxide to lose water. Our evidence suggests that the ageing of ferric hydroxide sols is connected with the slow formation of $\text{FeO} \cdot \text{OH}$ from $\text{Fe}(\text{OH})_3$. The existence of basic salts derived from both forms of the hydroxide should be possible. There is no apparent reason why the "liquid" micelles should not persist after this change has occurred though their capacity for being "curded" will be different.

(iv) Separation of a definite crystalline compound from the sol (or formation of its crystalloid solution) is another very important cause of instability. The type of crystalline compound which can separate from any given type of sol may well depend upon several factors such as concentration of sol, proportion of free and bound kations, and temperature. For example, with aluminium hydroxide sols there would seem to be the possibility of the sols being metastable towards one of several definite crystalline basic salts or towards either of the crystalline hydroxides $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ in either of the two forms in which these compounds occur. The tendency for such compounds to form or to crystallise varies widely with different metals, so the rate at which metal hydroxide sols change and age may be expected to vary greatly. Relatively stable sols can only be expected in those cases where there is a very small tendency to crystallise on the part of the compounds which might separate. Solubility is important in this connection. The case might arise of a sol which could be metastable towards more than one crystalline compound. The rate of ageing in such a sol would vary according to which particular compound was tending to separate.

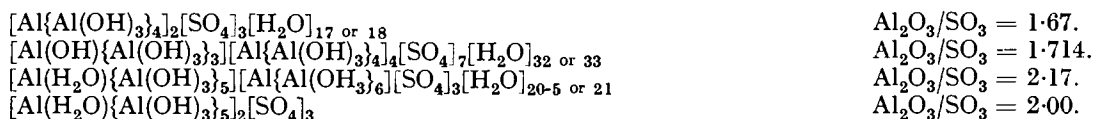
Most of these changes are very slow and do not lead to macroscopic crystals except over long periods of time. Even the microcrystalline material which is formed and is identifiable by means of X-rays may have a very imperfect lattice. It may still even be partly colloidal, in the sense that it may contain considerable portions of strongly adsorbing non-crystalline material. As the micelles of a sol become more crystalline and less adsorbing, their "solubility" gets less until finally the prevailing concentration of the oppositely charged (or "gegen") ions is able to cause flocculation (cf. Bassett and

Durrant, *loc. cit.*, pp. 2927—2933). The precipitate which slowly separates from many sols is, for this reason, to be regarded as being a partly crystalline gel. The case has some similarity to that of the formation of graphite from coke considered by Riley (*Chem. and Ind.*, 1939, 58, 391).

Preparation of Crystalline Basic Aluminium Sulphates.—The observation that certain basic aluminium sulphates are well crystallised and sparingly soluble in water has enabled information of value to be obtained about the nature and conditions of the basic ions formed in aluminium hydroxide sols. The experimental evidence is given on pp. 290, 293. These compounds can be obtained by several methods *via* sols prepared as follows so as to have the basicity of the compound desired: (1) by peptisation of aluminium hydroxide (precipitated from boiling solution) with aluminium chloride, but not with hydrochloric acid; (2) by peptisation of aluminium hydroxide (precipitated at room temperature in the translucent form) with either aluminium chloride or hydrochloric acid; (3) by adding the calculated amount of ammonia, slowly and with constant stirring, to a solution of aluminium chloride. The last is the best and simplest method of preparation, for it avoids the tedious filtration and washing of the precipitated hydroxide. The precipitate first formed rapidly redissolves owing to peptisation and a faintly turbid solution is obtained. This is a true sol, nevertheless, and if it is treated at once with a solution of ammonium sulphate a typical amorphous curd is precipitated. Sooner or later the sol breaks down, so that if some time elapses before addition of the sulphate, the precipitate obtained may be either partly or entirely crystalline.

The spontaneous breakdown of the sol at room temperature is uncertain, however, but if the sol is boiled for a short time it becomes absolutely clear and then gives an entirely crystalline precipitate on treatment with ammonium sulphate. The crystalline basic salts can be easily separated from any coprecipitated amorphous curd by treatment with a little dilute hydrochloric acid before filtration. This dissolves the latter without affecting the former.

From the details given for the preparation of basic aluminium sulphates, it is clear that basic salts and ions must play an important part in metal hydroxide sols. A complete study of all the compounds involved would be very prolonged and only a beginning has been made with the aluminium compounds isolated in the form of sulphates. The number of these salts which exist is evidently large and only provisional statements as to their formulæ, etc., can yet be made. The information now available suggests that at least four very basic aluminium sulphates can be obtained. Those with molecular ratios $\text{Al}_2\text{O}_3/\text{SO}_3 = 1.67, 1.71, \text{ and } 2.17$, and another with a ratio which is probably 2.0 give distinct X-ray powder diagrams suggestive of chemical individuality; their general crystallographic appearance and other characteristics also support this view. Several basic sulphates with very low $\text{Al}_2\text{O}_3/\text{SO}_3$ ratios are already known from other work, not yet published, but these are not considered now. The preparative data given make it probable, however, that there also exist other basic sulphates with $\text{Al}_2\text{O}_3/\text{SO}_3$ ratios below 1.67 and there is probably a number between the salt with this ratio and aluminium sulphate (ratio 0.33). It is hoped that determinations of the structures of all these compounds will be possible by X-ray methods. Various structures could be suggested, but for each of the four *compounds* indicated above one is given which is not incompatible with data for cell weights deduced from X-ray powder diagrams:



The last is included because the X-ray powder diagram of a preparation with $\text{Al}_2\text{O}_3/\text{SO}_3 = 1.90$ was distinctive and did not correspond to a mixture of the other three basic sulphates.

EXPERIMENTAL.

Preparation of Sols (see p. 282).—The hydroxides required were prepared by the action of excess of ammonia, generally in the cold, on a solution of the chloride, and were well washed, first with dilute ammonia and then with cold water. The ammonia washing is essential with lanthanum and neodymium hydroxides, for otherwise autopeptisation occurs when all but a small amount of the chloride has been removed. The washed hydroxide was thoroughly mixed by means of a spatula or pestle into the hydrochloric acid or metal chloride solution used for peptisation. By using solutions of suitable concentrations and allowing for the water and any chlorion (see p. 281) in the wet hydroxide, it was possible to prepare sols of concentrations and metal hydroxide/metal chloride ratios which were very close to those intended.

Appearance of the Sols.—Lanthanum and aluminium hydroxide sols are translucent or milky, though the latter may be quite clear and transparent; the neodymium hydroxide sols are translucent, blue by reflected, reddish by transmitted, light. [The most concentrated neodymium sol prepared was only 0.23N with respect to $\text{Nd}(\text{OH})_3$.]

Thorium hydroxide sols prepared by boiling are clear and transparent, whereas more concentrated ones, prepared in the cold, may be clear and transparent or translucent; if well below n with respect to $\text{Th}(\text{OH})_4$, they remain transparent for years. They show the Tyndall beam. The ferric and chromium hydroxide sols are reddish-brown and green, respectively, and clear and transparent, but show a Tyndall beam. The ferric sols gradually become yellower and less transparent with age and slightly turbid, and the chromium sols very slowly become less transparent.

Thixotropy was very marked in the aluminium sols and in the most concentrated lanthanum sols. All the sols considered in this paper give glass-like residues on evaporation at room temperature over sulphuric acid. These redissolve in water.

Analysis of Sols.—2, 5, 10, or 20 C.c. were used for analysis according to the concentration.

Total metal and total chloride. The sol is boiled with a considerable excess of ammonia, and the precipitate washed with hot dilute ammonia till free from chloride; it is then ignited and weighed as oxide. The estimation of total metal in lanthanum or neodymium hydroxide sols is best done by curdling it with a small excess of ammonium oxalate, igniting the washed curd, and weighing as oxide.

The filtrate from the hydroxide or oxalate precipitate is acidified with nitric acid, and the chloride precipitated and weighed as silver chloride. Alternatively, the chloride is determined in a separate portion of the sol after digestion with nitric acid. The extent to which results obtained by the two methods may differ is shown on p. 287.

"Free" metal ion. The sol is curdled with a solution of a suitable salt added with shaking from a burette. In some cases it is better not to wash the curd, but the volume of filtrate is determined, compared with the volume before filtration, and the necessary allowance made. Lanthanum or neodymium is precipitated from the filtrate and washings as oxalate, the other metals as hydroxide by ammonia. The precipitate is filtered off, washed, ignited, and weighed as oxide.

Ammonium sulphate is the best coagulant for all the sols except those of chromium hydroxide, which it does not precipitate completely. Excess of the sulphate may be used without danger in most cases, but separation of sparingly soluble, crystalline, basic sulphates may occasionally lead to errors. Such separation may be almost entirely avoided by using the minimum amount of a dilute solution of the ammonium salt. Microscopic examination of the curd will show whether any crystals of basic salt have separated. Only a slight excess of ammonium sulphate should be employed with lanthanum and neodymium sols, for excess tends to dissolve the precipitate, and it is best not to wash this. Potassium ferrocyanide is used to curd the chromium hydroxide sols, since it precipitates the micelles quantitatively when added in amounts equivalent to the "bound" chromium ions and does not precipitate "free" chromium ions. The ferrocyanide curd must be well washed with water. The potassium ferrocyanide solution should be freshly prepared with boiled-out water, for otherwise a little alkali may be present owing to oxidation to ferricyanide: this alkali might precipitate some of the free metal ion along with the micelles. The ferrocyanide should be added until no further curd is produced—a point not always easy to determine—for excess should be reduced to a minimum. Any such excess is carried down by the chromium hydroxide when this is subsequently precipitated by boiling the filtrate from the curd with ammonia, and after ignition the chromium sesquioxide is contaminated with ferric oxide, leading to high results for free Cr^{+++} . Ferrocyanide can be used similarly for the aluminium sols, as it does not precipitate free aluminium ions; ammonium sulphate is preferable, however.

The results given in the tables are expressed in mg.-equivs./l. Those for total metal, "free" metal ion, and total chloride were determined directly, whereas the figures for "bound" metal ion were obtained by deducting ("free" metal ion + H) from total chloride, and the figures for "un-ionised" metal (in the micelles) by deducting ("bound" + "free" metal ions) from "total" metal. The ratio n has been defined on p. 281.

Hydron recorded in the tables for thorium and chromium hydroxide sols was determined by titration of the filtrate from curds produced by the minimum amount of metaphosphate. Glass-electrode determinations with the thorium hydroxide sols and the diluted chromium hydroxide sol 3 show that the determinations by the titration method are probably fairly accurate.

"Bound" metal ion includes that present as complex basic ions in solution in the micelles as well as hydrated or basic cations adsorbed on the surface of the micelles (see p. 280). "Free" metal ion includes all metal recovered from the curd filtrate, part of which in some cases may have been present as basic ions. "Un-ionised" metal includes that of metal hydroxide co-ordinated to metal ions in the micelles and in some cases consists almost entirely of this.

Masking of Chloride in Old Sols (see p. 281).

$\text{La}(\text{OH})_3$, sol 9.

Age of sol, days.	Composition, mg.-equivs./l.		
	La.	Cl (after curdling sol with ammonium oxalate and washing precipitate).	Cl (after destruction of sol with HNO_3).
3	1049	157.6	159.1
143	1049	151.2	159.4

$\text{Fe}(\text{OH})_3$, sol 27. The nitric acid method is very troublesome with old ferric and aluminium hydroxide

sols, for the curd produced can only be dissolved with great difficulty and care has to be taken not to lose chlorine during the operation.

Age of sol, days.	Composition, mg.-equivs./l.		
	Fe.	Cl (after curding sol and washing precipitate with ammonia).	Cl (after destruction of sol with HNO ₃).
3	509.7	61.4	—
58	509.7	58.4	61.6
Al(OH) ₃ , sol 3.			
Age, days.	Al.	Cl (by ammonia method).	Cl (by HNO ₃ method).
1785	1242	184	186

A similar result was obtained with another aluminium hydroxide sol 860 days old.

Aluminium Hydroxide Sols.

When aluminium hydroxide is precipitated from boiling solution, it is translucent and is essentially Al₂O₃.H₂O (Böhm, *loc. cit.*). It can be filtered off and washed comparatively easily and can be peptised readily by either hydrochloric acid or aluminium chloride to give translucent sols. A translucent precipitate is obtained also at room temperature if the minimum amount of ammonia is used, but it is filtered off and washed only with extreme slowness.

