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AMMONIUM PHOSPHOMOLYBDATE AND THE REDUCING ACTION OF ZINC IN THE REDUCTOR.

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AMONG the problems presented to the sub-committee on Methods of the International Steel Standards Committee, in the choice of a method for the determination of phosphorus in steel, none seemed more important than those involved in the composition of ammonium phosphomolybdate, and the reducing action of zinc on the molybdic acid of this salt under different conditions. The object of this investigation was to present data for the settlement of this question.

COMPOSITION OF AMMONIUM PHOSPHOMOLYBDATE.

In the preparation of ammonium phosphomolybdate the method usually followed was to precipitate the salt by adding a solution of microcosmic salt to a solution of ammonium molybdate in nitric acid; but Doolittle and Eavenson[1] showed that ammonium phosphomolybdate precipitated from a solution containing a large excess of ferric nitrate had essentially the same composition as that obtained by following the usual method of procedure.

In the investigation which we have made, we prepared a number of samples under different conditions and made careful analysis of each as a basis for our work.

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[1] This Journal, 16, 234.

Sample 1.—Prepared by dissolving twenty grams of steel free from arsenic in nitric acid, adding twenty-five cc. of a saturated solution of microcosmic salt, evaporating to dryness, heating until the ferric nitrate was decomposed, dissolving in hydrochloric acid, diluting, filtering, evaporating to syrupy consistency, and then evaporating three times with excess of nitric acid to remove the hydrochloric acid. The solution was diluted to one liter, heated to about 60° C., and poured into one liter of molybdate solution. The precipitate was allowed to settle, the supernatant liquid was decanted, and the precipitate was washed by decantation with water containing one per cent. of nitric acid and finally filtered, washed, dried, removed from the filter, and heated to 150° C. for five hours.

Sample 2.—Prepared by partially neutralizing the first decantation from sample 1, adding twenty-five cc. more of the same microcosmic salt, washing, and drying the precipitate as above.

Sample 3.—Prepared by pouring a solution of microcosmic salt acidulated by nitric acid into molybdate solution, washing with water containing one per cent. of nitric acid, and filtering. A portion of this precipitate was dried at 150° C. for eight hours for sample 3.

Sample 4.—Prepared by taking a second portion of the precipitate above, washing with ice-water and drying over potassium hydroxide at the ordinary temperature for three months.

Sample 5.—Prepared by taking a third portion of the same precipitate, washing again with water containing one per cent. of nitric acid, and drying in the same manner as sample 4.

Sample 6.—The same as sample 5, but digested and washed before drying with water containing five per cent. of nitric acid.

Sample 7.—The same as sample 5, but digested and washed with water containing ten per cent. of nitric acid.

Sample 8.—Prepared by dissolving ferric oxide (obtained by igniting pure ferric oxalate) in hydrochloric acid, adding five per cent. of pure phosphoric anhydride, evaporating off the hydrochloric acid with nitric acid, heating to 80° C., adding an excess of molybdate solution at 20° C., shaking in a large flask for three minutes and washing with water containing one per cent. of nitric acid. After thorough washing, the precipitate was digested with consecutive portions of water, containing varying amounts of nitric acid and with water containing nitric acid and ammonium nitrate. Then after standing two months with half a liter of water, containing five per cent. of nitric acid, it was filtered, washed with water containing five per cent. of nitric acid, and heated to 100° C. for five hours.

Sample 9.—Prepared from the same reagents, and in the same manner as sample 8. Washed by decantation with water containing five per cent. of nitric acid, dried at 100° C. for eight hours.

Sample 10.—Prepared and washed in the same manner as sample 9, but dried at 100° for twelve hours.

The methods employed in the analyses of these samples are the usual ones except that for the determination of water, and a general description will be sufficient.

As the salt is very hygroscopic the samples were in all cases placed in drying tubes with glass stoppers, heated to the temperature indicated, cooled over fused potassium hydroxide, and weighed out by difference.

DETERMINATION OF PHOSPHORIC AND MOLYBDIC ACIDS.

