3. In continuous dialysis, the ratio of chromium to chlorine in the diffusate increases from 1 to a maximum of 1.57, then gradually diminishes and approaches zero.

4. In intermittent dialysis, as conducted in this research, about 6% of the original colloid, still associated with considerable electrolyte, remains in the membrane at the end of 56 days, and colloid still diffuses. This dialysis could have been continued until no colloid remained within the membrane.

5. In the continuous dialysis, 75% of the original colloid remains in the membrane. Continuing the process beyond 35 days, increases the purity of the colloid without loss of chromium, *i. e.*, only hydrochloric acid diffuses.

6. If the intervals in intermittent dialysis are made smaller, more satisfactory results are to be expected. In fact, by conducting the entire process in very short intervals, the efficiency may even exceed that of continuous dialysis. The latter procedure, however, is impractical.

7. The variations of the ratios of chromium to chlorine in the diffusates are accounted for. They indicate a gradual growth of the particles. In the intermittent process, the particles did not grow sufficiently to be retained by the membrane, whereas in continuous dialysis they did.

8. The growth of the particles is explained partly by aid of Bredig's theory of colloid precipitation and partly by assuming that the nuclei of the particles grow as the adsorbed chromic chloride is hydrolyzed by the adsorbed water.

PITTSBURGH, PA.

[CONTRIBUTION FROM THE SEVERANCE CHEMICAL LABORATORY OF OBERLIN COLLEGE.]

THE COLLOIDAL ARSENATES AND PHOSPHATES OF IRON.

BY HARRY N. HOLMES AND R. E. RINDFUSZ.

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The usual method of analysis of sulfide ores requires the dissolving of the sample in aqua regia and the addition of potassium chlorate or bromine to oxidize separated sulfur. After evaporation to dryness, addition of hydrochloric acid, filtration and treatment of the filtrate with ammonium hydroxide, any iron present is precipitated as ferric hydroxide.

In attempting to apply this method to arsenopyrite, as directed by Olsen,[1] we failed to get the expected precipitate of ferric hydroxide. Instead a rich red solution resulted.

Assuming that ferric orthoarsenate was formed in the process, we attempted to duplicate the final result by mixing solutions of ferric chloride and disodium arsenate and treating the precipitate thus formed with

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[1] Olsen's *Quant. Chem. Anal.*, 4th Ed., p. 172.

ammonium hydroxide. The same red solution resulted and, upon dialysis, we found it to be colloidal.

A search of the literature showed that Grimaux[1] had made colloidal ferric arsenate by the ammonium hydroxide peptization of precipitated ferric arsenate and, in similar manner, colloidal ferric phosphate. E. A. Schneider[2] also contributed something in this field but the two writers did little more than start the work.

We planned a more thorough study of the colloidal arsenates and phosphates of iron but at the very beginning found a serious difficulty. On treating ferric chloride solution with a solution of disodium orthoarsenate a rather gelatinous precipitate of $Fe_2(HAsO_4)_3$ forms. This formula is also written $2Fe_2O_3.(3As_2O_5).3H_2O$. Ordinary methods of washing failed to remove adsorbed ions. One sample washed "thoroughly" in the usual manner until the washings showed only a trace of excess arsenate was set away under water for four months. This water then contained so much soluble arsenate that it seemed as if the original precipitate had not been washed at all.

The problem of purifying the semigelatinous precipitates of ferric arsenate and phosphate was finally solved satisfactorily by mechanical disintegration of the wet precipitates. The results of that part of our investigation cast some doubt on the accuracy of many formulas given in the literature for the various phosphates of iron. Different degrees of washing precipitates that so strongly adsorb ions must certainly have given analytical evidence for many different formulas. Possibly this same doubt may extend to analysis in other fields. It was our custom to prepare the precipitate for peptization by adding a slight excess of a solution of disodium arsenate, for example, to a solution of ferric chloride and then removing this excess of soluble arsenate as well as the soluble salt formed by the reaction. The method we used has been described elsewhere.[3]

Peptization by Ammonium Hydroxide.—As observed by Grimaux,[4] the insoluble orthoarsenate and orthophosphate of ferric iron are quickly peptized by ammonium hydroxide into red colloids. In dilute ammonium hydroxide the action is slower, but in any case may be hastened by shaking. Several attempts to utilize the full power of a definite weight of ammonium hydroxide in peptization gave us interesting results. A sample of 24 cc. of the wet paste of ferric arsenate was shaken with 2 cc. of concentrated ammonium hydroxide in a stoppered vessel and, after a week of occasional shaking, was completely converted into a deep red sol.