When a large excess of ammonia is used in the precipitation at room temperature a white opaque hydroxide is obtained which is easily filtered off and washed, but some aluminium remains in solution. With smaller excess of ammonia, the translucent precipitate, on standing in contact with the ammonia, becomes white and opaque in from less than an hour to many hours according to the excess of ammonia employed. This precipitate gives an X-ray diagram characteristic of a microcrystalline solid but not of hydrargillite (gibbsite), the ordinary form of crystalline Al₂O₃.3H₂O. The diagram is identical with that of a preparation obtained and described by Böhm (*loc. cit.*, p. 208), who appears to have considered that it was a second form of Al₂O₃.3H₂O. We are of the same opinion, and have obtained a solid giving the same X-ray diagram by floating a solution of aluminium sulphate upon a concentrated solution of sodium aluminate. The precipitate formed at the junction of the two solutions was separated and well washed after 2 months.

One preparation of the microcrystalline hydroxide was obtained by adding 100 c.c. of approx. 8N-ammonia to 8 g. of aluminium chloride hexahydrate in 100 c.c. of water and leaving the mixture in a closed vessel for a month before filtration and thorough washing with cold water. After drying over concentrated sulphuric acid the water content was 35.3% (calc. for Al₂O₃.3H₂O : H₂O, 34.6%). The air-dried material contained H₂O, 35.7%, but this depends largely on the conditions of precipitation. Another sample, in the preparation of which a much smaller excess of more dilute ammonia had been used, contained H₂O, 44.5%.

The X-ray diagram of the fully dried compound (H₂O, 35.3%) was identical with that of the preparation which approximated to Al₂O₃.4.5H₂O and contained H₂O, 44.5%, so it is clear that no higher hydrate than Al₂O₃.3H₂O is involved.

The whole of the aluminium can be precipitated in the cold from concentrated solutions of the chloride by approximately five-sixths of the ammonia theoretically needed to produce the hydroxide. The precipitate can be regarded either as a basic salt or, as we consider, a gel in which the curding has been produced partly by hydroxyl ions and partly by chlorions. The proportion of the latter present depends upon the dilution of the initial solution, and some of it will be in solution in the micellar fluid. Most of the chlorion is easily replaceable by hydroxyl if more ammonia is added.

The translucent precipitate obtained in the cold is very reactive and is readily peptised by either hydrochloric acid or aluminium chloride to give translucent sols. The opaque, microcrystalline hydroxide is much less reactive, and although milky, opaque sols can be obtained from it by peptisation with either of the agents just mentioned, its behaviour is somewhat uncertain. It does not appear possible to peptise some samples, and the majority of those which can be peptised contain a portion which settles out very easily from the sols produced. We believe that peptisation is usually dependent upon the presence of a proportion of the amorphous material which acts as a protective colloid, so that the micelles of the sol produced contain a microcrystalline core with an emulsoid sheath formed from the amorphous material.

Two portions of the opaque, microcrystalline hydroxide from approx. 3.3 g. of the hexahydrated chloride (the X-ray diagram of which suggested freedom from amorphous material) were treated, one with 1.5 g. of the hexahydrate in 9 c.c. of water, and the other with the equivalent amount (9 c.c.) of 2N-hydrochloric acid. The former had given after 12 days a good, milky, opaque, thixotropic sol with no apparent sediment, but the latter did not give a sol in spite of occasional shaking for 6 days; a further shake then gave a good sol indistinguishable by eye from the other. If the hydroxide contained some of the amorphous form, a thin film of basic salt could be expected to form easily in the solution containing [Al(H₂O)₆]⁺⁺⁺ ions, but with greater difficulty in the acid solution. Addition of 10 c.c. of water after 5 days to the second sol caused it to "break" and a milky sol never re-formed. The other sol also broke spontaneously later and did not re-form.

It seems likely that this spontaneous "breaking" of the sols occurs when the emulsoid sheath either becomes detached from the micelles or, having become saturated with kations, passes into true solution as

basic kations. The experiments on the preparation of very basic sulphates (pp. 290, 293) show that, sooner or later, this will occur. The microcrystalline aluminium hydroxide particles after losing their protective sheaths will settle out as a normal precipitate. The liquid above this precipitate was still a sol, though only faintly turbid. With a small amount of ammonium sulphate it gave an amorphous curd, and the filtrate from this, with much more ammonium sulphate, gave an abundant deposit of small octahedra of ammonium alum. The solution from the sol which had been peptised by aluminium chloride gave more of the amorphous curd than did that from the sol peptised by hydrochloric acid. Conditions in both mixtures were evidently essentially similar to those prevailing in aluminium hydroxide sol No. 9 (Table I) which were studied in much more detail.

Proportion of Sulphate carried down by Different Varieties of Precipitated Aluminium Hydroxide.—Aluminium hydroxide was precipitated from solutions containing known amounts of pure aluminium sulphate in four different ways: (a), in the cold, only sufficient ammonia being used to give a mixture alkaline to litmus; (b) and (c), from boiling solution, about twice and ten times the theoretical amount of ammonia being used, respectively; (d), in the cold with a large excess of ammonia. The several precipitates were then thoroughly washed until apparently free from sulphate, cold water being used for preparations (a) and (d), hot water for (b), and hot dilute ammonia followed by hot water for (c). The washed precipitates were then dissolved in hydrochloric acid, and the sulphate present estimated as barium sulphate. Precipitate (a) had retained 6.13% of the total SO_3 , whence $\text{Al}_2\text{O}_3/\text{SO}_3 = 5.44$. This low value is not surprising, since the ammonia used to form the precipitate was less than that theoretically required for pure hydroxide: it must be regarded as consisting in part at least of basic salt. Preparation (b) had retained 2.06% of the total SO_3 , whence $\text{Al}_2\text{O}_3/\text{SO}_3 = 16.2$, and (c) had retained 0.054% of the total SO_3 , whence $\text{Al}_2\text{O}_3/\text{SO}_3 = 613$. The microcrystalline (d) precipitate, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, had retained 0.2% of the total SO_3 ; *i.e.*, $\text{Al}_2\text{O}_3/\text{SO}_3 = 163.4$: this may be reasonably attributed to surface adsorption. Chloride is less readily adsorbed than sulphate, and a sample of the microcrystalline hydroxide precipitated as in (d) but from the chloride instead of the sulphate contained, after thorough washing, only enough chloride to give an atomic ratio $\text{Al}/\text{Cl} = 1634$.

Preparation (c) gave the X-ray powder diagram characteristic of both natural and synthetic bauxite, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (Böhm, *loc. cit.*). Preparation (b) gave the same diagram, but only the strong lines were visible and they were rather diffuse, while even preparation (a) showed the same lines but very diffuse, indicating a partly amorphous condition.

According to this evidence preparation (c) was definitely microcrystalline, whereas (a) was amorphous with incipient formation of a bauxite lattice, and in (b) the bauxite lattice was still further developed. The large proportion of sulphate present in (a) and (b) did not give rise to any bands in the X-ray diagrams which could be attributed to basic sulphates. We have therefore obtained the bauxite form of the monohydrate both at room temperature and near the boiling point of water, whereas the second form of the trihydrate $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, which we have obtained at room temperature, was first obtained by Böhm at about 100° . It is probably to be regarded as the α -form corresponding to diasporé, $\alpha\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Both bauxite and the other form of the trihydrate (hydrargillite or gibbsite) occur in Nature and, according to Haber (*Naturwiss.*, 1925, 13, 1007), are corresponding γ -forms.

The gel obtained by precipitating an aluminium chloride solution with approximately five-sixths of the ammonia theoretically required to form hydroxide (see p. 287) gave an X-ray diagram showing the strong lines of hydrargillite, which were rather diffuse. This indicates that the gel was amorphous with incipient formation of a hydrargillite lattice. The gel thrown down by ammonium sulphate from old aluminium hydroxide sol No. 9 was a mixture of $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (see p. 289).

It would seem that the evidence is insufficient for any conclusions to be drawn regarding the relative stabilities of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ at different temperatures.

No satisfactory neutral coagulant for aluminium hydroxide sols has been found which will also precipitate the free aluminium ions. There is thus no titration method for determining their acidity. Only the glass electrode is satisfactory. No glass-electrode measurements were made on the earlier sols, but those made on later ones showed that the hydrion concentration was very small except in sol No. 8—a special case. It is therefore reasonable to assume that the hydrion concentration can usually be neglected in cases where no measurements are available.

The figures for "Free Al⁺⁺⁺" are not easily determined and are subject to an uncertainty of possibly about ± 5 mg.-equivs./l. In spite of this, it appears certain that on ageing both types of sol (*i.e.*, those prepared from hot- and from cold-precipitated hydroxide) there is a slow increase in the concentration of the free aluminium ions present: in some cases this is rapid. There is little indication of the attainment of any preferential value of n such as we have found with other hydroxides.

Table I shows our results for a number of sols. Glass-electrode measurements on sols 8 and 12 indicate that, when the hot-precipitated hydroxide is peptised by hydrochloric acid, a considerable hydrion concentration may persist for some days, though most of the free kations are aluminium ions. This suggests that in these translucent aluminium sols a portion, and perhaps the major portion, of the bound kations are hydrions, and that as the sols age these bound hydrions slowly react with the substrate to form aluminium ions which become free, in part at least. Unfortunately, we cannot distinguish between bound hydrions and bound aluminium ions.

Many of the aluminium hydroxide sols showed thixotropy. This applies to both milky and translucent

TABLE I.

Aluminium hydroxide sols.

Sol.	Total Al.	Un-ionised Al.	Bound Al ⁺⁺⁺ .	Free Al ⁺⁺⁺ .	H ⁺ .	Cl ⁻ .	η .	Age (days).
5	1221	1063	94	64	—	158	11.3	5
	"	"	86.2	71.8	—	"	12.3	11
	"	"	84.5	73.5	—	"	12.5	336
7	780	663.3	77.7	39	—	117	8.5	3
	"	"	77.0	39.7	—	"	8.6	12
	"	"	72.6	44.1	—	"	9.1	21
	"	"	71.1	45.6	0.3	"	9.3	96
8	247	146.1	67.9	33	—	110	2.1	1
	"	"	"	"	9.1	"	"	3
9	625.8	532.6	37.6	55.6	—	93.5	14.2	1
	"	"	45.4	47.8	0.3	"	11.7	3
	"	"	36.5	56.7	—	"	14.6	6
	"	"	34.1	59.1	—	"	15.6	42
	"	"	7.0	86.2	0.3	"	76.1	425
	338.0	244.0	6.9	86.8	"	91.7	35.4	980
11	1290	1098	120.2	71.8	—	192	9.1	2
	"	"	131.8	60.2	—	"	8.3	13
	"	"	129.7	62.3	—	"	8.5	34
12	1329	?	?	91.4	—	203.9	?	1
	"	1167.8	61.2	100	42.7	"	19.1	5
	"	?	?	113	—	"	?	7
	"	?	?	155	—	"	?	24
	"	1125.5	31.5	172	—	"	35.7	168
	"	—	—	—	0.4	"	—	172
13	2131.7	2010	121.7	0	0	121.7	16.5	12
14	2100	1555.6	123.8	420.6	—	544.4	12.6	6
	"	"	82.7	461.7	—	"	18.8	25
15	1510.6	872.5	203.1	(640)435	0.7	638.8	4.3	3
	"	"	192.1	(656)446	—	"	4.5	25
16	2007	1485.3	338.1	(918)183.6	0.2	521.9	4.4	—

Notes to Table I.—The figures given under "bound Al⁺⁺⁺" include any bound H⁺ that may have been present (see p. 288). Where this is present, the true values for bound Al⁺⁺⁺ would be less, and those for un-ionised Al greater, by the amount of H⁺; η would become (un-ionised Al)/(bound Al⁺⁺⁺ + H⁺) and would have a larger value than appears in the table.

Sol 5 was made from hydroxide precipitated from the chloride at 100° and peptised by cold hydrochloric acid. Sol 7 was made from hydroxide, prepared as for sol 5, added slowly to 0.2N-hydrochloric acid; in calculating η , the hydron concentration has been taken as 0.3 throughout.

