Guye and Moles[1] discuss surface condensation of moisture and other gases, and its effect upon the weights of substances weighed in the air, while Guye[2] emphasizes the bearing of this effect and of occluded gases upon the atomic weights of silver and other elements whose atomic weights have been found by reference to silver.

Moles[3] discusses critically the determinations of atomic weights published in 1916.

Sears[4] finds tantalum pentachloride unsuited for the very exact quantitative manipulation required for atomic weight experimentation.

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

THE PEPTIZATION OF FERRIC ARSENATE AND PHOSPHATE AND THE FORMATION OF THEIR GELS.

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The formation of colloids by peptization and the development of gel structure are two phenomena in need of further elucidation. Previous work with R. E. Rindfusz[5] has shown that ferric arsenate and phosphate have properties which make them unusually suitable for such a study.

In the present paper two main topics are presented: First, peptization by sodium hydroxide and by ferric chloride as influenced by concentration changes, rate of adsorption of the peptizing agent and the presence of certain salts and sugars; second, variations in the structure and time of formation of gels from dialysis of the various ferric chloride peptization products.

I. Peptization by Sodium Hydroxide.

In our earlier work we reported that it was necessary to use very dilute base to prevent coagulation of the colloid formed, but later we found that this was true only of thoroughly washed precipitates of ferric arsenate or phosphate. Unwashed precipitates are stabilized by any soluble arsenates or phosphates that may be present. Therefore, much more concentrated hydroxide may be used as peptizing agent, and added more rapidly and in greater excess. In fact, the total amount of base required is greater. We found *N* sodium hydroxide suitable for addition to the wet precipitate. Colloidal arsenates or phosphates that otherwise coagulate in a short time are stabilized by dilution after peptization. Potassium hydroxide shows a greater peptizing power than sodium hydroxide, a fact of great

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[1] *J. chim. phys.*, **15**, 360, 405 (1917).

[2] *Ibid.*, **15**, 549 (1917).

[3] *Ibid.*, **15**, 433 (1917).

[4] THIS JOURNAL, **39**, 1582 (1917).

[5] *Ibid.*, 38, 1970 (1916).

interest in connection with the influence of potassium salts as compared with sodium, lithium and ammonium salts.

Influence of Rate of Addition of the Base.—In the experiments recorded in Table I we peptized equal amounts of wet ferric arsenate. In general the process was carried out by slowly adding the base and shaking. In one series the total amount of base was added in 30 minutes while in the other this addition required 3 working days.

TABLE I.

Amounts of *N* Sodium Hydroxide Required to Peptize Equal Weights of Ferric Arsenate.

Excess of KH_2AsO_4 beyond that needed to form ferric arsenate. %.	Amounts required when time of addition was 30 minutes. Cc.	Amounts required when time of addition was 3 days. Cc.
No excess	4.9	4.0
15	5.6	4.2
25	6.1	4.8
75	8.6	5.0
100	10.0	5.5

From this table it is clearly evident that much less base is needed for peptization when considerable time between additions is allowed for diffusion. It is also plain that an increase in the excess of alkali arsenate throughout the precipitate forces a greater increase in the amounts of base needed for peptization if the base is added rapidly than if the base is added very slowly. Without doubt the influence of the alkali arsenate on the rate of diffusion of the base into the highly hydrated mass of fresh precipitate is a factor of importance.

The Stabilizing Influence of Alkali Arsenates and Phosphates.—If the ferric arsenate was precipitated by the action of the dihydrogen arsenate of potassium or sodium on ferric chloride, less sodium hydroxide is required for peptization than if the corresponding monohydrogen arsenate had been used in the precipitation. In general it may be stated that ferric arsenate precipitated by the action of ferric chloride on the corresponding arsenates of the alkali metals is peptized with the least base when ammonium arsenate has been used as the precipitating agent. In fact the ease of peptization of this series of products decreases in the order $NH_4 > K > Na > Li$. It is possible that there is a connection with the hydration of the alkali ions which increases in the reverse order from that just given. Ferric phosphate requires more base for peptization than does ferric arsenate and is less stable. A peculiar action was noted in this connection. Less sodium hydroxide than enough to peptize was added to some ferric phosphate. A part was filtered and the colloidal filtrate coagulated in two or three weeks. Another part allowed to stand over the unpeptized portion was stable indefinitely. This suggests the effect of mass action on a reversible reaction. Ferric phosphate peptized by just enough sodium hydroxide soon coagulated.