[1] *Compt. rend.*, 98, 1540 (1884).

[2] *Z. anorg. Chem.*, 5, 84 (1893); 7, 386 (1895).

[3] *J. Phys. Chem.*, 20, 522 (1916).

[4] *Loc. cit.*

After standing in a tightly corked tube several months the liquid turned into a smooth solid butter of yellow-red color. Other samples acted in the same way. One, left open after treatment with concentrated ammonia, soon deposited considerable sediment, not of a buttery character. Of course this was caused by a rather rapid escape of ammonia. Approximately quantitative experiments indicated that 1 cc. of concentrated ammonium hydroxide peptizes an amount of wet paste equivalent to 1 g. of ferric arsenate. This corresponds to about 15% more ammonium hydroxide than is enough to replace the remaining hydrogens of the $Fe_2(HAsO_4)_3$.

Wittstein[1] observed that ferric phosphate could not be peptized by ammonium hydroxide unless disodium phosphate was present. We found no difficulty whatever in peptizing the thoroughly washed precipitate of ferric phosphate.

During dialysis of the two colloids mentioned, considerable osmotic pressure developed. One sample of ferric arsenate sol rose, in a few weeks, to a level of 9.5 cm. above the water outside the dialyzing tube. After some time this dropped rather rapidly, not, however, because of any break in the dialyzing membrane (goldbeater's skin). It would seem that this action may have been influenced by changes in the size of the colloidal aggregates through removal of ions and instability of phases. Not long after the fall in osmotic pressure small lumps of gel appeared.

Ammonia was gradually removed during dialysis and the dialysates for some time showed a test for arsenate ion. This removal of ammonium arsenate is discussed in detail under the heading "Properties of the Colloid." After continued dialysis for a few months the sol of ferric arsenate formed an excellent dark red gel. Grimaux failed to obtain this gel. In a small dialyzer the gel was solid and like a good fruit jelly in texture but in a large dialyzer the gel was lumpy, possibly due to greater agitation in changing the water. This gel could not be peptized again by ammonium hydroxide. When dissolved in hydrochloric or nitric acid and dialyzed a poor gel resulted.

From this point on we will discuss ferric arsenate, but it is to be noted that all results, unless otherwise stated, were duplicated with ferric phosphate.

Properties of the Colloids.—The sol of ferric arsenate is quite like colloidal ferric hydroxide (or "hydrated ferric oxide") in appearance, varying from a light cherry to a black-red with increase in concentration. The question arose whether this is not, after all, merely colloidal ferric hydroxide with adsorbed arsenate. Experiments readily showed that the colloid was negatively charged whereas colloidal ferric hydroxide is positive. Subjected to prolonged electrolysis in a 25 cm. tube with 18

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[1] Comey's "Dictionary Chem. Solubilities," p. 304.

volts and less than 0.1 ampere current the red particles migrated to the positive pole and coagulated. Furthermore the ferric arsenate sol was extremely sensitive to an increase in valence of positive ions while an increase in valence of negative ions was without effect, a simple proof of the negative nature of the colloid. There was no difference in the amount of 0.02 *N* sodium chloride or 0.02 *N* disodium phosphate needed for coagulation of the colloid. Evidently the trivalent negative phosphate ion exerted just as little coagulating power as did the univalent negative chloride ion. On the other hand coagulation was produced by much less 0.02 *N* barium chloride and by very much less 0.02 *N* aluminium chloride.