Sol 8 was prepared as follows: 10 c.c. of 2N-hydrochloric acid were ground with a lump of still moist aluminium hydroxide precipitated at 100° which had been stored for 6 months, and the mixture diluted to 30 c.c. and placed in a graduated cylinder; after standing overnight there were a 7.5-c.c. zone of translucent jelly at the bottom of the cylinder, 15 c.c. of practically clear liquid at the top, and a 7.5-c.c. zone, somewhat milky, between the two. Analysis of the upper clear liquid showed that it was a solution of hydrochloric acid and aluminium chloride approx. 0.18N for aluminium and 0.62N for chlorine; 5 c.c. of the jelly from the bottom were shaken with water to yield 30 c.c. of a translucent sol which gave no deposit on standing. This was analysed 1 day after dilution of the jelly.

Sol 9 was prepared from cold-precipitated hydroxide peptised by 0.2N-hydrochloric acid. There was a small deposit from this sol which was shaken before removal of samples for analysis. The amount of this deposit was large in both the 425- and the 980-days old sol. The deposit from the latter gave an excellent X-ray powder photograph for α -Al₂O₃·3H₂O. It was not shaken before analysis of the slightly milky supernatant sol, which was found to contain the proportions of constituents shown in Table I. The sol was specially examined for the presence of basic kations. It was found that 0.15 c.c. of 0.95N-ammonium sulphate just sufficed to cause complete curdling of 20 c.c. of the sol. This corresponds to 6.9 mg.-equivs./l. of bound Al⁺⁺⁺, and gives an η value of 35.4 for the micelles. Much quicker filtration of the curd was obtained if 0.3 c.c. of the ammonium sulphate solution was used, the filtrate remaining quite clear and giving no crystals of basic aluminium sulphate after the addition of 12 g. of ammonium sulphate and 7 c.c. of water, even after several days' standing. This shows that the concentration of basic ions must have been very low. The hydron concentration being taken as still 0.3 mg.-equiv./l., the analytical data correspond to the "free aluminium" being distributed as 2.9 mg.-equivs./l. of [Al{Al(OH)₃}₄]⁺⁺⁺ and 83.9 mg.-equivs./l. of [Al(H₂O)₆]⁺⁺⁺. The value of η found after 425 days is fictitiously high owing to inclusion of the stirred-up deposit. It is possible, but not certain, that the analytical composition of the sol was already the same at that age as when 980 days old. The very low basic kation concentration in the 980-days old sol suggests strongly that, in systems of the general composition of sol 9, the basic kations are metastable and tend to deposit their co-ordinated hydroxide upon the microcrystalline hydroxide. It is of interest, in this connection, that the translucent gel obtained as above from this old sol gave an X-ray powder photograph with many fairly sharp lines which showed that it consisted essentially of α -Al₂O₃·3H₂O and γ -Al₂O₃·3H₂O (hydrargillite) in about equal proportions. The substance of the micelles in such a sol must be regarded as hydroxide rather than basic salt.

Sols 11 and 12 were peptised with hydrochloric acid, but the hydroxide used for sol 11 had been precipitated in

the cold and that for sol 12 at 100°. Sol 12 was thixotropic but not sol 11. Bound Al^{+++} and n could only be calculated for sol 12 for the two dates at which glass-electrode measurements were made owing to the large change in hydron concentration in this sol with age.

Sol 13 had been prepared from cold-precipitated hydroxide peptised by aluminium chloride. It was the only aluminium hydroxide sol in which no free hydron (by methyl-red) or aluminium ions could be detected in the filtrates from curds obtained with sodium metaphosphate and potassium ferrocyanide respectively. The sol gave a large proportion of gelatinous deposit on standing, and this was shaken up before analysis. The analysis gave an average n value of 16.5 for the micelles, but a filtration experiment in which three filter fractions and the residue were analysed indicated that the micelles could be subdivided roughly as follows: 10% with n value 8.4; 22% with n value 10.7; 27% with n value 14.6; 41% with n value 26.

Sol 14 was prepared from cold-precipitated hydroxide peptised by the chloride. It was fairly thixotropic and on standing gave a moderate deposit, which was shaken before analysis. The increase in the amount of free aluminium ions in the 25-days old sol is probably due to conversion of some free Al^{+++} into basic ions.

Sol 15 was prepared from some of the same hydroxide as was used for sol 14, but it was peptised with hydrochloric acid. This sol was not thixotropic and gave no appreciable deposit on standing: it has been discussed on p. 279. The figures show that the free aluminium ions must have been basic. The figures in parentheses for free aluminium ion are experimental. If 60% of this is supposed to be $[Al(H_2O)_4]^{+++}$ and 40% the basic ion $[Al\{Al(OH)_3\}_4]^{+++}$, the other figures give the equivalent amount of Al^{+++} , and these have been used for calculating the data for "bound" Al^{+++} , un-ionised Al, and n .

sols, prepared respectively from cold- and from hot-precipitated hydroxide. Very probably the thixotropic character is determined by the degree of crystallinity of the particular hydroxide, whether this be $\alpha-Al_2O_3 \cdot 3H_2O$ or $\gamma-Al_2O_3 \cdot H_2O$, but the statement sometimes made, that aluminium hydroxide sols prepared by precipitation and subsequent peptisation do not show thixotropy (cf. *Ann. Reports*, 1940, 37, 117), is clearly incorrect. It is not easy to prepare two samples of aluminium hydroxide with exactly the same physical properties, as may be judged from the data given on p. 288. This is mainly because the extent to which the crystal lattice of either $\alpha-Al_2O_3 \cdot 3H_2O$ or $\gamma-Al_2O_3 \cdot H_2O$ has been built up depends upon the exact conditions of precipitation, washing, etc., employed. The behaviour of different preparations of hydroxide, and of sols prepared from them, towards acid may vary considerably, as may the thixotropy shown by the sols. Most strong electrolytes, including acids, curd both types of aluminium hydroxide sol. Relatively high concentrations are required in the case of hydrochloric and nitric acids (generally above 0.5N). Clear, transparent sols of very small n value are not curded by these acids. Hydroxide which has been precipitated by means of a large excess of ammonia has a well-developed $\alpha-Al_2O_3 \cdot 3H_2O$ lattice and is very difficult to dissolve in any but hot concentrated hydrochloric or nitric acid, and this applies to the curds derived from the very milky type of sol. Much the same holds for hot-precipitated hydroxide when this has a well-developed $\gamma-Al_2O_3 \cdot H_2O$ lattice, and for the curds from its sols. Truly amorphous hydroxide dissolves readily even in quite dilute acid.

Dilution has a considerable effect on aluminium hydroxide sols, as illustrated by an experiment with sol 4. This had been prepared from aluminium sulphate, so must have contained some sulphate, but that is immaterial from the present point of view. The total Al content was 1038 mg.-equivs./l. When 8 days old, the sol contained 40 mg.-equivs./l. of free Al^{+++} ; it was then diluted four-fold, and after a further 2 days contained $59.4 \div 4$ mg.-equivs./l. of free Al^{+++} . This figure was unaltered 7 days later. The free Al^{+++} in the original sol was 48.8 mg.-equivs./l. when it was 20 days old. A ten-fold dilution was then made, and after 10 minutes the free Al^{+++} had risen to $55.3 \div 10$, and after 2 days to $64.7 \div 10$ mg.-equivs./l. The effect of dilution appears to be rapid.

Preparation of Crystalline Basic Aluminium Sulphates.—(i) Sol 16. Aluminium hydroxide, precipitated at 100° from chloride solution with a large excess of concentrated ammonia, was well washed with boiling water. It was mixed as a paste measuring 125 c.c. with a solution of aluminium chloride (3.5 g. of $AlCl_3$ in 21 c.c.) and the mixture was shaken occasionally for several days and then allowed to settle overnight. Much deposit was removed by decantation on the fifth day from the mixing, and a further moderate deposit after another 5 days; no further deposit formed during another 15 days. The translucent sol so prepared was not thixotropic, though the first deposit was. The analysis of this sol was made from 4 to 8 days after the last decantation. The two alternative methods gave the same values for the chlorine concentration. The data again show (cf. sol 15) that the free aluminium must be mainly, or largely, present as basic ions. Convincing proof of this was obtained as follows: 5 C.c. of sol 16 (9 days after last decantation) were curded with 53 c.c. of 0.05N-ammonium sulphate. The filtrate from the curd soon began to deposit small rosettes of minute prismatic crystals, which after 28 hours were filtered off, washed several times with cold water, air-dried, and analysed (Found: Al_2O_3 , 40.77; SO_3 , 16.48%; $Al_2O_3/SO_3 = 1.94$) (yield 0.05 g.); it did not contain chloride or ammonia, and seemed to be homogeneous under the microscope. Its aluminium content would account for nearly 30% of the total free aluminium in the sol, but the yield of crystalline basic salt was a minimum value, since the bulky curd had not been washed, so as to avoid dilution of the solution from which the basic salt crystallised. In calculating the n value given for sol 16 in Table I, it was assumed that all the "free" aluminium was present as the basic ion $[Al\{Al(OH)_3\}_4]^{+++}$ so that only one-fifth of the total "free" aluminium had to be considered as free Al^{+++} for the purpose of the calculation.

A week later the rest of the sol (44 c.c.) was worked up similarly, 470 c.c. of the ammonium sulphate

solution being used, but only 0.23 g. of slightly less basic salt was obtained (Found: Al_2O_3 , 39.47; SO_3 , 16.31%; $\text{Al}_2\text{O}_3/\text{SO}_3 = 1.90$). Sufficient solid ammonium sulphate was now added to the filtrate from the crystals (which had been kept separate from the washings) to double the concentration of this salt. After 8 days' standing a further deposit had separated. This was filtered off, washed with water, air-dried, and analysed (Found: Al_2O_3 , 37.00; SO_3 , 18.53%; $\text{Al}_2\text{O}_3/\text{SO}_3 = 1.57$) (yield 0.285 g.). Microscopic examination showed that the solid did not consist of the compound crystallising in minute prisms, and it appeared to be amorphous or glassy.

(ii) Two portions of aluminium hydroxide, precipitated by means of ammonia in considerable excess from boiling solutions of 21 g. of the hydrated chloride in 450 c.c. of water, were thoroughly washed with nearly boiling water. The very wet translucent precipitates, each measuring about 150 c.c., were transferred to two 400 c.c. beakers. To one portion were added 5 g. of hexahydrated chloride dissolved in 30 c.c. of water, and to the other, the equivalent (31 c.c.) of 2N-hydrochloric acid. Complete dispersion in the acid seemed to occur at once, but with the aluminium chloride some curd settled out for some time and 3 days were needed for complete dispersion. There was no visible difference in the appearance of the two sols, which were both translucent (but quite opaque), though the sol prepared by means of hydrochloric acid seemed distinctly more thixotropic than the other.

The two sols prepared in this manner were worked up, after a further two days, for the basic salt, a solution of 2 g. of ammonium sulphate in 100 c.c. of water being used for each. The curds were then filtered off, and soon after filtration was started, separation of crystalline basic salt began in the filtrate from the sol which had been peptised by aluminium chloride, but the other filtrate did not give crystals at any time.

The curd from the sol peptised by acid was microscopically free from crystals, whereas the other contained a considerable proportion. The amount lost in this way is unknown and only 0.203 g. of washed, air-dried crystals was obtained, although a further 2 g. of ammonium sulphate in 100 c.c. of water had been added to each filtrate before the crystals were filtered off. Analysis of the filtrate which gave no basic salt, made some time after the second addition of ammonium sulphate, showed it to be 0.138N with respect to aluminium and 0.149N with respect to chlorine. The crystals obtained as above contained Al_2O_3 , 40.07; SO_3 , 16.89%; $\text{Al}_2\text{O}_3/\text{SO}_3 = 1.85$. The filtrate from the crystals deposited, during 17 days' standing, a further 0.07 g. of amorphous or glassy solid (Al_2O_3 , 35.98; SO_3 , 19.57%; $\text{Al}_2\text{O}_3/\text{SO}_3 = 1.44$).

The reason for the different behaviour of the two sols prepared in the above experiment has already been discussed and attributed to the persistence of hydrion as such when bound to the micelle of hot-precipitated aluminium hydroxide. The glass-electrode measurement on sol 8 (Table I) also shows that hydrion can survive for a considerable time in sols prepared from this hydroxide.

(iii) Aluminium hydroxide precipitated cold in the amorphous translucent condition is so reactive that after adsorption of hydrion immediate reaction occurs so that a very good yield of basic salt can be obtained from it. The hydroxide was precipitated by the minimum amount of ammonia from a solution of 8 g. of hydrated chloride, filtered off, and washed on a Buchner funnel, the washing not being thorough owing to the slowness of filtration. The hydroxide, 7.5 c.c. of 2N-hydrochloric acid, and water to a total volume of 80 c.c. were well mixed with a spatula. After 3 days all but a little sediment had dissolved to give a faintly opalescent solution. To this were added 2.5 c.c. of an ammonium sulphate solution containing 0.924 g. in 50 c.c., and the mixture filtered. It was hoped that this treatment would remove any trace of residual colloid, though no obvious curding took place.