About two grams of the salt was weighed out by difference into a beaker, dissolved in twenty-five cc. of ammonia (0.96 sp. gr.) transferred to a carefully calibrated half liter flask and diluted to the mark with water. The solution was thoroughly mixed by pouring it into a dry beaker and back into the flask several times. By means of a pipette, which had been carefully tested against the flask, 100 cc. (containing about four-tenths gram of the salt) was measured into a beaker for the estimation of the molybdic acid, and 200 cc. (containing about eight-tenths gram of the salt) was measured into another beaker for the estimation of the phosphoric acid. To the latter was added, drop by drop, ten cc. of magnesia mixture with constant stirring, then fifty cc. of ammonia and the precipitated ammonium magnesium phosphate was allowed to stand over night. The precipitate was filtered, washed with ammonia water, dissolved on the filter in dilute hydrochloric acid, made slightly alkaline with ammonia, ammonium sulphide added, the solution acidulated with hydrochloric acid and hydrogen sulphide passed through the hot solution for half an hour. The precipitated molybdenum sulphide was filtered off, the filtrate was boiled to expel hydrogen sulphide and the ammonium magnesium phosphate reprecipitated as before. This precipitate was filtered off, burned and weighed as magnesium pyrophosphate, and the phosphoric acid and phosphorus calculated in the usual way.

The solution for the determination of molybdic acid was diluted to about three-fourths of a liter with hot water, heated to boiling, slightly acidulated with acetic acid and a boiling solution of lead acetate (containing about three grams of the salt) was added. After boiling for about fifteen minutes the precipitate was allowed to settle, decanted through an asbestos filter on a Gooch crucible, washed thoroughly by decantation with hot water, transferred to the crucible, dried at 120° C., and weighed as the mixed lead phosphate and molybdate.

The percentage of the mixed salts was calculated and from this amount was subtracted the percentage of lead phosphate found by multiplying the percentage of phosphorus previously found by 13.086. The difference (lead molybdate) multiplied by 0.39242 gave the percentage of molybdic acid.

DETERMINATION OF AMMONIA.

About one and a half to two grams of the salt was weighed out into a funnel inserted in the neck of a fractional distillation flask and washed down into the flask with water. The flask was fitted with a stopper carrying a bulb tube with a glass stopcock. The side tube of the flask was fitted into a glass condenser to the lower end of which was attached one arm of a large bulb U tube containing ten cc. of hydrochloric acid and twenty cc. of water. The other arm of the U tube was fitted with a small calcium chloride tube, containing broken glass moistened with water. Fifty cc. of pure potassium hydroxide (1.27 sp.

gr.) was admitted to the distillation flask through the bulb tube, and the ammonia was distilled over. The contents of the U tube were transferred to a beaker, platinic chloride added, and the ammonia determined in the usual way.

DETERMINATION OF WATER.

The determination of water in ammonium phosphomolybdate offered unexpected difficulties. After repeated trials to get satisfactory results by heating the salt with sodium tungstate the following method was adopted :

At the middle point of a tube of hard glass 200 millimeters long, and nineteen millimeters in diameter was fused at right angles a tube thirty-seven millimeters long and nine millimeters in diameter. In the small tube a thermometer was fitted with sheet asbestos. The bulb of the thermometer extended a short distance into the large tube. The tube was placed in a horizontal position across the ring of an iron retort holder, the middle of it being protected by a piece of sheet copper three inches long bent around it, but separated from it by sheet asbestos. The ends of the tube were fitted with perforated corks, one carrying a small glass tube for the passage of dry air, and the other a U tube filled with calcium chloride. A porcelain boat sixty-two millimeters long and twelve millimeters wide was provided to hold the salt.

The stand holding the tube now closed with solid stoppers was placed near the balance case, about two grams of the salt was weighed out by difference into the boat which was immediately placed in the tube, and the latter closed by the corks. It was then placed in position, the perforated corks substituted for the others and a current of dry air passed through while the tube was heated by a Bunsen burner until the thermometer registered 250° C. The increase in weight of the calcium chloride tube gave the amount of water.