The well-dialyzed sol of ferric arsenate is quite stable. One sample, over a year old at this date, shows no sign of settling. It is not coagulated by boiling but is very sensitive to polyvalent positive ions and is coagulated by considerable alcohol. A very little nitric or hydrochloric acid produces a coagulum, but this dissolves easily in a slight excess of the acid. Unless very dilute acid is used and added slowly no coagulum shows but the deep red color turns to the light yellow of a ferric chloride solution. Addition of excess ammonium hydroxide to this solution gives a precipitate, apparently ferric hydroxide, leaving a colorless liquid above. This point is discussed later. Evaporated spontaneously in the air the colloid is not reversible.

The thoroughly dialyzed colloid contains no free ammonia and on heating with sodium hydroxide not enough combined ammonia is released to affect litmus. Dialyzed colloidal ferric arsenate was evaporated to dryness on the water bath and duplicate samples analyzed. No. 1 contained 38.0% iron and 15.8% arsenic; No. 2 contained 38.3% iron and 15.6% arsenic. These values correspond to the formula $FeAsO_4.Fe_2O_3.xH_2O$ which might be called basic ferric orthoarsenate. Another sample prepared at a different time was dialyzed until lumps of gel appeared. The mixture of sol and gel was analyzed for the ratio of iron to arsenic, which was found in satisfactory agreement with the above formula. The removal of soluble arsenate, doubtless as ammonium arsenate as previously mentioned, accounts for the change in formula from $Fe_2(HAsO_4)_3$ of the fresh precipitate to $FeAsO_4.Fe_2O_3.xH_2O$ of the dialyzed colloid. It was suggested by W. Metcalf that the original precipitate was decomposed by water, thus accounting for the change in composition on dialysis. Lachowicz[1] states that such is the case. However, our precipitate after the special purification previously mentioned was kept under distilled water three months and this water gave no test for arsenate ion and only a slight test for chloride ion. It seems probable, therefore, that this precipitate is not decomposed by water and that Lachowicz's observation must have applied to an incompletely washed precipitate.

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[1] *Sitzb. kais. Akad. Wiss., Wien.*, **101, IIb,** 374.

Absorptive Power of the Colloids.

Ferric hydroxide was dissolved in a solution of ferric chloride in order to obtain colloidal ferric hydroxide and ferric ions in the same solution. Without dialyzing, this was treated with a solution of sodium arsenate. The white precipitate of ferric arsenate appeared an instant before the red coagulum of ferric hydroxide. Naturally the trivalent negative arsenate ions neutralized the positive charge on the colloidal ferric hydroxide and coagulation followed. But at the same time ferric ions from the ferric chloride reacted with arsenate ions to precipitate white ferric arsenate. This simultaneous precipitation and coagulation insured an intimate mixture of the insoluble ferric hydroxide and ferric arsenate. The entire precipitate was readily peptized by addition of ammonium hydroxide into a deep red sol.

The peptizing action of ammonium hydroxide on ferric arsenate has already been discussed, but even an excess of this base has no such effect on precipitated ferric hydroxide. The ferric hydroxide precipitate has simply been adsorbed by the colloidal ferric arsenate and thus carried into suspension. To test this point further a finely divided precipitate of ferric hydroxide was shaken in water with an excess of finely divided precipitate of ferric arsenate. Addition of ammonium hydroxide formed an excellent sol of unusually deep red color and with a greenish "bloom." A small amount of sediment slowly settled on standing. This deep color and bloom were duplicated by adding very little colloidal ferric hydroxide —less than enough for mutual precipitation—to the dialyzed ferric arsenate. The bloom was apparently due to the presence of aggregates somewhat larger than those of the clearer colloids.

The above experiments furnish further evidence that colloidal ferric arsenate is not colloidal ferric hydroxide with adsorbed arsenate. We have loaded our negative colloid with a positive colloid, ferric hydroxide, up to a point short of complete discharge. When that limit is reached adsorption ceases and precipitation results.