Another 32 c.c. of the sulphate solution were added with constant stirring to the clear filtrate, whereupon a permanent crystalline precipitate of minute prisms began to form. After 10 mins., during which these increased in amount and size, the rest of the 50 c.c. of ammonium sulphate solution was added. The precipitate was separated after 24 hours' standing, well washed with cold water, and air-dried (yield 3.15 g.) (Found: Al_2O_3 , 39.85; SO_3 , 14.55%; $\text{Al}_2\text{O}_3/\text{SO}_3 = 2.14$). This exceptionally well-crystallised preparation consisted mainly of (probably) orthorhombic prisms showing straight extinction, but as there seemed to be a trace of amorphous curd present the following treatment was given to remove this.

2.1 G. of the solid were gently stirred for 5 mins. with 50 c.c. of approx. 0.1N-hydrochloric acid, the mixture quickly filtered (pump), and the crystals washed with cold water till free from chloride. After air-drying, the crystals looked sharp and unaltered and there was now no sign of the presence of any amorphous material. As only 1.5 g. of solid were recovered, 0.6 g. had been lost by solution in the acid. The acid filtrate plus washings measured approx. 125 c.c., and after standing for 2 days had deposited crystals, which after washing and air-drying weighed 0.15 g. Microscopic and X-ray examination and chemical analysis showed these to be essentially identical with the original preparation and also with the acid-washed crystals (Found: for acid-washed crystals, Al_2O_3 , 40.57; SO_3 , 15.14%; $\text{Al}_2\text{O}_3/\text{SO}_3 = 2.10$; for crystals separating from acid solution, Al_2O_3 , 41.61; SO_3 , 15.09%; $\text{Al}_2\text{O}_3/\text{SO}_3 = 2.16$). This remarkable result indicates that the basic salt must have very considerable stability towards acid.

Crystalline basic salt, similar in appearance to that of other preparations, was also made on a small scale by the peptisation of cold-precipitated, translucent aluminium hydroxide with aluminium chloride, but it was not analysed.

Aluminium hydroxide freshly precipitated in the cold is peptised with extreme ease by aluminium chloride, and this is the basis of the modified and simpler procedure used in the following preparations.

(iv) To a solution of 10 g. of aluminium chloride hexahydrate in 75 c.c. of water were added slowly with

constant stirring 22.5 c.c. of approx. 3.2N-ammonia. This gave a perfectly clear sol to which, after 3 days' standing, was added a solution of 2 g. of ammonium sulphate in 30 c.c. of water. The precipitate which separated was mainly an amorphous curd with a proportion of prismatic crystals. After standing for several days, the mixture was diluted to about 150 c.c., and after another 5 days the curd was dissolved by slowly stirring in 2N-hydrochloric acid. After about 7 c.c. of acid had been added, microscopic examination showed that the residual crystals were free from curd. 1.12 G. of washed, air-dried crystals were obtained (Found : Al_2O_3 , 39.91; SO_3 , 18.91%; $\text{Al}_2\text{O}_3/\text{SO}_3 = 1.64$).

(v) The same quantities were used as in (iv), but directly after addition of the ammonia the mixture was gently boiled for 10 mins. This destroyed the sol, so that on addition of the ammonium sulphate a pure crystalline precipitate was obtained. After two days this was filtered off, washed, and air-dried (Found : Al_2O_3 , 39.56; SO_3 , 18.64%; $\text{Al}_2\text{O}_3/\text{SO}_3 = 1.67$); yield 2.3 g.

(vi) With a larger proportion of ammonia than was used in the above two experiments it is difficult, if not impossible, to get all the aluminium hydroxide to peptise, but by the following modification this can be done and a nearly theoretical yield of the basic salt obtained. A solution of aluminium chloride, prepared as in (iv), was treated similarly but 32.7 c.c. of ammonia were used, followed by 9 c.c. of 2.05N-hydrochloric acid, and the mixture gently boiled for 20 mins.; all the curd dissolved, and a clear solution was obtained to which, after cooling, were added 2 g. of ammonium sulphate in 30 c.c. of water (Found : Al_2O_3 , 40.03; SO_3 , 18.77%; $\text{Al}_2\text{O}_3/\text{SO}_3 = 1.67$); yield 4.16 g.

Two other experiments in which minor alterations were made in the general procedure used for the last two preparations gave varying yields of the well-crystallised prismatic crystals, but in both preparations the ratio $\text{Al}_2\text{O}_3/\text{SO}_3$ was 1.67 [Found : Al_2O_3 , (i) 40.11, (ii) 39.75; SO_3 , (i) 18.96; (ii) 18.66%]. The substance is undoubtedly $5\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 17$ or $18\text{H}_2\text{O}$ (Calc. : Al_2O_3 , 40.10, 39.53; SO_3 , 18.87, 18.61%, respectively). The hydrate is stable in the air under normal conditions, samples of the various preparations varying in weight by only $\pm 0.2\%$ over several weeks. The water is probably to be regarded essentially as "packing" water in the crystals, so the proportion of this would probably depend somewhat upon the size and habit of the crystals in different preparations, since they are small. The crystals are essentially rectangular prisms which extinguish at an angle of about 12° to the length. When the prisms are on edge the extinction appears to be straight.

The well-crystallised, basic salt with $\text{Al}_2\text{O}_3/\text{SO}_3 = 2.16$ consists mainly of rectangular prisms and modifications of these which show straight extinction. The reasons for regarding this as a definite compound $13\text{Al}_2\text{O}_3 \cdot 6\text{SO}_3 \cdot 76$ or $77\text{H}_2\text{O}$ are as follows: (1) Its general well crystallised and homogeneous appearance under the microscope: this differs from that of the 1.67 compound, though both are prismatic. (2) It crystallises unchanged from dilute acid. (3) It has a distinctive X-ray diagram. (4) The $\text{Al}_2\text{O}_3/\text{SO}_3$ ratio is practically identical with that (2.17) of the mineral felsöbányite though the degree of hydration differs. The well-crystallised mineral appears to be one of the best-defined basic aluminium sulphate minerals, in spite of the fact that Hintze ("Handbuch der Mineralogie," Vol. 1, p. 4435, 1929-30) casts some doubt upon it. The 76- or the 77-hydrate would require Al_2O_3 , 41.77, 41.54; SO_3 , 15.12, 15.04%, respectively, whereas the analytical data for felsöbányite correspond to a 61- or a 62-hydrate: Haidinger (*Wien. Sitzungsber.*, 1854, 12, 188) reported von Hauer as finding: Al_2O_3 , 45.63; SO_3 , 16.47; H_2O , 37.27%, and regarded the mineral as $2\text{Al}_2\text{O}_3 \cdot \text{SO}_3 \cdot 10\text{H}_2\text{O}$ (Calc. : Al_2O_3 , 44.0; SO_3 , 17.2; H_2O , 38.8%).

Filtrates from the basic salt $5\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot x\text{H}_2\text{O}$, on standing for several weeks at room temperature, frequently deposit very characteristic crystals of a third basic salt. The crystals are Maltese-cross twins shaped remarkably like those of the mineral staurolite. They are usually very well developed though rather small. Very often there is only a small re-entrant angle between the two arms of the cross, and the appearance of the crystals then suggests an octahedron at first glance. In other cases the arms of the cross are much more obvious. The two components of the twin extinguish at a few degrees on either side of the diagonal of the Maltese cross. When the crosses are standing on an arm they present a barrel-shaped outline. Very well-formed crystals of the new compound mixed with much amorphous or "glassy" solid had separated from the filtrate of preparation (v) during 15 weeks' standing in a covered beaker, evaporation having reduced the volume of liquid by about one-fifth. The liquid and most of the amorphous solid were decanted, leaving most of the crystals and some amorphous solid adhering to the vessel. Treatment with 50 c.c. of approx. 0.1N-hydrochloric acid dissolved the amorphous curd almost at once, leaving the crystals, which were filtered off (pump), washed with cold water, and air-dried (Found : Al_2O_3 , 38.78; SO_3 , 17.70%; $\text{Al}_2\text{O}_3/\text{SO}_3 = 1.72$); yield 0.239 g. Even 2N-hydrochloric acid only attacked the crystals very slowly in the cold, though they dissolved rapidly on heating.

(vii) 16.9 C.c. of approx. 3.2N-ammonia were added with constant stirring to a solution of aluminium chloride as in (iv). The clear solution was boiled for 15 mins., diluted to approx. 400 c.c., and 1.5 g. of ammonium sulphate in 25 c.c. of water were added to the warm solution. No precipitate had separated after 12 hours, so a further 1 g. of sulphate was added. A relatively small, bulky precipitate (apparently amorphous or glassy) had separated after 2 days and was removed by filtration. After standing for 19 weeks in a covered beaker, the filtrate deposited a considerable amount of solid. This consisted in part of the coarse Maltese-cross twins and in part of much finer material which showed no definite structure under the microscope and may have been "glassy solid." The mixture was well stirred, and the bulk of liquid (now about 300 c.c.) decanted together with most of the fine solid; the latter was filtered off (pump), washed

with water, and air-dried (0.25 g.). To the 50 c.c. of mixture which contained the coarse crystals were added 5 c.c. of 2*N*-hydrochloric acid which dissolved the fine material rapidly. After a few minutes the coarse crystals were similarly filtered off, washed, and dried (0.68 g.).

The fine crystals, slightly contaminated with the coarse, had $\text{Al}_2\text{O}_3/\text{SO}_3 = 1.64$ (Found: Al_2O_3 , 35.72; SO_3 , 17.06%), and the latter had $\text{Al}_2\text{O}_3/\text{SO}_3 = 1.72$ (Found: Al_2O_3 , 39.16; SO_3 , 17.85%). The hydrate $12\text{Al}_2\text{O}_3 \cdot 7\text{SO}_3 \cdot 75$ or $76\text{H}_2\text{O}$, for which $\text{Al}_2\text{O}_3/\text{SO}_3 = 1.714$, requires Al_2O_3 , 39.06, 38.84; SO_3 , 17.87, 17.77%, respectively.

The following experiment shows that a relatively large proportion of ordinary aluminium ions can coexist in solution with very basic ions. The procedure was as in experiment (vi) except that 20 c.c. of 2.05*N*-hydrochloric acid were added and the mixture was boiled till clear, 2.75 g. of ammonium sulphate in 10 c.c. of water being added to the hot solution; yield of washed, air-dried solid 2.7 g. (Found: Al_2O_3 , 35.90; SO_3 , 17.79%; $\text{Al}_2\text{O}_3/\text{SO}_3 = 1.58$). 10 G. of ammonium sulphate were added to the filtrate (without washings), and after standing for a week a considerable separation of well-formed square and octahedral crystals had occurred. These were separated by settling and decantation from much fine amorphous solid which had also formed. 0.6 G. of washed, air-dried crystals was obtained and another 0.1 g. after a further 3 months' standing, but much was lost during decantation and washing. Probably about 2.5 g. of these crystals in all had been formed. They gave a strong reaction for ammonia, were isotropic, and consisted of ammonium alum contaminated with a little of the insoluble basic material (Found: Al_2O_3 , 11.62; SO_3 , 35.44. Calc.: Al_2O_3 , 11.26; SO_3 , 35.32%).

An *X*-ray rotation photograph about the cube axis of one of the crystals proved conclusively that these did in fact consist of ammonium alum, for the atomic spacings calculated from the photograph agreed with those given for this alum by Lipson and Beevers (*Proc. Roy. Soc.*, 1935, *A*, 148, 666).

Under certain conditions an ammonium basic aluminium double sulphate separates as small very brilliant crystals from the filtrates of sols treated with ammonium sulphate. Under the microscope these resemble regular octahedra, but they are strongly double refracting. They are single crystals and not twins, though there is a slight superficial resemblance to the maltese-cross twins formed by the basic sulphate $12\text{Al}_2\text{O}_3 \cdot 7\text{SO}_3 \cdot 75$ or $76\text{H}_2\text{O}$.

