

the behavior of a solution of potassium chromico-molybdate upon dialysis, have favored the assumption that we have here a complex inorganic acid.

The mercurous salt of the chromico-molybdic acid, obtained by using an excess of mercurous nitrate, contains eight molecules of Hg_2O . Since the preparation of this salt would liberate ten molecules of nitric acid it can scarcely be a basic salt, but is either the normal salt or one in which nearly all of the replaceable hydrogens have been replaced.

Alkali salts of ferrico-molybdic acid analogous in composition to those of the aluminico- and chromico-molybdic acids were obtained. These are undoubtedly constituted in a similar manner, the R_2O_3 oxide being a part of the acid portion of the salt. These sesquioxides have more characteristic basic than acid properties. With Al_2O_3 and Cr_2O_3 the acid properties are developed in the presence of strong bases, but in their compounds prepared and described above the MoO_3 must influence their nature, causing them to lose their basic properties, since here they, together with the MoO_3 , function as an acid, and they are not replaceable by metallic oxides, although in an acid environment, a condition adapted to bring out their basic character.

The derivatives of manganoso-molybdic acid obtained had that portion of the manganese combined with the molybdenum to form the acid, present as the dioxide, confirming the work of Friedheim and Samuelson in this respect. Derivatives of a nickeloso- and of a cobaltoso-molybdic acid containing the nickel and the cobalt as the dioxide and analogous in composition to the similar manganoso-molybdates were prepared. There can be little doubt as to the state of oxidation of the nickel and cobalt contained in them, and the fact that they contain the dioxides of these elements make them of especial interest.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY NO. 133.]

SOME NEW DOUBLE PHOSPHATES OF IRON (FERRIC) AND ALUMINUM¹

BY LOUIS J. COHEN.

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In an unpublished paper J. L. Danziger states that by the addition of a large excess of diammonium phosphate to a solution of ferric chloride strongly acid with hydrochloric acid, he obtained a white powder which on analysis so closely approximated the formula $\text{NH}_4\text{H}_2\text{PO}_4 \cdot \text{FePO}_4$ as to warrant the belief in the existence of such a double phosphate of ferric

¹ Read at the December meeting of the New York Section of the Am. Chem. Society.

iron. By the same method of precipitation, the existence of corresponding sodium and potassium salts was indicated, although the latter products were not quantitatively analyzed.

The verification and extension of this preliminary work of Danziger, served as the object of this investigation.

The Double Phosphate of Iron.



By closely following the method of Danziger, difficulty was at once met with in washing the precipitate formed entirely free of phosphoric acid with cold water; for after hours of washing, the wash water still gave a decided test for phosphate. Further washing gave the same result. From the persistence of phosphate in the wash water in apparently uniform amounts, after considerable water had been employed, it became evident that the phosphoric acid in the wash water was derived from some other source than either the excess of the reagent or by-products of the initial reaction. Accordingly a series of precipitates was prepared and washed with a limited though sufficient quantity of water. The products after drying at 100° were analyzed. Results low in phosphorus and ammonia were obtained. Repeated attempts to obtain a salt of normal composition by washing with water the products formed under slightly varied conditions, gave substantially the same low figures for phosphorus and ammonia as shown below:

	Found			Theory per cent.
	A per cent.	B per cent.	C per cent.	
Fe	21.20	21.10	21.20	21.05
P	22.83	22.40	22.75	23.30
NH ₄	6.31	6.31	5.96	6.76

These results are in agreement with those obtained by Danziger.

	per cent.
Fe	21.15
P	22.95

After considerable experimentation, the following method was found to yield a salt of normal composition.

A solution consisting of 200 cc. of ferric chloride (containing 20 grams FeCl₃) 80 cc. hydrochloric acid (sp. gr. 1.2) and 120 cc. water, was heated to about 70°. To this was added gradually and with constant stirring a hot solution of diammonium phosphate (120 grams in 200 cc. of water). The color of the iron solution weakened with the addition of the phosphate and finally disappeared. Further addition of diammonium phosphate produced a creamy white flocculent precipitate which on prolonged heating on a boiling water-bath, or with constant stirring on an asbestos pad heated by a Bunsen burner, was observed to change (at from 91° to 95°) to a perfectly white and powdery form resembling barium sulphate, leaving a clear, colorless supernatant liquid. After digestion

on a boiling water-bath for one-half hour, the supernatant liquid was siphoned off and the residual compact mass washed several times by decantation with an alcoholic solution (1 part 95% alcohol to 2 parts water) containing 0.1 per cent. ammonium chloride, and finally washed on a filter with alcohol (1:1) till free of chlorides.¹ It was then dried at 100° in a water oven and analyzed.