Ferric chloride solution, as discussed later, dissolves precipitated ferric arsenate. If less than one-tenth enough to dissolve the precipitate is added the further addition of ammonium hydroxide forms a red colloid. Of course the ammonium hydroxide peptizes the ferric arsenate and at the same time forms some ferric hydroxide which is adsorbed by the colloidal ferric arsenate. If more than enough ferric chloride to peptize the arsenate is added there is some precipitation with ammonium hydroxide, but a red sol may also form. If still more ferric chloride is used, addition of ammonium hydroxide may cause complete precipitation, leaving a colorless liquid above. The excess ferric hydroxide, if formed first as a positive colloid, has coagulated the negative colloid, ferric arsenate, formed at the same time. Less than enough ferric hydroxide to discharge completely the negative colloid results in the adsorption of the ferric hydroxide and little or no precipitation.

This phenomenon, also observed in the adsorption of aluminium hydroxide and other hydroxides by colloidal ferric arsenate, is similar to that reported by Fisher and Herz.[1] They found that if, in a mixture of solutions of ferric and chromium salts, the chromium salt is in large excess, the addition of an excess of a solution of sodium hydroxide forms colloidal chromium hydroxide carrying into the sol all the iron as adsorbed ferric hydroxide. With a much smaller excess of the chromium salt both sol and precipitate may result while if the ferric salt is in excess there is no sol but complete precipitation.

We found other examples of hydroxide adsorption. A small amount of a solution of aluminium chloride was added to an excess of precipitated ferric arsenate and upon addition of ammonium hydroxide a sol resulted with no precipitation. An excess of aluminium chloride resulted in complete precipitation. Chromium chloride and lead nitrate were substituted for the aluminium chloride with similar results.

These adsorption experiments lead to an explanation of the fact that dialyzed colloidal ferric arsenate treated with excess hydrochloric or nitric acid yields a precipitate when ammonium hydroxide is added. In this case the ammonium hydroxide does not exert its usual peptizing action. If a fresh precipitate of $Fe_2(HAsO_4)_3$ is dissolved in hydrochloric or nitric acid and ammonium hydroxide added the same precipitation results with some sol remaining. If considerable excess arsenic acid is mixed with ferric chloride solution and excess ammonium hydroxide added, both the white insoluble ferric arsenate and the red insoluble ferric hydroxide are seen. On shaking a deep red sol forms. If a smaller amount of arsenic acid is used the addition of ammonium hydroxide precipitates ferric hydroxide with possibly a little of the sol remaining.

$$Fe_2(HAsO_4)_3 + 6HCl \rightleftarrows 2FeCl_3 + 3H_3AsO_4.$$

In the equilibrium indicated above most of the iron is on the right of the equation. Addition of ammonium hydroxide must neutralize the hydrochloric acid and thus disturb the equilibrium to the left, causing the appearance of white insoluble ferric arsenate. At the same time ammonium arsenate is formed but this reacts readily with ferric chloride to form more ferric arsenate. Some ferric hydroxide must also be formed by the action of the base. An excess of ammonium hydroxide may peptize the white precipitate of ferric arsenate into a red colloid. However, unless considerable excess of arsenic acid is used any colloidal ferric arsenate formed is adsorbed and precipitated, at least in part, by the coagulum of ferric hydroxide. This needed excess of arsenic acid is not obtained when a precipitate of $Fe_2(HAsO_4)_3$ is dissolved in hydrochloric

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[1] *Z. anorg. Chem.*, 31, 352 (1902).

acid but it must be added. The ability of peptized ferric arsenate to adsorb ferric hydroxide is limited, as previously stated. It is also probable that the equilibrium

$$FeCl_3 + 3NH_4OH \rightleftarrows Fe(OH)_3 + 3NH_4Cl,$$

is shifted to the left by the action of excess arsenate ion on the ferric ion.

In the case of the dialyzed sol, $FeAsO_4.Fe_2O_3.xH_2O$, treated with hydrochloric acid the excess of ferric chloride over the arsenic acid formed is too great to yield a colloid on treatment with ammonium hydroxide. In other words, the ratio of three atomic weights of iron to one of arsenic gives too great an excess of ferric chloride when dissolved in hydrochloric acid. This is the ratio in the dialyzed colloid but it must be remembered that this is not the ratio of iron to arsenic that existed when the sol was formed in the presence of ions. That ratio was represented by the formula $Fe_2(HAsO_4)_3$ and the change to $Fe_2AsO_4.Fe_2O_3.xH_2O$ came about slowly as the ions dialyzed out.