(viii) To 10 g. of hydrated aluminium chloride in 80 c.c. of water were added fairly quickly 32.7 c.c. of approx. 3.2*N*-ammonia, which gave a faintly alkaline mixture. This was then poured into about 80 c.c. of boiling water, and the whole boiled for 10 mins. A translucent suspension was obtained which was set aside over the week-end. A bulky gel had settled out, with a moderate amount of clear liquid above it. The filtrate from the gel was treated with a solution of 1 g. of ammonium sulphate in 10 c.c. of water. This caused separation of a small amount of non-crystalline curd, which was filtered off to give an absolutely clear filtrate. To this were added 10 g. of solid ammonium sulphate, which dissolved without producing any further precipitate. After 16 days' standing a small deposit of crystals with the above-described characteristics was filtered off. Unfortunately, the crystals were washed with water, which caused decomposition and rendered them opaque—the partly decomposed crystals weighed 0.055 g. The volume of solution from which they had separated was approx. 125 c.c. The filtrate from these (without washings), after 6 weeks' standing, had given a further small deposit of the crystals, which was filtered off, washed (without decomposition) with 3 c.c. of 50% alcohol, and air-dried. The crystals were quite unaltered in appearance by this treatment; yield 0.037 g. (Found: NH_3 , 4.2; Al_2O_3 , 31.3; SO_3 , 24.8. $[\text{NH}_4]_4[\text{Al}\{\text{Al}(\text{OH})_3\}_4]_2[\text{SO}_4]_5[\text{H}_2\text{O}]_{22}$ requires NH_3 , 4.2; Al_2O_3 , 31.4; SO_3 , 24.6%). As the ammonia estimation had to be made colorimetrically with Nessler reagent, it is probably subject to an uncertainty of $\pm 10\%$.

The conditions needed for the separation of this double *salt* appear to be a low concentration of the basic ion and a relatively very high concentration of ammonium and sulphate ions.

Chromium Hydroxide Sols.

Chromium chloride and hydrochloric acid are equally effective as peptising agents for chromium hydroxide: the sols produced are identical which ever agent is employed, and they are very stable. We have found no indications of any liberation of bound kation due to either age or dilution. Chromium hydroxide sols gave no precipitate with hydrochloric acid in any circumstances. Table II gives some of the results obtained with these sols. All those listed were peptised by means of chromium chloride, except No. 7 for which hydrochloric acid was used. The most striking feature of the table is the marked tendency for the sols to have an *n* value close to 4. This appears to show that the micelles are adsorptively saturated and that this condition can be attained with little if any excess of peptising agent. It may be concluded that the charge on the micelles is due, almost entirely, to adsorbed chromium ions, since the sols have such a very small acidity.

Differences found in the free chromium-ion content of several of the sols at different ages are attributed to uncertainties in the analytical methods. High results for free chromium when little or none is present are due to the use of slightly too little ferrocyanide for precipitation of the micelles.

All the hydrion figures given in the table were obtained by the titration method after curding with metaphosphate. They are probably too high, since metaphosphate causes hydrolysis of chromium chloride (see p. 279), and their chief value is in showing that the hydrion concentration of those sols is very low.

Only one glass-electrode measurement was made on a chromium sol, *viz.*, on a 5-fold dilution of sol 3 when this was 1470 days old. Analysis of the diluted sol gave :

Total Cr.	Un-ionised Cr.	Bound Cr ⁺⁺⁺ .	Free Cr ⁺⁺⁺ .	H ⁺ (by glass electrode).	Cl ⁻ .	<i>n</i> .
1728	1299	319	111	1.16	431	4.07
whence the undiluted sol contained						
8640	6495	1595	555	5.8	2155	—

It is seen that 5-fold dilution caused no separation of previously bound kations. The diluted sol underwent no further appreciable change on ageing.

TABLE II.

Sol.	Total Cr.	Un-ionised Cr.	Bound Cr ⁺⁺⁺ .	Free Cr ⁺⁺⁺ .	H ⁺ .	Cl ⁻ .	<i>n</i> .	Age (days).
1	1580	1184	232	164	3	399	5.1	3
2	1944	1595	350	0	0	351	4.6	3
3	8640	6483	1636	521	3.8	2163	3.96	38
"	"	6476	1609	555	6	2170	4.03	83
"	"	6482	1618	540	(38)	2164	4.01	379
"	"	6502	1618	520	(77)	2144	4.02	510
"	"	(6523 ?)	(1562 ?)	(627)	7.6	2123	4.17	1270
				(555 ?)				
4	4372	3538	818	16	3	837	4.33	7
	4435	3600	835	0	0.9	836	4.31	18
	4432	3502	830	0	1.5	832	4.22	52
	4555	3693	852	10	0.9	863	4.34	322
6	6786	5442	1318	26	0	1344	4.13	7
"	"	"	1338	6	0	"	4.07	56
"	"	"	1319	26	0	"	4.13	165
7	3294	2594	625	75	8	708	4.15	3
"	"	2587	623	74	0.8	"	4.15	161
"	3255	2542	603	110.5	0.9	714	4.21	323

Sol 3 became somewhat more concentrated with increasing age owing to slight evaporation. The figures given in the table were obtained from the experimental figures by recalculation to a constant average figure for total chromium. The hydrion figures 38 and 77 for this sol are clearly much too high. A constant value of 6 for the hydrion concentration, based on the glass-electrode measurement on the diluted sol, has been assumed in calculating the bound Cr⁺⁺⁺. The value 627 for free Cr⁺⁺⁺ at age 1270 days must be wrong. A value 555 derived from the diluted sol analysis has been used to calculate the bound Cr⁺⁺⁺. The chlorion concentration at age 1270 days was also determined by direct precipitation with silver nitrate of a nitric acid digestion of the sol. The value 2113 so obtained does not support the view that the low value 2123 obtained by the usual method was due to some chlorion having become "masked" in the old sol.

Sols 3 and 4 showed strikingly different behaviour in two respects which can be attributed to the great difference in the amount of free chromium ion in the two sols. Sol 4 was much more viscous than sol 3, though the latter was nearly twice as concentrated. The viscosities were measured in an Ostwald viscometer at 16° with the following results :

	Specific gravity (<i>S</i>).	Time readings (<i>N</i>), secs.	<i>S</i> × <i>N</i> .	Relative viscosity, $\frac{SN}{S_w N_w}$.
Water	1.000	62	62	1
Sol 3	1.257	344	432.4	6.97
Sol 4	1.129	524	591.6	9.54

The lower viscosity of sol 3 appears to be due to the presence of free chromium chloride, which was 6.4% of the total chromium. Sol 3 retained its highly mobile character for 3½ years with no deposit. Sol 6 was also much more viscous than sol 3 though less concentrated. It is well known that when a sol approaches "purity" by means of dialysis its viscosity increases often up to a point at which spontaneous coagulation occurs. On evaporation over sulphuric acid at room temperature, sol 3 gave a glassy residue which dissolved in cold water on standing for several hours.* Analysis of the regenerated sol so obtained gave :

Total Cr.	Un-ionised Cr.	Bound Cr ⁺⁺⁺ .	Free Cr ⁺⁺⁺ .	H ⁺ .	Cl ⁻ .	<i>n</i> .
609.5	457.9	151.6	0	1.7	153.3	3.02

showing that the whole of the chromium ions which were free in sol 3 had become bound, with corresponding reduction in the *n* value. If the hydrion (determined by the titration method) is taken to be zero, the *n* value becomes 2.98. The high concentration of chromium ions produced by the evaporation may have caused some less basic kation to be formed than is present in the micelles which have an *n* value of 4.

When sol 4 was similarly evaporated, the glassy residue was only very slowly dissolved by cold water, about 3% having dissolved after 24 hours, but all dissolved slowly in warm water. This sluggishness may be due simply to greater initial dehydration and consequent slower rehydration and dispersion. Very insoluble green products with a conchoidal glassy fracture are often obtained as deposits during the preparation of

* Some of the glassy residue which had been kept for 3 years took 3 days to disperse completely in cold water.

chromium hydroxide sols, but only if the proportions of hydroxide and of chromium chloride or hydrochloric acid employed are such as would represent a ratio $\text{Cr}(\text{OH})_3 : \text{CrCl}_3$ of more than 4. Several such deposits obtained during the preparation of sols 4 and 6 had compositions between about $[\text{Cr}(\text{OH})_3, x\text{H}_2\text{O}]_{5.86}\text{CrCl}_3$ and $[\text{Cr}(\text{OH})_3, x\text{H}_2\text{O}]_{6.33}\text{CrCl}_3$, where the value of x depended upon the precise conditions of drying but was about 3 for "air-drying" at room temperature. The deposits obtained during the preparation of sol 7, where hydrochloric acid was the peptising agent and in which successive amounts of the hydroxide were added to the acid, had smaller n values, however. These ranged between 4.43 for the earlier deposits and 6.04 for the last deposit. The sols finally produced contained little if any free chromium ions, as can be seen from the tables, and their micelles had an n value of about 4. The nature of these glassy products has been discussed on p. 281.

Ferric Hydroxide Sols.

We have prepared and examined two different types of ferric hydroxide sol: (a) those prepared by peptisation of cold-precipitated ferric hydroxide with either ferric chloride or hydrochloric acid, and (b) those obtained by addition of boiling water to ferric chloride.

It is not generally realised how difficult it is to obtain pure iron compounds. Most of those usually found in laboratories, even when of "AnalaR" quality, contain more or less manganese, and the commercial ferric chloride is often very impure: zinc as well as manganese may be present in considerable amount. Ferric hydroxide sols prepared from such materials contain most of the zinc or manganese as free kations. A sample of Kahlbaum's ferrous ammonium sulphate, stated to be free from manganese, was actually free from both manganese and zinc but contained a large amount of aluminium. This was about 2.5 equivs. % of the total (Fe + Al) and was present as crystals of ammonium alum (identified by refractive index and other optical properties). Some of our sols were prepared from this material, which was purified by precipitation, hot, with excess of sodium hydroxide after oxidation with nitric acid. After washing, digestion with more hydroxide, and further washing, the precipitate was dissolved in the minimum amount of concentrated hydrochloric acid, and the diluted solution precipitated cold with excess of ammonia. Most of our sols were, however, prepared from "AnalaR" anhydrous ferric chloride, which was found to be the purest purchasable iron compound, containing only 0.07 part by weight of manganese per 100 parts of iron. The statements on the labels of this material that "sodium and other metals" amount to 0.04% is misleading, since any manganese present would be carried down by the iron and missed by the method of analysis used for label purposes.

TABLE III.

Sol 20 ($n = 0.5$ or 1.5). Prepared by addition of 500 c.c. of boiling water to 3 c.c. of approximately 30% ferric chloride solution (Found: Total Fe, 43.9; total Cl, 43.7 mg.-equivs./l.).

Ageing shown by the increase of total free iron in solution:

Age, days	1	3	21	31	55	73
Free iron, mg.-equivs./l.	16.3	18.8	23.8	25.4	25.2	24.7

Free H⁺ by the glass electrode was 5.9 mg.-equivs./l. when 55 days old. Sols 28, 29, and 30 were prepared in a similar manner.

Sol 28; $n = 6.1$ or 7.1 ; total Fe = 83.

Total free Fe ⁺⁺⁺	Free H ⁺	Cl ⁻	Age (days)	Total free Fe ⁺⁺⁺	Free H ⁺	Cl ⁻	Age (days)
42.8	—	83	3	—	23.6	83	9
—	22.9	"	4	50.8	—	"	11
47.8	—	"	5	53.8	25.1	"	33
50.4	—	"	7				

Sol 29; $n = 1.3$ or 2.3 (at 21 days); total Fe = 117.4.

53.1	—	117.1	2 (hours)	70.9	24.0	117.1	10
56.6	—	"	1	72.4	28.8	"	12
61.0	—	"	2	73.5	—	"	15
63.2	—	"	3	74.9	28.2	"	17
66.3	38.0	"	5	76.6	22.9	"	21
68.4	31.6	"	7	87.3	—	"	276

Sol 30; $n = 6.2$ or 7.2 ; total Fe = 136.8.