The only danger apprehended was that of decomposing the salt and liberating its ammonia, but careful experiments made by passing the air over the salt heated to 250° C. and into Nessler's solution showed that no trace of ammonia was given off.

The results of the analysis of the samples are as follows:

Sample.	Phosphoric acid. Per cent.	Molybdic acid. Per cent.	Ammonium oxide $(NH_4)_2O$. Per cent.	Water. Per cent.	Ratio of Phosphorus to 100 molybdic acid.
1	3.79	91.88	3.33	1.02	1.799
2	3.79	91.63	3.39	1.30	1.805
3	3.80	91.67	3.34	1.22	1.810
4	3.59	88.06	3.56	5.02	1.778
5	3.63	89.07	....	....	1.786
6	3.57	86.44	....	....	1.802
7	3.56	86.89	....	....	1.789
8	3.73	91.37	2.64	1.96	1.780
9	3.79	92.33	3.12	0.71	1.790
10	3.81	91.96	3.03	1.17	1.807
				Average for the ten samples,	1.7946

These results are sufficient to show remarkable uniformity in the composition of ammonium phosphomolybdate precipitated under varying conditions and may be considered as practically answering the question as to the effect of the presence of ferric nitrate in the solution from which the precipitation is effected.

There are two points worthy of remark in these results. First, the variation in the amounts of water in the different samples, and second, the variation in the amounts of ammonia.

The explanation of the first point is found probably in the temperature of drying, that of the second in the washing of the precipitated salt. Sample 8, which was digested for a long time with dilute nitric acid, had lost most ammonia. This is borne out by the fact that the ammonia can all be destroyed by digestion with aqua regia and phosphomolybdic acid crystallized out from the solution. In this connection the following table of calculated composition compared with results obtained by analysis may be of interest:

SAMPLE 10.

		Theory. Per cent.	Actual determination. Per cent.
24 MoO_3	3456	91.19	91.96
P_2O_5	142	3.74	3.81
3 $(NH_4)_2O$	156	4.12	3.03
2 H_2O	36	0.95	1.17
	4790	100.00	99.97
Phosphorus ratio		1.794	1.807

SAMPLE 4.

		Theory. Per cent.	Actual determination. Per cent.
24 MoO_3	3456	87.45	88.06
P_2O_5	142	3.59	3.59
3 $(NH_4)_2O$	156	3.95	3.36
22 H_2O	198	5.01	5.02
	3952	100.00	100.03
Phosphorus ratio		1.794	1.778

The last trace of water seems to go off between 150° and 250° C., but the samples having been prepared and analyzed after drying at or below 150° C it was not deemed necessary to prepare the anhydrous salt especially as it is very hygroscopic. In view of the fact that the variation in the ratio of molybdic acid to phosphorus is so small (the average of the ten samples being 1.7946) we may without hesitation adopt the theoretical ratio of 1.794.

Samples 4, 5, 6, and 7 were prepared to test the accuracy of the statement made by Hundeshagen[1] that the precipitated ammonium phosphomolybdate washed with dilute acid and dried in a desiccator over calcium chloride and potassium hydroxide had the composition

$$12MoO_3, P_2O_5, 3(NH_4)_2O, 4HNO_3, 2H_2O.$$

Actual tests of these samples made by dissolving weighed amounts in a standard solution of potassium hydroxide and titrating back with standard nitric acid gave the following results:

	Standard alkali required to neutralize one gram of salt.
No. 3	130.53
" 4	119.14
" 5	121.25
" 6	123.59

Sample 7 was unfortunately used up in the preliminary analysis and none remained for this test, but as No. 3 was heated to 150° C., and the others were dried as described above, No. 4 having been washed with water, No. 5 with one per cent. nitric acid, and No. 6 with five per cent. nitric acid the results do not seem to bear out Hundeshagen's statement.

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[1] *Chem. News*, 60, 168.