Peptization by Substituted Ammonias and Other Bases.—A water solution of pure methyl amine quickly converted the precipitate of ferric arsenate into the characteristic dark red colloid. On dialysis a firm red gel formed after a few weeks. Aqueous solutions of dimethylamine and tetramethyl ammonium hydroxide showed just as great peptizing power, but the action of our trimethyl amine was much less marked. To vary the series of substituted ammonias we used diethyl amine with success. Aniline and pyridine were shaken with the wet precipitates but with little or no result.

Sodium hydroxide or potassium hydroxide solutions, carefully used, peptized ferric arsenate to a red sol, contrary to the statements of Grimaux. Very dilute base, about 0.1 *N*, must be added, drop by drop, with shaking, and great care taken to avoid an excess. Otherwise the colloid is precipitated as fast as formed. Doubtless such a lack of caution accounts for Grimaux' failure to obtain the colloid by sodium hydroxide peptization. Dialysis yields a rough coagulum rather than a compact gel.

Attempts to employ calcium hydroxide or barium hydroxide as peptizing agents failed, although the white precipitate of ferric arsenate developed a red tint. If there was an intermediate colloidal state it was not apparent, for the bivalent positive ions quickly coagulated the negative colloid. Solutions of sodium carbonate and ammonium carbonate showed a slight peptizing power.

These results suggest the possibility that the hydroxyl ion is a peptizing agent.

Peptization by Ferric Chloride.—Grimaux[1] states that a ferric chloride solution dissolves precipitated ferric arsenate and that, on prolonged

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[1] *Loc. cit.*

dialysis, a transparent reddish yellow gel is formed. He did not pursue this line of investigation, not even experimenting with ferric phosphate.

We duplicated his work in making the sol and gel of ferric arsenate and obtained similar results with ferric phosphate. Grimaux records a difference in color of the ferric arsenate precipitated from ferric chloride, depending on whether sodium or potassium arsenate was used, the latter, he observes, giving a yellower precipitate. We found no such difference when care was taken to use a slight excess of the alkali arsenate. However, a very slight excess of ferric choride exerts a peptizing action, developing a yellow to red tint. This, doubtless, accounts for the difference in color observed by Grimaux.

The amount of ferric arsenate peptized by ferric chloride solution is greatly increased by heating and the sol is a deeper red. Such a sol is not so stable and coagulates, in part, on dialysis.

The fact that ferric arsenate is so easily peptized by ferric chloride is good reason for using a slight excess of disodium arsenate solution on a solution of ferric chloride in preparing the precipitate. This excess of disodium arsenate can be removed by the method previously described.

The gel formed by the peptization of ferric arsenate by a solution of ferric chloride and subsequent dialysis is of excellent texture and looks much like a good fruit jelly. A sample retained its shape for several months when placed in 95% alcohol. Exposed to the air it dries down to a coarse powder. On standing sealed the gel slowly contracts. A change to a less hydrated phase is shown by the appearance of water around the gel. One gel had stood in a sealed tube for three months and had squeezed out considerable water. The water was rich in hydrochloric acid but gave only a slight test for iron. This shows that ferric chloride, included in the gel, had been hydrolyzed, the resulting colloidal ferric hydroxide being adsorbed, while the hydrochloric acid readily diffused throughout the water. Of course longer dialysis would have removed more of the hydrochloric acid. The gel may be dissolved in ammonium hydroxide to the characteristic sol which behaves exactly like that formed by the ammonium hydroxide peptization of ferric arsenate. It forms a good gel on dialysis and may then be redissolved in ferric chloride and a second gel formed on dialysis. A better structure of gel is secured if the ferric arsenate is peptized by ferric chloride solution immediately after precipitation. Delay from any cause, washing or otherwise, seems to permit an unfavorable change in physical condition. The gel forms after about two weeks' dialysis.