72.9	—	135.7	2 (hours)	88.9	30.9	135.7	10
76.3	—	"	1	90.8	30.9	"	12
82.1	31.6	"	2	103.5	—	"	119
84.4	30.9	"	4	103.5	27.6	"	220
88.2	33.9	"	7				

Sols prepared by the action of boiling water upon ferric chloride contain relatively more free hydrion than do those prepared by peptisation of ferric hydroxide. They also age more rapidly by some process which leaves the concentration of free hydrion practically constant while the amount of free ionic iron increases. The red sols become more orange with age. It is suggested that initially these sols contain micelles of (FeO·OH) carrying adsorbed hydrion. On standing at room temperature, the bound hydrions slowly react with the micelles to set free ordinary ferric ions. If one assumes that no bound hydrions were left but only bound Fe⁺⁺⁺ when the last readings on each sol were made, the smaller n values shown against the sol numbers can be calculated for the dates of the last readings. The presence of basic ions in the intermicellar

liquid would lower the n values still further. If, however, it is supposed that all the bound kations were hydrions, then the larger values of n may be calculated for the dates of the last readings. We consider that the higher n values are the more probable, and that in this type of sol, the charge on the micelles is due mainly to bound hydrion. The change which occurs on ageing is, of course, a sort of reversal of the original hydrolysis by which the sol was formed. This reversible process is less simple than is represented by such equations as (i) $\text{Fe}^{+++} + \text{HOH} \rightleftharpoons [\text{FeOH}]^{++} + \text{H}^+$ or (ii) $\text{Fe}^{+++} + 3\text{HOH} \rightleftharpoons \text{Fe}(\text{OH})_3 + 3\text{H}^+$, and is more in keeping with the complex equation (iii) $n\text{Fe}^{+++} + 3n\text{HOH} \rightleftharpoons [\text{Fe}(\text{OH})_3]_n \text{H}^+_{3n}$. It would seem that the actual reversible hydrolysis involves reactions similar to (i) and (ii) but occurring between the bound kations and the hydroxide substrate of the micelles.

The hydrion concentrations were all obtained by means of the glass electrode. The variations for any one sol are probably within the limits of error of the measurements.

Table III gives our results with some of these hydrolysis sols.

The results shown in Table IV for sols prepared by the cold method suggest that the micelles would be approximately saturated with bound kations at an n value of about 7. The values for free hydrion which are enclosed in parentheses in Table IV were obtained by the metaphosphate method and are therefore probably too high. They are given because they serve to show that there is almost certainly a slow but definite increase in the acidity of these sols on ageing.

An unsuccessful attempt was made to peptise, by means of hydrochloric acid, ferric hydroxide which had been precipitated at about 100° and washed with ammonia and water at this temperature. The mixture on the first day was found to contain total Fe, 1341; total Cl, 340 mg.-equivs./l., the chlorine being determined after solution of the mixture in nitric acid. Even after 39 days with frequent shakings, the mixture gave a

TABLE IV.

Sol no.	Bound Fe ⁺⁺⁺	Free Fe ⁺⁺⁺	Free H ⁺	Cl ⁻	n	Age (days)	Bound Fe ⁺⁺⁺	Free Fe ⁺⁺⁺	Free H ⁺	Cl ⁻	n	Age (days)
Sol no. 19, peptised by 2N-HCl; total Fe = 1886; un-ionised Fe = 1689.												
170	27	(5.5)	210	9.9	8	168.8	28.2	(6.5)	—	10.0	150	
184	13	(2.5)	—	9.2	11	150	47	(9.5)	—	11.2	241	
179	18	(3.5)	—	9.4	14	137	60	(18.0)	—	12.3	610	
167	30	(4.5)	—	10.1	84	125	72	—	211.3	13.5	1134	
						—	—	12.9	—	—	1176	
Sol no. 22, peptised by 2N-HCl; total Fe = 2554; un-ionised Fe = 1988.												
255	311	—	584	7.8	1	230	336	—	584	8.6	24	
257	309	—	"	7.7	3	225	341	19.1	"	8.8	46	
264	302	—	"	7.5	5	213	353	—	"	9.3	71	
255	311	—	"	7.8	7	196	369	17.0	"	10.1	115	
221	345	—	"	9.0	14	180 *	378	—	576	10.3	492	
Sol no. 23, peptised by FeCl ₃ ; † total Fe = 2819; un-ionised Fe = 2173.												
273	373	—	666	8.0	1	266	380	—	666	8.2	24	
274	372	—	"	7.9	3	242	404	24	"	9.0	46	
294	352	—	"	7.4	7	241	405	—	"	9.0	72	
277	369	—	"	7.8	9	—	—	15.5	"	—	116	
279	367	—	"	7.8	14	—	—	—	—	—	—	
Sol no. 24, peptised by FeCl ₃ ; ‡ total Fe = 2348; un-ionised Fe = 1893.												
221	235	—	470	8.6	2	187	269	—	470	10.1	20	
216	240	—	"	8.8	5	174	282	13.8	"	10.9	29	
200	256	—	"	9.5	12	187	269	—	"	10.1	62	
194	262	—	"	9.8	15	—	—	14.5	—	—	98	
Sol no. 24a, peptised by FeCl ₃ ; § total Fe = 2333; un-ionised Fe = 1890.												
165	278	—	472	11.5	3	138	305	—	472	13.7	16	
151	292	—	"	12.5	6	140	303	29	"	13.5	30	
147	296	—	"	12.9	9	123	320	—	"	15.4	63	
141	302	—	"	13.4	12	126	317	—	"	15.0	96	

* A heavy sediment had settled out from this sol after 490 days and, though vigorously shaken, some remained adhering to the flask when a portion of the sol was removed for analysis, so it then had total Fe = 2407, un-ionised Fe = 1849. The yellow sediment was shown to retain 19% of its total chlorine content after digestion with hot ammonia. In calculating the n values of sols 19 and 22 a steady value of 13 and 18 respectively has been taken for the hydrion concentration. The bound kation has been assumed to be only Fe⁺⁺⁺.

† Free H⁺ taken as 20 throughout in calculating n values for this sol.

‡ Free H⁺ taken as 14 throughout in calculating n values for this sol.

§ After sol 24 had been prepared half of it was heated to 85° and then kept at about 60° for 14 hours. This sol (24a) was very opaque. Heating has increased the free hydrion and free iron. Although this is somewhat similar to the effect of age, there is a difference, for in sol 24 little if any of the chlorine was masked even after 62 days, whereas sol 24a after 3 days gave 472 mg.-equivs./l. of chlorine by the method in which the sol was first destroyed by nitric acid, while precipitation of the sol by ammonia and thorough washing of the curd by ammonia only gave in the filtrate chlorine equivalent to 419 mg.-equivs./l. in the sol. When the sol was 96 days old a value of 441 mg.-equivs./l. of chlorine was found by the direct ammonia method.

TABLE IV (contd.).

Bound Fe ⁺⁺⁺ .	Free Fe ⁺⁺⁺ .	Free H ⁺ .	Cl ⁻ .	n.	Age (days).	Bound Fe ⁺⁺⁺ .	Free Fe ⁺⁺⁺ .	Free H ⁺ .	Cl ⁻ .	n.	Age (days).
Sol no. 25, peptised by FeCl ₃ ; total Fe = 2740; un-ionised Fe = 2452.											
260	28	—	299	9.4	1 (hr.)	263	25	—	299	9.3	13
267	21	—	..	9.2	1	261	27	—	..	9.4	21
274	14	(1.6)	..	8.9	2	237	51	11	..	10.3	58
276	12	(3.8)	..	8.9	5	210	78	—	..	11.7	229
271	17	—	..	9.0	7						
Sol no. 26, peptised by slow addition of Fe(OH) ₃ to 0.2N-HCl; ¶ total Fe = 487; un-ionised Fe = 441.											
35	11	(0.8)	57	12.6	4	35	11	10.6	57	12.6	71
35	11	(6.2)	..	12.6	11	33	13	(11.6)	..	12.4	118
36	10	(6.6)	..	12.3	19	33	13	8.9	..	12.4	125
33	13	(7.0)	..	12.4	35	30	16	(11.9)	..	14.7	243
Sol no. 27, prepared by adding Fe(OH) ₃ to 0.2N-HCl; total Fe = 510; un-ionised Fe = 455.7.											
43	11.3	(8.5)	61.4	10.6	5	41	13.3	—	61.4	11.1	60
43.5	10.8	—	..	10.5	7	38.3	16.0	—	..	11.9	130
42	12.3	7.1	..	10.9	11	24.6 **	24.4	(12.4)	..	18.7	265

Sol 31 and its dilutions. No glass-electrode measurements were made on this sol, but results with other sols indicate that the hydrion concentration of sol 31, prepared by peptisation of Fe(OH)₃ with 2N-HCl, would have been about 11 mg.-equivs./l. This value has been assumed in calculating the *n* value of this sol.

Total Fe = 2468; un-ionised Fe = 2184.

Bound Fe ⁺⁺⁺ .	Free Fe ⁺⁺⁺ .	Cl ⁻ .	n.	Age (days).	Bound Fe ⁺⁺⁺ .	Free Fe ⁺⁺⁺ .	Cl ⁻ .	n.	Age (days).
226.2	57.8	295	9.7	3	224.4	59.6	295	9.7	17
232.7	51.3	..	9.3	5	219.4	64.6	..	10.0	21
225.6	58.4	..	9.7	13					

5-Fold dilution.			10-Fold dilution, when sol 31 was 13 days old.		20-Fold dilution, when sol 31 was 13 days old.	
Age of sol 31 at dilution, days.	Time since dilution, days.	Free Fe ⁺⁺⁺ .	Time since dilution, days.	Free Fe ⁺⁺⁺ .	Time since dilution, days.	Free Fe ⁺⁺⁺ .
13	3	60	1	51.2	1	35
13	5	66.5	3	58.4	3	41.7
17	1	64	5	55.7	6	45.3
19	1	64.9				

Actual results for free Fe⁺⁺⁺ have been multiplied by 5, 10, and 20, respectively, so as to make the effect of dilution clearer. The results, taken in conjunction with that of the single dilution of sol 26, suggest that the effect of dilution is to upset the hydrolytic equilibria with replacement of a certain amount of the free [Fe(H₂O)₆]⁺⁺⁺ ions by the equivalent amount of hydrion, the hydroxide so produced presumably becoming attached to the micelles. This would indicate that there are practically no free basic kations in these ferric hydroxide sols, but only ordinary ferric ions and hydrions.

|| About 2% of the chlorine was held up by the curd obtained with ammonia at age 58 days. Hydrion concentration taken as 11 throughout in calculating *n*.

¶ Sol 26 gave a slight deposit on standing until about 40 days old, when peptisation seemed complete. Hydrion concentration taken as 11 in calculating *n*. Ageing of this sol appears to be very slow. The curd obtained with ammonia when it was 4 days old held up no chlorine, whereas that at 118 days held up about 1% of the total. A 10-fold dilution of sol 26 was made when it was 125 days old, and after 2 days the dilution contained 4.3 ÷ 10 mg.-equivs./l. of Fe⁺⁺⁺ and 16.6 ÷ 10 mg.-equivs./l. of H⁺.

** In this solution, un-ionised Fe = 461.

large deposit on standing and contained 270 mg.-equivs./l. of free Fe⁺⁺⁺; 7.4% of the total chlorine was held up by the curd obtained by addition of ammonia after repeated washing with ammonia.

Lanthanum Hydroxide Sols.

Lanthanum hydroxide is such a strong base that it is extremely difficult to prepare its sols quite free from carbonate. This was not fully realised until much work on these sols had been done. Apart from this difficulty, they are among the easiest hydroxide sols to prepare, and in fact, auto-peptisation occurs so readily on washing the hydroxide that this is not easily obtained pure; in order to prevent this, a sufficient concentration of hydroxyl ions must be maintained in washing out the chloride. Addition of ammonia does not always suffice for this purpose, and some pure sodium hydroxide should be added in such cases; washing can be completed with pure water.

The oxalate, La₂(C₂O₄)₃·10H₂O, was ignited in platinum, and a neutral solution of the chloride prepared by dissolving the lanthana in the calculated amount of hydrochloric acid. This solution was used for preparing lanthanum hydroxide, and also for peptising it in sols 7 and 8, hydrochloric acid being used for this purpose for all the other sols given in Table V. When protected from carbon dioxide, lanthanum hydroxide sols are very stable and the bound lanthanum ions then only become free very slowly. Treatment

of the sols with carbon dioxide liberates lanthanum ions rapidly and causes a gel to separate. This is not the normal effect of a coagulating anion for this does not displace the bound kations. Carbonic acid, even in very low concentration, probably acts on these sols as follows: (a) on account of the strongly basic character of lanthanum hydroxide, bound lanthanum kations are displaced by the equivalent amount of hydrion with relative ease; (b) the bound hydrion then reacts with the substrate to produce more lanthanum ions which probably remain bound unless displaced by more hydrion; (c) carbonate ions exert the well-known effect of bivalent anions and ultimately cause curdling of the sol; (d) continued action of carbonic acid will cause complete carbonation of the original hydroxide.