In Table II is shown the stabilizing influence of potassium dihydrogen arsenate when intimately mixed with the colloidal ferric arsenate (peptized by sodium hydroxide). Strangely enough this salt added *after* peptization by the base coagulated the colloid. A series of samples of this colloid containing different amounts of excess potassium dihydrogen arsenate used in the first precipitation of ferric arsenate were prepared and all peptized with just enough sodium hydroxide. In all experiments equal amounts of ferric arsenate suspended in 30 cc. of water were used. About 0.5 cc. additional N sodium hydroxide was required for each succeeding sample. This agrees with our statement that the greater the excess alkali arsenate present the greater the amount of base required for peptization.

Table II.

Stabilizing Effect of KH_2AsO_4 when Intimately Mixed with Colloidal Ferric Arsenate.

Excess KH_2AsO_4 present from the first. %.	Time of coagulation. Days.
None	7
25	10
50	20
75	40
100	60

A duplicate series was prepared and to each sample one cc. of 10% potassium dihydrogen arsenate was added after peptization. The sample containing no excess of arsenates, present from the first, coagulated at once and the others a few days laters in the same order as given in Table II. Here it is plainly evident that colloidal ferric arsenate peptized by just enough sodium hydroxide is stabilized towards the coagulating power of potassium dihydrogen arsenate if this same salt is thoroughly adsorbed before and during peptization. Of course, part of the base must react with the first addition to form potassium sodium hydrogen arsenate, the monohydrogen arsenate. The negative colloid probably adsorbs the polyvalent negative arsenate ions and with this increase in the charge on the particles a greater concentration of oppositely charged ions is required for precipitation.

Influence of Sugar and Sodium Chloride.—Ferric phosphate is much more difficult to peptize than the arsenate, yet, in the presence of relatively small amounts of sugar, peptization by sodium hydroxide to a rich red colloid is a simple matter. Without sugar the sodium hydroxide peptization of ferric phosphate forms a rather unstable colloid but in the presence of much sugar not even a high concentration nor a great excess of the base is sufficient to coagulate the colloid. Very concentrated base can be added rapidly with production of a stable sol. The effect on the arsenate is similar.

Glycerol acts in much the same manner as sugar but is not so potent.

It can prevent the precipitation of colloidal ferric arsenate by great excess of conc. sodium hydroxide but cannot prevent such coagulation of the phosphate.

We failed to obtain gels by dialysis of the colloidal ferric arsenate or phosphate peptized by sodium hydroxide or potassium hydroxide, yet if the peptization took place in the presence of sugar or glycerol, dialysis resulted in the formation of deep red gels in about two months.

Sodium chloride exerts an influence opposite to that of sugar. Even relatively small amounts of sodium chloride added to the unwashed precipitate of ferric phosphate entirely prevented peptization by sodium hydroxide. Yet in the presence of sugar this hindering effect of sodium chloride was nullified and the ferric phosphate peptized easily to a rich red sol.

II. Gels from Ferric Chloride Peptization.

Precipitated ferric arsenate is readily peptized by ferric chloride, ferric nitrate or ferric sulfate. On dialysis these colloids yield gels of excellent clearness and texture except in the case of ferric sulfate. As mentioned in a previous paper, ferric arsenate peptized by ferric sulfate, chromic sulfate or aluminum sulfate coagulates as a powder on dialysis.

As a rule it is best to use rather concentrated solutions of ferric chloride for peptization. A colloid peptized by 10% ferric chloride, for example, yields an inferior gel on dialysis. The gels formed when a considerable excess of ferric chloride is used as a peptizing agent are deep red in color, rather weak (or thin) in structure, and form more slowly than when less ferric chloride is used. In fact these differences are proportional to the excess of ferric chloride. Dialysis of this excess ferric chloride must form deep red colloidal ferric hydroxide. This is adsorbed by the ferric arsenate with increase in the depth of red color, decrease in viscosity, delay in set of the gel, and increase in the amount of solution separating on long standing. Attempts to use just enough ferric chloride for peptization produce a remarkable change in the appearance of the gel. Instead of requiring a few weeks' dialysis to form, the gel sets in two or three days. But the beautiful clearness of the yellow-red gels is lost. Although still somewhat transparent, the gel has a smoky or opalescent appearance. By transmitted light the color is a light yellow-brown, but by reflected light a dirty yellow-gray. With distinctly less than enough ferric chloride and filtration before dialysis an opaque butter often results. This indicates that attempts to add just enough ferric chloride for peptization really secure a very slight excess. This is all the more probable since with slower addition less peptizing agent is needed.