We next tried treating the precipitates of the arsenates of the common metals with a solution of ferric chloride. The arsenates of lead and mercurous mercury gave sols and white precipitates of the chlorides. On dialysis after filtration these sols gave the characteristic gels of ferric arsenate. We found, also, that the arsenates of other metals gave the same gels containing none of the metal whose arsenate was used. This was true of arsenates of all the common metals except stannic tin and the soluble arsenates of the alkali group. Dialysis removed all the soluble products of the reaction, thus disturbing the equilibrium and leaving the insoluble ferric arsenate in the highly hydrated gel form. Ferrous arsenate dissolved in a solution of ferric chloride gave, on dialysis, an excellent red gel which contained both ferrous and ferric iron. In most cases these gels formed when nearly all the chloride ion was gone but there were a few instances where considerable remained. This then dialyzed out very slowly.

A sample of ferric arsenate in a solution of chromium chloride on dialysis gave a good green gel which contained only a trace of iron. This shows that in the relation of chromium to iron, at least, it is a matter of mass action, depending on which salt is in excess to determine whether we get the arsenate of iron or of chromium in the gel form.

Two samples of cadmium arsenate in ferric chloride solution were dialyzed. One gave an excellent red gel in about three weeks; the other in a few days gave a yellowish butter. This contracted but little and took three months to dialyze out all the chloride ions. At the end of that time it was more nearly a gel in texture but was still quite buttery and light yellow in color. This same difference was observed with two samples of lead arsenate in ferric chloride solution. The probable explanation is that we get the quickly formed butter when there is not enough excess ferric chloride solution, and on dialysis this slight excess is removed too suddenly for the change to gel form to take place. This is substantiated by the fact that some of the butter from the lead arsenate was redissolved in a large excess of ferric chloride solution and gave, on dialysis, a splendid red gel. The behavior of the mixture of solutions of ferric chloride and arsenic acid greatly strengthens this view.

After this work on gels had been completed we found that E. A. Schneider[1] had already done a small amount of work along the same line. He had dialyzed the sol of calcium phosphate in ferric chloride solution and had gotten the gel of ferric phosphate as soon as nearly all the chloride ion was removed. He had also observed that this gel dissolved in ammonium hydroxide and on dialysis lost phosphate. This agrees with our observations on this gel and on the original sol of ferric phosphate or arsenate in ammonium hydroxide. He found that if the gel was treated with potassium hydroxide there was a precipitation of ferric hydroxide, while nearly all the phosphate went into solution. We had not tried the addition of the base directly, but found similar results with the ammonia gel or sol when treated with acids and the base added. Schneider sug-

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[1] *Loc. cit.*

gested this as a method for the separation of iron and phosphorus and extended it to calcium. The calcium phosphate dissolved in ferric sulfate giving a precipitate of calcium sulfate. On addition of potassium hydroxide solution to the filtered sol the iron was precipitated as hydroxide, leaving the phosphate in solution. His aim was to get a method of analysis applicable to humus.

Sodium metaphosphate treated with excess ferric chloride solution gave the characteristic sol and, on dialysis, a good gel of ferric metaphosphate. The pyrophosphate on similar treatment yielded a most excellent deep red gel of ferric pyrophosphate. Ferric hypophosphite gave sols with ferric chloride solution, hydrochloric acid or nitric acid. On dialysis each of these sols yielded a rather poor gel.

Peptization by Sulfates.—Aside from any connection with Schneider's work we had already tried using sulfates instead of ferric chloride solution as peptizing agents. On adding to a solution of sodium arsenate an excess of a solution of ferric alum, or of aluminium sulfates, or of chrome alum, the same results were observed as when the chlorides of these metals were used. The sols were apparently very stable. One sample made by treating sodium arsenate with excess of ferric ammonium sulfate solution has stood undialyzed for four months with no sign of settling. On dialysis, however, there is great difference. Inside of a few days a powder begins to form on the walls of the dialyzer and then on the membrane and after a few more days the colloid settles out entirely as a powder. This was found to be the case every time a sulfate was used as a peptizing agent.