The ageing of lanthanum hydroxide sols is shown in Table V. Sols 7 and 8 were preserved in stoppered bottles in a desiccator containing soda-lime, and sol 3 was kept in a stoppered bottle, but not in a desiccator. Sols 9 and 10 were kept in flasks, closed by tightly fitting rubber bungs, but not in a desiccator.

There had been some contact with the atmosphere during the preparation of these sols; it was probably least with sols 9, 11, and 13, but nevertheless, treatment of sol 9 with acid showed the presence of traces of carbonate. The experiment with sol 10 shows the marked effect of carbon dioxide deliberately introduced into the system. It is relatively easy to protect the sols from this gas once they are prepared. The chief difficulty arises in the preparation of the hydroxide, especially in its collection and washing.

The following conclusions follow from our experiments. (i) Peptisation by either hydrochloric acid or lanthanum chloride is complete after 3 days or less. (ii) The sols age extremely slowly when protected from carbon dioxide (sols 7 and 8) but more rapidly when slow access of this gas can occur (sol 9). (iii) The sols are completely precipitated, with formation of crystalline lanthanum carbonate, when deliberately treated with carbon dioxide (sol 10). (iv) Dilution with conductivity water has a negligible ageing effect in liberating lanthanum ions (sol 10); ordinary distilled water has a marked effect on account of the carbon dioxide present (sol 3a). (v) Sols with an average n value at least as low as 7.1 can be prepared, although in most cases the value was much greater than this.

TABLE V.

Lanthanum Hydroxide Sols.

Sol. No.	Total La.	Un-ionised La.	Bound La ^{'''} .	Free La ^{'''} .	Cl ['] .	n .	Age (days).
3	1778	1539	88	151	239	17.5	9
	"	"	87	152	"	17.7	14
	"	"	"	"	"	"	25
	"	"	80	159	"	19.2	163
3a	1844	1606	84	156	240	19.1	17
dilution {	10	Free La ^{'''}	73 ÷ 10	167 ÷ 10	—	—	—
	20	ordinary	66 ÷ 20	173 ÷ 20	—	—	—
	40	distilled	58 ÷ 40	181 ÷ 40	—	—	—
	50	water	dilution	47 ÷ 50	192 ÷ 50	—	—
7	468	431.8	20.2	16.0	36.2	21.4	3
	"	"	20.9	15.3	"	20.7	9
	"	"	17.4	18.8	"	24.8	119
	"	"	17.9	18.3	"	23.9	561 *
8	1352	1063	33	256	289	32.2	1
	"	"	57	232	"	18.6	2
	"	"	65	224	"	16.3	3
	"	"	60	229	"	17.7	5
	"	"	58	233	291	18.2	116
9	1064	904.9	105.1	54	159.1	8.6	3
	"	"	104.6	54.5	"	8.7	4
	"	"	103.9	55.2	"	"	5
	"	"	97.3	61.8	"	9.3	7
	"	"	87.3	71.8	"	10.4	35
	"	904.6	79.7	79.7	159.4	11.3	143
10	1007	848.5	54.1	104.4	158.5	15.7	3
	"	"	47.9	110.6	"	17.7	12
dilution 50 {	with conductivity water when sol		46.3 ÷ 50	112.2 ÷ 50	—	18.3	—
	10 was 12 days old: two separate experiments one day after dilution		55.6 ÷ 50	102.9 ÷ 50	—	15.3	—
11	142.4	124	6.4	12.0	18.4	19.4	3
	"	"	6.2	12.2	"	20	8
	"	"	5.9	12.5	"	21.0	16
13	72.6	44.3	6.2	22.1	28.3	7.1	1
	"	"	"	"	"	"	13

* Evaporation in sodium hydroxide desiccator between 119 and 561 days had raised the concentration of total La to 593. Experimental figures have been reduced in the ratio 468/593.

Table V shows that the n values of the sols are usually large even when a high concentration of lanthanum ions is present, but there is no simple relationship between the value of n and the concentration of lanthanum ions. This suggests that some factor other than a simple adsorption of lanthanum ions is involved. We

consider that the large n values are due to partial carbonation of the micelles. If this is correct, it follows that the lanthanum (and neodymium) hydroxide sols are not strictly comparable with the other hydroxide sols dealt with in this paper. They are sols in which the micellar charge has been partly neutralised by addition of carbonate ions. It is probable, from the amount of free lanthanum or neodymium ions present, that the micelles of all the sols were adsorptively saturated.

A few of the lanthanum sols (*e.g.*, No. 13) were translucent, but most had a milky appearance and had a marked tendency to form deposits on standing for even a short time. They behaved, in fact, more like suspensions of charged particles than true sols. For instance, by filtering sols 9 and 10 through a Whatman No. 50 (hardened) paper on the pump, a gel and a clear solution of lanthanum chloride were obtained.

The data in the table refer to sols which had been shaken up immediately before removal of samples for analysis. The tendency of many of the lanthanum sols to give deposits on standing and their lack of homogeneity can be illustrated by the behaviour of sols 9 and 11. The remainder of sol 9, after the data recorded in Table V had been obtained, was kept without shaking, and the translucent liquid above the deposit was analysed when the sol was 163 and 453 days old. The results obtained were :

Total La.	Un-ionised La.	Bound La ⁺⁺⁺ .	Free La ⁺⁺⁺ .	Cl ['] .	n .	Age (days).
595.3	440.6	70.4	84.3	154.7	6.3	163
173.4	41.6	27.4	104.4	131.8	1.5	453

It is evident that only micelles with very small n values were left in the 453-days old sol. The sol still gave a white precipitate (which soon dissolved) on addition of 2*N*-nitric acid, which suggests that the micelles were still large in spite of the small n value.

100 C.c. of sol 11 when 8 days old were allowed to settle in a tightly corked, graduated cylinder, and the upper 95 c.c. separated from the lower 5 c.c.; the deposit in the latter was washed twice by decantation and both this and the upper sol were analysed. The results for the latter after 4 days' settling were :

Total La.	Un-ionised La.	Bound La ⁺⁺⁺ .	Free La ⁺⁺⁺ .	Cl ['] .	n .
121.9	104.4	5.7	12.2	17.9	18.2

and the washed deposit corresponded closely to $[\text{La}(\text{OH})_3]_{50}\text{LaCl}_3 \cdot x\text{H}_2\text{O}$. The total La_2O_3 in the deposit from the original 100 c.c. was about one-tenth of that in the settled sol, so the n value of the original sol agrees closely with that calculated from the values for settled sol and deposit.

Addition of more hydrochloric acid to the sols with high n values has little effect on this value, but there is an increase in the amount of free La^{+++} which is roughly equivalent to the added acid. This agrees best with the view that the micelles are adsorptively saturated but partly carbonated. In spite of the tendency of these sols to become carbonated, a very small crystalline deposit from a sol which was 130 days old may have been lanthanum hydroxide. After being washed and dried at about 35°, its loss on ignition was 15.1% [Calc. for $\text{La}(\text{OH})_3 : 1\frac{1}{2}\text{H}_2\text{O}$, 14.2%]. It contained a trace of chloride but was free from carbonate. It consisted of small spherulitic nodules and also many square to barrel-shaped crystals. Some of these showed straight extinction, others oblique. The crystals were probably either orthorhombic or monoclinic. The birefringence was low with two indices about 1.71 and 1.73 in the case of the larger crystals and the spherulites had a mean refractive index of about 1.72. The crystals were too small for detailed examination. These values and the general behaviour are not inconsistent with the crystals' being crystallographically similar to the monoclinic gibbsite, $\gamma\text{-Al}(\text{OH})_3$, which has refractive indices, α 1.566 and γ 1.587, but they may have consisted of basic chloride. The index of the orthorhombic plates of $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ is considerably lower than 1.7, β being 1.58 and γ 1.60.

Sol. No. 13 was much more translucent than a 5-fold dilution of sol No. 11.

Treatment of sol no. 10 with carbon dioxide. 90 C.c. of sol No. 10 when 3 days old were placed in a 250-c.c. flask. The air in this was displaced by carbon dioxide which was not bubbled through the sol. The next day a sample was withdrawn for analysis, and more carbon dioxide passed into the flask. This treatment was repeated at intervals of two days.

Total La = 1007; un-ionised La = 848.5.

Bound La ⁺⁺⁺ .	Free La ⁺⁺⁺ .	Cl ['] .	n .	Age of sol (days).	Time of action of CO_2 (days).	Bound La ⁺⁺⁺ .	Free La ⁺⁺⁺ .	Cl ['] .	n .	Age of sol (days).	Time of action of CO_2 (days).
42.7	115.8	158.5	19.6	4	1	17.5	141.0	158.5	48.4	9	6
37.5	121.0	"	22.4	5	2	14.2	144.3	"	59.7	11	8
26.6	131.9	"	31.9	7	4						

In the above tables bound La^{+++} refers to lanthanum ions which are still balanced by chlorions. The unknown amount of carbonated lanthanum ion attached to the micelles is not included, but has been counted in with the un-ionised lanthanum. After standing for a year, the mixture from the above experiment was filtered and the solid washed, air-dried, and analysed. It consisted of well-formed rhombic plates and gave CO_2 , 21.09%; loss on ignition, 45.10% [Calc. for $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O} : \text{CO}_2$, 21.94; loss on ignition, 45.85%]. The figures suggest that a small amount of hydroxide was still present.

Neodymium Hydroxide Sols.

Böhm and Niclassen (*Z. anorg. Chem.*, 1923, **132**, 6) prepared a sol, described as having a beautiful blue colour, by peptising the hydroxide in hydrochloric acid. We have prepared and examined a number of such sols, starting from some very pure $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ which had been prepared by the late Professor C. James (0.1255 G. gave on ignition 0.0574 g. of Nd_2O_3 . Calc. : 0.0576 g.).

Apart from their blue colour, the neodymium sols are very similar to those of lanthanum in their general characteristics, and are equally sensitive to the action of carbon dioxide. They can be prepared by peptisation of the hydroxide with the chloride or, better, hydrochloric acid, and readily result, in a dilute form, by autopeptisation on washing the hydroxide precipitated by ammonia from chloride solution.

The following figures for sol 7 may be taken as typical of the results obtained with these sols. No strict precautions had been taken to exclude carbon dioxide. The rate of ageing was certainly much too great, and if carbon dioxide were rigidly excluded, there can be little doubt that these sols would be as stable as those of lanthanum hydroxide.

The "bound Nd^{+++} " is that still balanced by chlorions and does not include any carbonated neodymium ions which may be attached to the micelles.

Total Nd.	Un-ionised Nd.	Bound Nd^{+++} .	Free Nd^{+++} .	Cl'.	<i>n</i> .	Age (days).
230	199	17.4	13.6	31.0	11.4	6
226	185.2	16.8	14.0	30.8	11.0	18
222	181.2	15.4	15.4	30.8	11.1	26
226	185.2	11.8	19.0	30.8	15.7	52
219	188.2	11.5	19.3	30.8	16.3	63
220	189.2	5.5	25.3	30.8	34.4	245

A very small crystalline deposit was obtained from this sol after 245 days, by which time all the sol had been used in analyses. This deposit still contained a trace of chloride but was free from carbonate. It seemed to consist of the hydroxide but may have been a basic chloride. The only optical measurement which could be made was that of the refractive index. The very small violet crystals were weakly birefringent and the values were practically the same as for the corresponding lanthanum crystals, *viz.*, about 1.71 and 1.73. The crystal system was probably either orthorhombic or monoclinic.

Thorium Hydroxide Sols.

These sols can be prepared either at room temperature by peptisation of the cold-precipitated hydroxide with a solution of thorium chloride or hydrochloric acid or by Desai's method (*Kolloid-Chem. Beih.*, 1928, **26**, 357), in which a suspension of the hydroxide in water is kept near the boiling point while dilute hydrochloric acid is added very gradually until a transparent sol is obtained, for which many hours may be needed: any water lost by evaporation should be replaced at intervals. The results are recorded in Table VI.

Sols 15 and 16 show that the same results are obtained whether thorium hydroxide is added gradually to the hot acid or *vice versa*. It is evident that thorium hydroxide sols are remarkably stable towards ageing or dilution whether they have been prepared by the hot or the cold process. The two methods of preparation do not give sols of identical character, however, as is shown by their very different behaviour towards added acid. All sols prepared by the hot process give a heavy precipitate when made 5*N* with regard to hydrochloric acid, whereas none of the sols prepared by the cold process does so. The precipitate obtained with the hot-process sols disappears on considerable dilution.