It was hoped also, that the neutralization (Handy's) method might offer some advantages over the reduction method for the determination of phosphorus in steel, but the hygroscopic charactor of the ammonium phosphomolybdate and the lack of agreement in the results obtained caused us to abandon this part of the investigation.

THE REDUCTION OF MOLYBDIC ACID BY ZINC.

When a solution of ammonium phosphomolybdate in ammonia is acidulated with sulphuric acid and the molybdic acid is reduced by metallic zinc it was claimed by Wericke that the reduction was not to the form Mo_2O_3 but to $Mo_{12}O_{19}$. This theory was adopted by Emmerton and has been generally accepted by chemists as the formula to be used in the determination of phosphorus by the reduction method. When Jones' reductor came into general use it was noticed that the green color of the reduced solution was more permanent and the oxidation with potassium permanganate was from this color and not from the port-wine color referred to by Emmerton. Babbitt[1] claimed that the reduction was to a point between Mo_2O_3 and $Mo_{12}O_{19}$ but Noyes[2] claimed that the reduction was to Mo_2O_3.

The reactions may be indicated as follows for the subsequent oxidation by potassium permanganate:

$$5Mo_{12}O_{19} + 17K_2Mn_2O_8 = 60MoO_3 + 17K_2O + 34MnO,$$
$$5Mo_{24}O_{37} + 35K_2Mn_2O_8 = 120MoO_3 + 35K_2O + 70MnO,$$
$$5Mo_2O_3 + 3K_2Mn_2O_8 = 10MoO_3 + 3K_2O + 6MnO,$$

then as

$$10FeSO_4 + K_2Mn_2O_8 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O;$$

or one molecule $K_2Mn_2O_8$ oxidizes ten molecules of iron to the ferric condition, and we have for the ratio of iron to molybdic acid 100 to 90.756 in the first case, to 88.163 in the second, and to 85.714 in the third.

In other words, we must multiply the value of the permanganate solution in iron by 0.90756, by 0.88163, or by 0.85714 according to the theory we adopt for the reducing action of zinc on the solution of ammonium phosphomolybdate.

[1] *J. Anal. Appl. Chem.* 7, 165.

[2] This Journal, **16**, 553.

The differences are certainly too great to be disregarded, and it becomes necessary to decide which theory we must adopt.

We have, therefore, sought to discover in the following experiments, first, what conditions affect the reduction, and secondly, whether the methods in ordinary use are capable of giving uniform results.

First, sample 10, containing 91.96 per cent. molybdic acid was selected for these experiments and a number of glass stoppered weighing tubes were filled with the carefully ground and dried salt. About two grams of the salt was weighed by difference into a beaker, dissolved in five cc. ammonia (0.96 sp. gr.) washed out into a half liter flask, diluted to the mark with distilled water, mixed by pouring back and forth into a dry beaker, and measured out by means of a twenty-five cc. pipette, carefully tested with the flask into beakers. Twenty cc. ammonia (0.96 sp. gr.) were added, the solution was acidulated with twenty-five cc. sulphuric acid (1–4) and passed through the reductor. The reduced solution was titrated with standard permanganate and the molybdic acid calculated by the proper formula.

The reductor shown in the accompanying sketch was used. This form of reductor was suggested by Mr. W. P. Barba of the Midvale Steel Co., a member of the sub-committee on Methods of the International Steel Standard Committee, and has been found most convenient.

In the bottom of the reductor tube A was placed a spiral of platinum wire, on top of this a piece of platinum gauze, a wad of glass wool six millimeters thick, and then a thin film of asbestos. The tube was filled with granulated zinc to within thirty-seven mm. of the top and a wad of glass wool twelve millimeters thick filling the diameter of the tube placed on top. This served to distribute the acid and to prevent the liberated hydrogen from spattering the solution on the upper part of the tube. The solution having been placed in the beaker B, the latter was placed on the stand C, and the tube D placed in position. The flask F having been attached, the block E was placed under it, and the pump having been connected the liquid was drawn over from B.[1] When the liquid in B was almost all