The iron was determined volumetrically with a standard potassium permanganate solution by the Zimmermann-Reinhart method; the phosphorus was separated from the iron in the usual way with ammonium molybdate solution, and ultimately weighed as magnesium pyrophosphate. The ammonia was determined by distillation with caustic potash into a standard acid solution.

	Found per cent.	Theory for $\text{NH}_4\text{H}_2\text{PO}_4\text{FePO}_4$ per cent.
Fe	20.89	21.01
P	23.20	23.30
NH_3	6.60	6.76

Having obtained a salt of normal composition, it was thought desirable to ascertain the effect of water on this salt with a view to account for the low results obtained for phosphorus and ammonia in the first products which had been subjected to excessive washing with water. To this end 3 grams of the salt were treated in a flask with about a liter of water (at room temperature 28°), the contents thoroughly agitated, allowed to settle and the clear liquid filtered. This was repeated until the combined washings measured six liters. The residual salt was dried at 100° and on comparison with the untreated sample appeared yellowish, thus indicating hydrolysis. Analysis of the residue gave:

	per cent.
Fe	21.43
P	22.40
NH_3	6.35

Comparison of these figures with those obtained for the normal salt conclusively shows that the water dissolved out phosphorus and ammonia.²

An examination of the washings concentrated to 250 cc. showed the absence of iron and the presence of ammonia and phosphorus; but the amounts of the latter were insufficient for an accurate quantitative estimation.

To intensify the hydrolytic effect of water 0.9921 gram of the normal salt was treated in a similar way as above with a liter of hot water 90°; (the average temperature of the water at the time of filtration 66°) the operation was repeated with another liter of hot water. The residue was

¹ The final washings though free of chlorides gave a test for PO_4 with ammonium molybdate solution.

² An explanation of this fact will be given at the end of this section.

noticeably brownish yellow after the first treatment. The filtrates were combined and evaporated in a platinum dish on a water-bath to dryness, then placed in a water-jacketed oven and finally weighed.

Weight of total residue was 0.1038 gram equal to 11.25 per cent. of the original salt. This residue was dissolved in water,¹ the solution made up to 250 cc. and aliquot portions analyzed for phosphorus and ammonia.

Found :

	per cent.
P.	35.56
NH ₄	14.94

The amount of phosphorus in the filtrate is in excess over that necessary to form monammonium phosphate with the ammonia found. This excess as will be explained below is due to the hydrolysis of the ferric phosphate. The analysis of the residual salt after treatment with hot water gave :

	per cent.
Fe	21.95
P.....	21.46
NH ₄	5.61

The deficiency in phosphorus and ammonia here indicated was found to be exactly compensated by the ammonia and phosphorus found in the wash water.

The above experiments conclusively show that the action of water on the salt consists in dissolving out some phosphorus and ammonia accompanied by a change in color of the compound. The alcoholic solution (1:1) employed in the final washing of the salt also removed phosphorus, as shown by the presence of the latter in the washings after the complete removal of chloride. Inasmuch as the amount of phosphoric acid found in the wash water is in excess over that required to form monammonium phosphate² with the ammonia found, this excess must have been derived from the ferric phosphate. This conjecture is borne out by the investigations of Caven,³ and verified by Cameron and Hurst,⁴ which establish the hydrolysis of ferric phosphate by water beyond a doubt. That the darkening of the compound is also due to the hydrolysis of ferric phosphate is confirmed by the work of Caven,⁵ who treated his white variety of ferric phosphate with hot water and obtained a yellowish or brownish basic phosphate.

¹ This solution was faintly acid to litmus and to congo-red and gave no test for iron.

² As the solution was acid to congo-red, no diammonium phosphate could have been present.

³ J. Soc. Chem. Ind., 15, 17-19.

⁴ This Journal, 26, 885.

⁵ loc. cit.

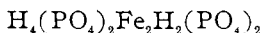
The presence of ammonia and the greater part of the phosphoric acid found in the water with which the normal salt was treated, may be accounted for by the slight solubility of the double salt with the subsequent dissociation into the soluble diammonium phosphate and the insoluble ferric phosphate; the latter yielding additional phosphoric acid by hydrolysis with the simultaneous formation of an equivalent amount of ferric hydroxide.

The behavior of this double salt when subjected to excessive washing with water is not peculiar to this particular compound, but rather characteristic of a class of double alkali phosphates to which it belongs. A double phosphate of sodium and copper prepared by Steinschneider,¹ and having the same type formula as the iron and ammonium salt, was observed when treated with water to undergo changes precisely similar to those already described for the double phosphate of iron and ammonium. In this case the loss of sodium and phosphoric acid was accompanied by a change in color from a beautiful blue to a greenish white. A corresponding double phosphate of ammonium and aluminum next to be described showed a similar behavior when treated with water.