Peptization by Hydrochloric or Nitric Acids.—The question naturally suggests itself whether the salt (such as ferric chloride) or the acid from hydrolysis does the peptizing. The dialysates from ferric arsenate in ferric chloride solution were acid for ten days. Evidently the way to settle the point was to try hydrochloric acid instead of ferric chloride solution as a peptizing agent. We found that on dialysis of the colorless solution of well washed precipitate in hydrochloric or nitric acid ferric ion diffused through the membrane for about four days. Then a color began to devlop and after a few more days a light yellow gel of excellent texture was formed. This gel could be redissolved in acid and the gel obtained again on dialysis or the gel from ferric chloride dissolved in acid and another gel obtained on dialysis. It has been mentioned before that the gel from the ammonium hydroxide peptization could be dissolved in acid and formed again on dialysis. The gel from the pure acid was not so red as the one from ferric chloride solution because, no doubt, of the lack of adsorbed ferric hydroxide. In the case of the ferric chloride peptization the large excess of ferric chloride, the probability that the hydrochloric acid from hydrolysis reacts to dissolve the arsenate, thus causing more hydrolysis, and the fact that so much acid dialyzes out, led us to expect a very considerable adsorption of ferric hydroxide. Nitric acid may be used instead of hydrochloric but sulfuric acid gives, on dialysis, the powder described under sulfate peptization.

Hydrochloric acid on ferric arsenate probably forms ferric chloride and arsenic acid, or an acid ferric arsenate. The solution thus formed passes from reddish yellow to light yellow to colorless as the acid is added and, on dialysis, this color change reverses. The removal of the hydrochloric acid by dialysis disturbs the equilibrium, reversing the reaction and slowly reforming ferric arsenate, first in the sol and later in the gel condition. We thought it possible to duplicate these results by starting with the substances on the other side of the equilibrium. Arsenic acid was added to ferric chloride solution until the color was nearly gone and the solution dialyzed. In about two weeks there resulted a splendid gel of about the same color as the gel from ferric arsenate in hydrochloric acid. Similar results were obtained using diluted phosphoric acid in ferric chloride solution. If too concentrated solutions were used a powder and then a butter was obtained. This confirms our conclusions about the butter as given above.

Peptization of Other Salts by Ammonium Hydroxide.—The pyrophosphate of ferric iron peptized readily in ferric chloride solution forming a red sol. After two months' dialysis an excellent compact deep red gel resulted. Ferric metaphosphate was also peptized to a red sol by a little very dilute ammonium hydroxide but was coagulated again by any excess. It yielded no gel on dialysis. Efforts to peptize ferric hypophosphite by ammonium hydroxide failed. Ferric arsenite was readily peptized by ammonium hydroxide to a red-yellow sol. Dialysis did not produce a real gel. Chromium arsenate and phosphate were peptized to a slight extent only by ammonium hydroxide. The same is true of the arsenate of aluminium. The arsenates of zinc and nickel were peptized by this base but on dialysis these colloids were precipitated.

Sols and Gels of Aluminium and Chromium Salts.—When a solution of aluminium chloride was added in excess to sodium arsenate solution the precipitate first formed was redissolved and, on dialysis, a colorless gel formed on the dialyzer. This gel seemed to retard the diffusion of ions, for when there was about one-fourth inch of gel on the membrane the dialysates showed almost no chloride ions while the sol above the gel was rich in chlorides. On changing this sol to another dialyzer a gel formed. However, the disturbance at the time of transfer caused the gel to be lumpy. We tried one sample with which we shook the dialyzer every day to keep the sol uniform. The gel developed from top to bottom but in lumps. The aluminium arsenate gels were not nearly as good as those of iron. With chromium arsenate the results were very like those with aluminium. The gels were perhaps a little better and of greenish color.

Summary.

1. The precipitated arsenates and phosphates of ferric iron are rather gelatinous and difficult to wash free from adsorbed ions. However, they may be purified by repeated shaking with sand and a large amount of water followed by decantation or filtration.

2. Ferric orthoarsenate and orthophosphate may be peptized by comparatively small amounts of ammonium hydroxide, yielding stable colloids. On long-continued dialysis these were found, contrary to the experience of Grimaux, to form excellent deep red gels. The composition of both sol and gel of the arsenate correspond closely to the formula $FeAsO_4.Fe_2O_3.xH_2O$. The change in composition from that of the precipitated arsenate and the formation of the final sol and gel are brought about by the removal of ammonium arsenate during dialysis. The same is true of the phosphate.