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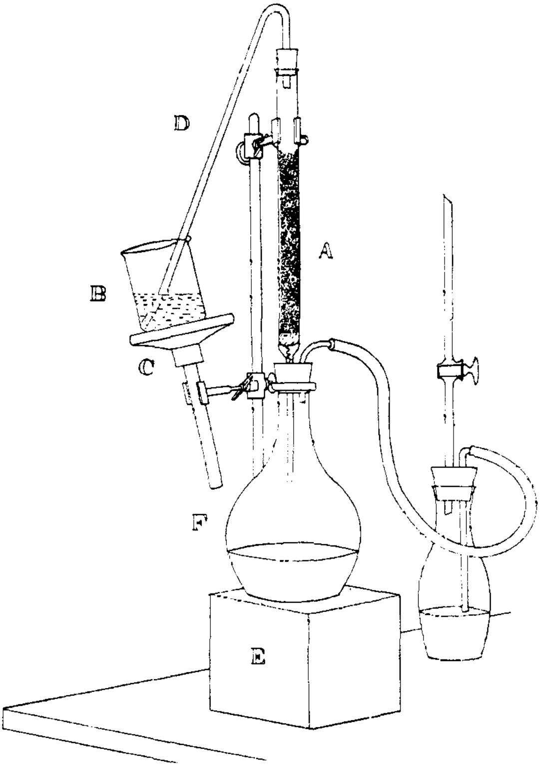
[1] See seq. for use of dilute sulphuric acid for washing.

drawn over, the sides of the beaker were washed down and then the beaker was filled with water, and when this was all drawn over, the stopper carrying the tube D was removed and the reductor tube was filled with water to thoroughly wash out the top of the tube. The flask was removed, the end of the reductor tube washed into it, the sides of the neck of the flask washed down with water, and the reduced liquid was titrated in the flask.



In making a blank determination, the solution was made up as nearly as possible to the composition of the solution of the salt; *viz.*, twenty cc. ammonia, twenty-five cc. sulphuric acid (1–4) and water to the same volume.

In giving the results of our experiments, it seems unnecessary to give all the figures as they comprise several hundred in number, extending over a period of six months. Only those illustrating the facts of interest are therefore annexed.

The most curious result obtained was in an effort to get the greatest possible reduction of the solution by repassing it through the reductor, heating it nearly to boiling after each passage. In the third passage, the solution instead of coming through green in color, was almost colorless and the green oxide of molybdenum was found deposited on the zinc in the reductor. In another attempt to reduce the molybdic acid by treating the solution in a flask with zinc in a current of hydrogen at a boiling temperature, redissolving the excess of zinc by sulphuric acid admitted through a funnel tube, allowing the solution to cool in the current of hydrogen after diluting by means of the funnel tube with boiled distilled water and titrating in the flask, the following results were obtained:

Weight of phosphomolybdate	0.08784 grams.
Volume of permanganate required	24.9 cc.–24.9 cc.
Molybdic acid on Mo_2O_3 theory.....	84.86 per cent.
" " " $Mo_{24}O_{37}$ "	87.28 "
" " " $Mo_{12}O_{19}$ "	89.85 "
" " " Mo by grav. det	91.96 "

showing that the reduction was not even to $Mo_{12}O_{19}$.

A series of determinations was made to test the best rate of speed for passing the solution through the reductor, and for a column of zinc from two hundred to two hundred and fifty mm. no appreciable difference was noticed between a speed of two minutes and one of ten minutes for the passage of a solution made up in the usual way, except that it was necessary to follow the solution of phosphomolybdate by dilute sulphuric acid when the rate of speed was very slow to avoid leaving some molybdenum trioxide in the zinc. This precaution was finally made a part of every determination and the beaker which contained the solution to be reduced, was washed down with a hot solution of sulphuric acid (ten cc. of sulphuric acid (1–4) diluted to 100 cc.) and the operation was completed by washing with water. A speed of about two minutes was finally adopted with a hot solution. It was also found advisable to pour fifteen cc.

of sulphuric acid (1–4) into the titrating flask, before attaching it to the reductor.