Properties of $NH_4H_2PO_4, FePO_4$.—The double phosphate of ferric iron and ammonium readily dissolves in hydrochloric acid to a yellow solution; with nitric, sulphuric and phosphoric acids, colorless solutions are obtained. It is practically insoluble in 50 per cent. acetic acid. When treated with ammonia in the cold, partial hydrolysis takes place as indicated by the change in color from white to light brown; on prolonged heating, particularly when the ammonia is in great excess, the double phosphate completely dissolved to a reddish brown solution. Caustic alkalis completely hydrolyze the double salt. The solubility of the compound in phosphoric acid is noteworthy, because of its inability to reprecipitate on the addition of ammonia. If to a solution of the double salt in phosphoric acid, ammonia be added drop by drop, it acquires a yellow tint which deepens with the further addition of the reagent, but no precipitate was observed to form, even when sufficient ammonia had been added to render the solution strongly alkaline. A similar deportment was observed in a phosphoric acid solution of ferric phosphate prepared by adding dilute phosphoric acid to ferric chloride until the precipitate which first formed redissolved. From this solution ammonia failed to precipitate either the hydroxide or phosphate of iron. These results find their explanation either in the solubility of the phosphate in ammonium phosphate, or as being due to the combination of ferric phosphate with phosphoric acid to form a complex phosphoferric acid, $H_3Fe(PO_4)_2$, the iron of which is not precipitable by ammonia and of which the iron salt just described is a derivative. The latter supposition

¹ "Ueber die Phosphate des Kupfers" - Dr's. Dissertation Halle, a. S., 1850.

appears to be confirmed by the work of Erlenmeyer,¹ who prepared a compound to which he assigned the formula $\text{Fe}_2\text{O}_3(\text{P}_2\text{O}_5)_2 \cdot 8\text{H}_2\text{O}$, and which is resolved into $(\text{H}_2\text{PO}_4)_2\text{Fe}_2(\text{HPO}_4)_2$, and called the primary secondary ferriphosphate, and monodiferric phosphate. Arranged somewhat differently the structural formula becomes :



and simplified $\text{H}_2\text{PO}_4\text{FeHPO}_4$ or $\text{FeH}_3(\text{PO}_4)_2$. It is manifest that this is the hypothetical phosphoferric acid referred to above. When ignited, the double salt decomposes, giving off ammonia and water.

Further Study of the Action of Ammonia.—As the action of an excess of hot strong ammonia on the double salt seemed anomalous, further study was undertaken with a view to throw some light on the complex phosphate which doubtless formed, and which appeared to be soluble in an excess of ammonia. Freshly prepared ammonium ferric phosphate, after partially drying in the air, was treated in a beaker with a large excess of strong ammonia and heated on an asbestos pad. The white double salt first became brown, and on prolonged heating, finally dissolved with the formation of a deep reddish brown solution. A portion of this solution was poured into a crystallizing dish and allowed to evaporate spontaneously in the hope of crystallizing out a dissolved complex phosphate. On standing for several days the concentrated solution was cleared up by the addition of more ammonia, and on further evaporation a syrup was obtained, which on prolonged exposure was converted to a brown mass, but no crystals appeared.

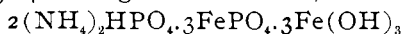
Spontaneous evaporation of the ammoniacal solution having thus failed to yield a crystalline body, another portion was treated with 95 per cent. alcohol with the object of diminishing the solubility of any dissolved complex phosphate that the solution might hold. A brown voluminous gelatinous precipitate formed when an excess of 95 per cent. alcohol was added.

This was filtered and slightly washed with 95 per cent. alcohol and dried at 90°. The filtrate possessed a slightly yellowish tint and gave a strong test for phosphate.

Analysis of brown precipitate gave :

	A	B	Combining ratio	Calculated per cent. for formula below.
	per cent.	per cent.		
Fe	32.64	32.86	0.581	32.37
P.....	14.94	15.00	0.482	14.93
NH ₄	6.94	6.96	0.385	6.93

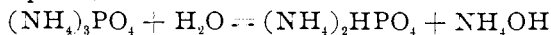
from which it appears that the ratio of iron to phosphorus to ammonia is 1.5 : 1.25 : 1 or 6 : 5 : 4 leading to the formula,



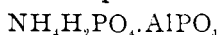
which is a basic double ammonium ferric phosphate. That this com-

¹ Studien über phosphosäure Salze, Ann., 194, 188.

pound is basic might have been surmised from its color, and by the presence of phosphoric acid in the alcoholic filtrate. The assumption of the secondary ammonium phosphate instead of the tertiary in the formula seems justified because of the instability of the latter; for on drying, the tertiary salt would be hydrolyzed by the water or alcohol, to form the secondary phosphate, thus:



The Double Phosphate of Aluminum.