3. The peptization mentioned in (2) is probably due to the action of the hydroxyl ion since, with limitations, other hydroxides may be substituted for ammonium hydroxide and substituted ammonias may be used as peptizing agents. The colloid formed by using a water solution of methyl amine yielded, on continued dialysis, a splendid gel of a deeper red color than the others.

4. Either colloid has great adsorptive power, carrying into suspension with it other insoluble hydroxides at the time of its peptization. This power, however, is greatly lessened by the removal of arsenate during dialysis.

5. Ammonium hydroxide also peptizes ferric pyrophosphate, ferric metaphosphate and ferric arsenite. With arsenates and phosphates of chromium and aluminium there seems to be very little peptization. With the arsenates and phosphates of zinc and nickel unstable sols are formed, settling out on dialysis.

6. Ferric orthoarsenate or orthophosphate is peptized by ferric chloride solution as found by Grimaux and yields, on dialysis, an excellent red gel after removal of most of the chloride ion. In similar manner the orthoarsenate or orthophosphate of chromium or aluminium are peptized by solutions of chromium chloride or aluminium chloride and form gels on dialysis.

7. The precipitated orthoarsenates or orthophosphates of any of the common metals are peptized in ferric chloride solution and yield, on dialysis, gels of ferric arsenate or phosphate. If the ferric chloride solution is overloaded with the arsenate or phosphate, a butter is formed which is very slow to give up its adsorbed ions.

8. If a solution of a sulfate is used as the peptizing agent, instead of a

chloride as mentioned in (6), a sol is formed stable on standing but forming a powdery sediment on dialysis and completely settling out.

9. In all examples of peptization by salts as mentioned in (6), (7) and (8) the action is due to acid hydrolysis, as shown by the fact that hydrochloric or nitric acid may be used as peptizing agents with equally good results. The sols formed by acids give excellent gels on dialysis but lighter in color than those formed from ferric chloride solution. If sulfuric acid is used the results are those observed in the use of any sulfate as the peptizing agent. There are at least two kinds of peptization of these arsenates and phosphates, that by acids and that by bases.

10. The formation of the sol and gel in the case of the acid peptizations is due to the disturbance of the equilibrium by dialysis. This is shown by the fact that good gels may be formed by dialyzing dilute mixtures of ferric chloride solution and arsenic or phosphoric acid, the phosphoric acid giving a gel excellent in clearness as well as in texture.

11. The metaphosphate, pyrophosphate and hypophosphite of ferric iron behave like the orthophosphate in peptization by acids and ferric chloride. Ferric pyrophosphate in ferric chloride solution formed a splendid deep red gel on dialysis.

OBERLIN, OHIO.

THEORY OF COLLOIDS.

BY JOHN ARTHUR WILSON.

Received July 27, 1916.

The object of the present paper is the promulgation of further reasoning in favor of the "complex" theory of colloid formation and the elucidation of the very interesting and important conclusions which follow. The fundamental assumption of this theory is that the colloidal state in sols owes its stability to the formation of a complex between the particles of the disperse phase and certain substances present or formed in the dispersion medium during the preparation of the colloid. The sols of the noble metals have been cited as an argument against this theory, but Beans and Eastlack[1] have shown that the presence of chloride, bromide, iodide, or hydroxide ions in concentrations from 0.00005 N to 0.005 N has a marked stabilizing effect on gold sols and that the colloid particles become negatively charged. In concluding, these authors consider that the electrical synthesis of colloids consists of a thermo-mechanical dispersion of the metal, followed by the formation of a colloidal complex between the dispersed metal and certain ions present in the medium.

The assumption of the formation of such a complex between any colloid particles and electrolytes present in the dispersion medium is not unreasonable. Carbon is a typical *adsorbing* agent and happily one, the stability of whose compounds has been extensively investigated. The

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[1] THIS JOURNAL, 37, 2667–83 (1915).