The Influence of Alkali Arsenates and Phosphates on Gel Formation.—Since ferric chloride exerts such a powerful peptizing influence on ferric arsenate our usual procedure was to add more than enough alkali arsenate to react with the ferric chloride. This excess could be washed out later, or known amounts of it allowed to remain.

Gels formed when a distinct excess of ferric chloride peptizes unwashed ferric arsenate and the product is dialyzed, are firm and very clear, forming in from one to four weeks' dialysis. Gels formed in similar manner from the washed ferric arsenate are dark red, weak, shrinking greatly with the separation of more solution than the other type and requiring from two or three times as long to set. Washed ferric arsenate peptized with just enough ferric chloride requires from 3 to 30 times longer dialysis to form a gel than when unwashed. Even mere peptization is slower on a washed precipitate. Phosphate gels are lighter in color than the arsenate, and form more quickly.

It is evident that the presence and later the slow removal by dialysis of the ions from the excess alkali arsenate greatly aid the distribution of water between the two phases necessary for a good gel structure.

In a series of experiments with ferric arsenate precipitated by the action of ferric chloride on diammonium hydrogen arsenate, potassium hydrogen arsenate and the other dialkyl hydrogen arsenates it was found that these precipitates peptized by ferric chloride and dialyzed formed gels in the same order as observed with sodium hydroxide peptization. For example, unwashed ferric arsenate made by starting with diammonium hydrogen arsenate was dialyzed (after ferric chloride peptization), and set to a gel in 6 days. The dipotassium and disodium products set more slowly while the gel derived from dilithium hydrogen arsenate set in 49 days. The series $NH_4 > K > Na > Li$ represented the order of influence. It is noteworthy that this reverses the order of hydration of the ions of these metals.

The gel starting from diammonium hydrogen phosphate (in a series of unwashed precipitates) set in 3 days, the gel from the disodium salt in 8 days and, as might have been expected, that from a combination of these two, sodium ammonium hydrogen phosphate, in intermediate time, 5 days.

Gels originating from the dihydrogen arsenates as a class form in much less time than those from monohydrogen arsenates. In fact, arsenic acid may be added with ferric chloride as a peptizing agent, and gel formation hastened. Of course the presence of any arsenic acid guarantees the formation of dihydrogen arsenates. This agrees with the observation of Diess that manganese dihydrogen arsenate sets to a gel without dialysis. We secured a good gel of zinc dihydrogen arsenate in less than one hour without dialysis.

The Influence of Sugar and Salts on Gel Formation.—The presence of sugar is an aid to gel formation on dialysis. It makes more difference with the washed precipitates than with the unwashed. However, ferric phosphate suspended in water saturated with sugar was peptized by ferric chloride and, on standing two months without dialysis, set to a somewhat opaque gel. Copper arsenate was peptized by ferric chloride and dialyzed to a gel in 6 weeks, but part of the same copper arsenate mixed with sugar and arsenic acid was peptized by ferric chloride and dialyzed to a clear blue gel in a few hours. In time this gel disintegrated.

Gels containing sugar separated a great deal of solution on standing. Urea, substituted for sugar, caused the separation of very little solution. A ferric phosphate-urea gel developes a striking growth of moulds. Naturally this was not true of arsenate gels.

Sodium chloride, even in low concentrations, greatly delayed the time of set of gels on dialysis as did other alkali chlorides. Under similar conditions a number of salts were added before peptization by ferric chloride. In general, they delayed the set.

Summary.

Ferric arsenate or phosphate can be peptized by sodium hydroxide or ferric chloride. With sodium hydroxide the action is greatly aided by sugar or glycerol but hindered by sodium chloride.

The presence of thoroughly adsorbed alkali arsenate in precipitated ferric arsenate forces the use of more sodium hydroxide for peptization but the resulting colloid is stable in direct proportion to the amount of alkali arsenate present. Furthermore, if it is ammonium arsenate that is present in excess, less base is required for peptization than in the case of other alkali arsenates, the order being NH_4, K, Na, Li.

On dialysis of the colloids formed by the action of sodium hydroxide on ferric arsenate or phosphate no gels form except in the presence of sugar or glycerol.

Dialysis of the colloids formed by the ferric chloride peptization of ferric arsenate or phosphate yields excellent gels. With barely enough ferric chloride for complete peptization the gels are opalescent and yellow-gray, forming in a few days. With excess ferric chloride the gels are red, weaker in structure, and slower in formation in direct proportion to this excess.

Gels form in much less time when the original precipitate of ferric arsenate contains thoroughly adsorbed alkali arsenate. Moreover, this accelerating influence of alkali arsenates decreases in the order $NH_4 > K > Na > Li$.

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