It does not seem possible to prepare by the cold process sols having high *n* values such as are normally obtained by the hot process. In order to confirm the striking result observed in sol 11, where the *n* value was as low as 1.15, a mixture was made from 10 c.c. of sol 12 and 10 c.c. of 0.38*N*-hydrochloric acid. This should give a sol with *n* = 1.24 if all the acid reacted and the final sol contained no free Th^{++++} or H^+ . Analysis of the mixture after 1 day gave:

Total Th.	Un-ionised Th.	Bound Th^{++++}	Free Th^{++++} .	H^+ .	Cl'.	<i>n</i> .
854	473.9	318.6	61.5	0.9	381	1.49

It thus appears that, in sols prepared by the cold process, the micelles behave towards acid in much the same way as did the original hydroxide used in preparing the sols. This result should be compared with that given by a mixture of 100 c.c. of sol 7, when 835 days old (see Table VI), with 10 c.c. of 0.2*N*-hydrochloric acid. Two days after mixing, analysis gave:

Total Th.	Un-ionised Th.	Bound Th^{++++} .	Free Th^{++++} .	H^+ , by NaPO_3 method.	H^+ , by glass electrode.	Cl'.	<i>n</i> .
127.7	105.7	11.0	11.0	9.6	10.0	31.6	9.6

and after 5 hours' heating at 90°, the mixture then being 4 days old, the results were:

127.7	102.8	11.3	13.6	6.7	—	31.6	9.1
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The amount of acid added was sufficient to give 18 mg.-equivs./l. in the mixture, so it is evident that only about half of it had reacted with the micelles after 2 days at room temperature to give an equivalent amount of free Th^{++++} . Since the value of *n* has remained practically unaltered, it would seem that some solution of

TABLE VI.

Thorium hydroxide sols prepared by Desai's hot process.

Sol.	Total Th.	Un-ionised Th.	Bound Th ^{****} .	Free Th ^{****} .	H'.	Cl'.	<i>n</i> .	Age (days).
7	140.1	126.1	14.0	0	0.3	14.3	8.9	1
	—	—	—	0.3	—	—	—	3
	—	126.1	13.7	—	0.3	—	—	7
	—	—	13.8	0.2	—	—	—	53
8	—	—	13.2	0.8	0.3	—	—	835
	240.1	219.9	19.6	0.6	0.7	20.9	11.2	2
	240.0	219.5	20.2	0.4	0.4	21.1	10.9	178
13	250.5	229.0	21.2	0.3	—	21.9	10.8	587
	907.5	701.0	76.2	130.3	12	218.5	9.2	1
	—	694.0	78.5	135.0	5	—	8.9	19
14	907.6	693.4	68.5	145.7	3.8	218.0	10.1	1178
	730.0	638.7	89	2.3	0	91.3	7.2	1
	—	—	88	3.3	0	—	7.3	28
(Sol 14. When 27 days old diluted 12.5 times)	730	—	86.7	4.6	0	91.3	7.4	2 (from dilution)
15 *	439.4	368.0	53.0	18.4	0	71.4	6.9	1
[Th(OH) ₄ added gradually to hot HCl]	—	—	53.9	17.5	0	—	6.8	3
—	—	368.3	51.9	19.3	0.3	—	7.1	74
—	—	—	50.7	20.4	0.3	—	7.3	94
—	—	368.2	50.4	20.8	0.2	—	—	506
16 *	451.5	381.9	51.6	18.0	0	69.6	7.4	2
[HCl gradually added to hot mixture of Th(OH) ₄ and water]	—	—	53.6	16.0	0	—	7.1	4
—	—	—	55.4	14.2	0	—	6.9	29
—	—	—	51.9	17.7	0	—	7.4	74
—	—	—	49.4	20.2	0	—	7.7	507

Thorium hydroxide sols prepared by the cold process.(Sols 9, 10, 11 peptised by ThCl₄, sol 12 by 5N-HCl.)

9	1641	1271	370	0	0	370	3.43	3
10	2500	1685.2	794.8	20	1.8	816.6	2.12	2
11	2163	985.4	852.4	325.8	0.3	1178.2	1.15	2
12 †	{ 1755	1372	383	0	0	383	3.58	1
	{ 1709 ‡	1327.5	381.5	0	0	381.5	3.48	6

* "H'" results for sols no. 15 and 16 obtained by means of the glass electrode were 1.9 mg.-equiv./l. at 62 days in each case. Any effect of the 12.5-fold dilution on sol 14 is within the limit of experimental error.

† No free Th^{****} or H' could be detected in sol 12 after 75 days' or after 100 days' ageing, nor were any of these ions liberated when the 6-days old sol was diluted 12.5 times even after the diluted sol had stood for 14 days.

‡ A small deposit had settled out after 6 days and this was not shaken up before the analysis.

the micelles as a whole has occurred. This supports the view that the micelles are of a liquid nature, and that the *n* value is determined by their bulk composition much more than by adsorption on their surface. Were the latter the case, then any marked increase in the free Th^{****} ion must have led to a reduction in the *n* value when all bound ions are assumed to be Th^{****} ions as in our calculations. This result would be obtained whether the additional free Th^{****} ions are supposed to come directly from the un-ionised substance of the micelle or from Th^{****} ions previously adsorbed on the surface and displaced by hydrions. In the calculation such displaced ions would be deducted from the total thorium to obtain the figure for un-ionised thorium and so would thorium equivalent to the bound hydrion.

It seems likely that hydrions bound to the micelles of these hot-process sols only react slowly with the substrate in view of the length of time for which a relatively high hydrion concentration can persist in such sols. The micelles may normally contain a proportion of bound hydrions for this reason (see p. 283). On heating the acid sol a small reduction in the *n* value does occur. This may well be due to changes in distribution between the two liquid phases (*i.e.*, liquid micelle and intermicellar fluid) owing to change of temperature, and the new value of *n* is closer to that of the sol when freshly prepared at 90–100°. The relative steadiness of *n* suggests that the micelles of sol 7 were almost adsorptively saturated in spite of the fact that the sol contained hardly any free Th^{****} or H' ions.

Concentration of thorium hydroxide sols prepared by Desai's method causes a diminution of the *n* value due to some of the free thorium ion becoming bound. The micelles of the original sols were evidently not adsorptively saturated though very nearly so. The following experiments were performed in this connection.

Expt. I: (a) 50 c.c. of sol 13 when 14 days old were evaporated by gentle boiling to just under 20 c.c.; (b) 100 c.c. of sol 13 when 16 days old were similarly reduced to about 24 c.c. This method of evaporation was employed, as the sols had been produced by gentle boiling. The analyses gave:

	Total Th.	Un-ionised Th.	Bound Th ^{****} .	Free Th ^{****} .	H'.	Cl'.	<i>n</i> .
Original sol	907.5	694	78.5	135	5	218.5	8.8
(a)	2292	1763	215.4	314	22	551.4	8.2
(b)	3738	2857	345.4	523	33	901.4	8.3

The relatively large amount of H' in the concentrated sols is probably connected with the very large amount of free thorium ion present. The glass-electrode result quoted on p. 300 shows that the determinations, made by the sodium metaphosphate method, are probably reliable.

Expt. II: 60 c.c. of sol 15 when 94 days old were evaporated by gentle boiling to 18 c.c.:

	Total Th.	Un-ionised Th.	Bound Th ^{'''} .	Free Th ^{''''} .	H'.	Cl'.	<i>n</i> .
Original sol	439.4	368.3	50.7	20.4	0.3	71.4	7.3
Conc. sol	1450	1215.8	185.7	48.5	1.4	235.6	6.55
„ ÷ 3.3	439.4	368.3	56.3	14.7	0.4	71.4	6.55

Expt. III: 20 c.c. of sol 7 when 835 days old were evaporated to dryness at room temperature over concentrated sulphuric acid. The glassy residue was somewhat hygroscopic, increasing in weight by 5% on exposure to air for 24 hours. It dissolved rapidly in water to a clear sol. After this had been curded with 5 c.c. of 0.5*N*-ammonium sulphate, the trace of thoria obtained from the filtrate with ammonia weighed only 0.0003 g., corresponding to 0.2 mg.-equiv. of free thorium per l. of the original sol. Another 20 c.c. of the sol analysed in exactly the same way without any evaporation gave 0.0011 g. of thoria, corresponding to 0.8 mg.-equiv. of free thorium per l. The drastic concentration effected in this experiment led to the binding of three-quarters of the free thorium and a reduction of the *n* value of the micelles from 9.5 to 9.1.

Coagulation of Thorium Hydroxide Sols.—0.01*N*-Solutions of the ions OH', F', IO₃', HCO₃', C₂O₄'', Fe(CN)₆'''', PO₄'''', P₂O₇'''', and PO₃' coagulate the whole of the thorium from thorium hydroxide sols when added in amounts equivalent to, or slightly greater than, the total thorium ion present; SO₄'', S₂O₃'', Fe(CN)₆'''', Co(CN)₆'''', and citrate ions coagulate only the micelles in similar circumstances. Higher concentrations of BrO₃', S₂O₆'', and S₄O₆''' cause coagulation of the sols, and very high concentrations of Cl', Br', I', ClO₃', ClO₄', and MnO₄' cause complete or partial coagulation but the curds disperse again readily on dilution.

The great efficiency of iodates has been noted by others. A rough determination has been made of the relative efficiencies of ClO₃', BrO₃', and IO₃' as precipitants for a thorium hydroxide sol containing 90 mg.-equiv./l. of total thorium with about one-tenth of that amount of free and bound thorium ion. Table VII gives the results, together with the corresponding figures for the precipitation of a thorium nitrate solution of concentration equal to that of the (free + bound) thorium ion in the sol. The relative solubilities of the barium salts are also shown. There is an obvious similarity in the three sets of figures, and the inference is that solubility is at least one of the factors in sol coagulation.

TABLE VII.

Precipitating ion.	Relative concn. of K salt required for precipitation of		Relative solubility of Ba salts at 15°.
	Th(OH) ₄ sol.	Th(NO ₃) ₄ solution.	
ClO ₃ '	190	>800	2290
BrO ₃ '	3.8	48	39.3
IO ₃ '	1	1	1

Crystalline Basic Thorium Chloride.—Approximately 20 g. or 17.3 c.c. (*d* 1.158) of thorium hydroxide sol No. 10, after 6 years' storage in a tightly corked flask, had deposited 0.463 g. of dense, strongly doubly refracting crystals. These consisted of minute prisms which showed straight extinction and had a tendency to form St. Andrew's crosses and other groups. The crystals were filtered off, washed with a small amount of cold water (by which they were unaffected), and air-dried (Found: Th, 63.66; Cl, 9.74; Th : Cl = 0.999. [Th{Th(OH)₄}₃]Cl₄.10H₂O requires Th, 63.85; Cl, 9.76%; Th : Cl = 1.0).

The mother-liquor from which the crystals had separated was absolutely clear and transparent, but still behaved like a sol in giving a typical amorphous curd when treated with ammonium sulphate in amount equivalent to its chloride content. Analysis of the mother-liquor gave: total Th, 11.47; Cl, 2.43% and free Th^{''''} (in the filtrate and washings from the ammonium sulphate coagulum), 0.45%. These figures correspond (in mg.-equiv./l.) to:

Total Th.	Un-ionised Th.	Bound Th ^{'''} .	Free Th ^{''''} .	H'.	Cl'.	<i>n</i> .
2290	1497.2	783.7	9.05	—	792.8	1.91

which should be compared with those for sol 10 in Table VI.

When the relative weights of crystalline solid and residual sol are considered, the analyses indicate that evaporation to the extent of about 4% by wt. must have occurred from the sol during the 6 years' storage.

It is noteworthy that the crystalline basic salt has a higher *n* value (= 3) than have the micelles of the sol from which it has separated.

The ultramicroscope showed the presence in the mother-liquor of only a very small proportion of very heavy particles with slow Brownian movement, and this liquor showed only a relatively weak Tyndall beam. It must be concluded, therefore, in view of the large total thorium content, that the micelles present are too small to cause appreciable scattering of light and hence do not show up in the ultramicroscope. The dissolved material is in a state intermediate between that of a typical sol and that of a crystalloidal solution.

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