As no mention is made in the literature of a double phosphate of aluminum corresponding in composition to the double phosphate of iron just described, an attempt was made to prepare it. The method which yielded this salt was similar to that employed in the preparation of the iron salt, except as regards acidity, which in this case was somewhat greater.

Preparation—Ten grams of C.P. aluminum chloride were dissolved in 300 cc. of hydrochloric acid (1:1) and the resulting solution heated to about 65°. To this was added, with constant stirring, a hot saturated solution of diammonium phosphate and finally the solid salt till precipitation occurred. The volume at the time of precipitation was approximately 1000 cc. and the amount of diammonium phosphate added 230 grams. The precipitate when first formed was gelatinous in character, resembling aluminum hydroxide; but on continued heating on an asbestos pad over a bunsen burner, and constantly stirring (to avoid bumping), the precipitate was observed to change at 90° to a dense powder, which rapidly settled on standing. The rise in temperature from 65° to 90° consumed one half hour. The precipitate and clear solution were then heated on a boiling water bath for one half hour and then allowed to stand over night. The next day the clear solution was siphoned off and enough warm water added to dissolve the primary ammonium phosphate which crystallized over the white mass on the bottom of the beaker. The clear solution was again siphoned off and the residual white compact mass washed several times by decantation with an alcoholic solution (1:2) containing 0.1% of ammonium chloride and finally transferred to a filter and washed with alcohol (1:1) till free of chlorides.¹

It was then dried at 96°–98° in a water-jacketed oven and analyzed.

The ammonia and phosphorus were determined by the same method employed in the analysis of the iron salt. The aluminum was determined, with slight modification, by the method given by Crookes.² About one gram of the salt was dissolved in the least amount of concentrated hydrochloric acid, diluted somewhat, and an excess of a strong solution of sodium hydroxide (free from aluminum) added. The clear resulting

¹ The final washings though free of chloride gave a test for phosphate.

² Crooke's Select Methods in Chemical Analysis, 4th Ed., p. 520.

solution was warmed and barium chloride added till no further precipitation occurred. The mixture was then digested at a gentle heat for one-half hour, filtered and the precipitated barium phosphate washed free of chlorides with a very dilute solution of sodium hydroxide. The filtrate after being slightly acidified with hydrochloric acid was concentrated to 250 cc. ; 100 cc. of this solution were pipetted out, and after removing the barium with sulphuric acid, the aluminum was precipitated with ammonia and ignited to Al_2O_3 .

	Found per cent.	Theory for $NH_4H_2PO_4 \cdot AlPO_4$ per cent.
Al	11.53	11.42
P.	26.16	26.13
NH_4	7.79	7.61

A salt prepared under slightly different conditions of acidity and concentration of the precipitant gave substantially the same results.

Properties of the aluminum salt—A qualitative study of the action of water on this salt, showed that it was hydrolyzed in precisely the same way as was noted in the case of the iron salt. Its solubilities are the same as those for the iron salt, except toward alkalies ; in the latter it dissolves completely, behaving like aluminum phosphate. On ignition it gives off ammonia and water.

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Feb. 1907.

PHASE RELATIONS OF THE SYSTEM : SODIUM CARBONATE AND WATER

By R. C. WELLS AND D. J. MCADAM, JR.
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The experiments described in this paper concern the phase relations of sodium carbonate between 25° and 45° , an interval which includes all the known transition points of the hydrates. Somewhat over a year ago, Dr. L. F. Witmer and one of us were determining the solubility of this salt for the purpose of ascertaining the number of hydrates. We had made certain of at least two quadruple points when the new edition of Landolt and Börnstein's tables brought to our attention the inaugural dissertations, dealing in part with this very subject, by Herman Epple, Heidelberg, 1899 and C. H. Ketner, Leiden, 1901. After securing Epple's dissertation, we were surprised to find that he described the lower hydrates as octa and dihydrates. Our own analyses had led us to decide that they were hepta and monohydrates, although in order to get those results we had to take special precautions to prevent enclosed mother liquor from crystallizing as decahydrate and thus giving too high a percentage of water. Ketner, however, settled the matter very conclusively by analyzing a ternary mixture (sodium carbonate, alcohol and water) according to the method of Schreinemacher, and could obtain no other hydrates than those with 10, 7, and 1 molecule of water.