The following results will illustrate the effect of dilution:

Weight of phosphomolybdate.	Volume of solutions in cc.	Permanganate required in cc.	MoO_3 by $Mo_{24}O_{37}$ theory. Per cent.
0.03095	175	9.0	88.83
0.03095	175	0.2	90.80
0.06190	175	18.35	90.55
0.06190	175	18.40	90.80
0.15475	175	46.40	91.59
0.15475	175	46.35	91.49
0.03589	500	10.1	85.76
0.14356	500	42.6	90.64
0.07178	500	20.9	88.94
0.14356	250	43.1	91.71
0.07178	250	21.0	89.36
0.14356	125	43.05	91.60
0.07178	125	21.5	91.49
0.09720	50	29.1	91.45
0.09720	50	29.05	91.29
0.09720	75	29.2	91.77
0.09720	75	29.1	91.45

These results all point to the fact that it is desirable to have the solution sufficiently concentrated, and a volume of 100 cc. was finally adopted as being most satisfactory for general use and for weights of phosphomolybdate up to two-tenths gram. With greater amounts of phosphomolybdate it is necessary to increase not only the volume of the solution but also the amount of sulphuric acid in order to prevent the reprecipitation of the ammonium phosphomolybdate in the acid solution.

Many variations in the manipulation were tried, such as passing a small volume of dilute sulphuric acid through the reductor, following this with the solution of phosphomolybdate without allowing any air to pass in and completing the operation by washing with dilute sulphuric acid and water which had been boiled to expel the air, but no higher results were obtained, and we concluded that the reduction was practically to $Mo_{24}O_{37}$ and not to Mo_2O_3.

Secondly, to determine whether the methods in ordinary use would give results agreeing with these, it was determined to send portions of this sample to the members of the sub-committee and also to Prof. Noyes and Mr. Doolittle. These samples were sent in the weighing tubes with the request that the tube be dried at 100° C. for about an hour and cooled in a desiccator. Then that about one gram be weighed out by difference, dissolved in ammonia, diluted to 250 cc. and portions of twenty-five cc. each measured off, acidulated and titrated in the usual manner; then that the results be returned in the following way; weight of phosphomolybdate used for the reduction, corrected volume of permanganate required for the oxidation, value of permanganate in iron. These returns were then calculated, giving the following interesting results.

MoO_3 IN SAMPLE 10 PHOSPHOMOLYBDATE.

	Mo_2O_3 theory. Per cent.	$Mo_{24}O_{37}$ theory. Per cent.	$Mo_{12}O_{19}$ theory. Per cent.	Gravimetric. Per cent.
Blair	88.91	91.45	94.14	91.96
Dudley	88.61	91.11	93.83	
Drown	88.68	91.21	93.90	
Shimer	88.22	90.74	93.41	
Doolittle (Job)	90.47	93.05	95.80	
Noyes	89.95	92.52	95.25	
Average		91.68		91.96

May we not conclude from these results—

First, that the ratio of phosphorus to molybdic acid is 1.794?

Second, that the value of molydic acid as compared with iron is 0.88163 according to the theory of reduction of the molybdic acid to $Mo_{24}O_{37}$?

MOLYBDATE SOLUTION.

In the course of this investigation, our attention was naturally called to the stability of molybdate solutions and the composition of the yellow precipitate which forms sooner or later in nearly all these solutions.

This precipitate carefully collected, washed with dilute nitric acid and then with cold water and dried over sulphuric acid was bright orange colored and contained by analysis,

Molybdic acid	90.43
Water at 250° C	9.61
Phosphoric acid	None
Ammonia	Traces

When heated the precipitate became white and was in fact molybdic anhydride. As ammonium phosphomolybdate is much less soluble in dilute nitric acid containing ammonium nitrate than in dilute nitric acid alone, we considered it possible that the excess of ammonium nitrate might be the cause of the instability of these solutions and an experiment showed this to be the case. We found that the solution prepared according to the following formula remained practically unaltered for several months and gave exactly the same results as a fresh solution when used for the determination of phosphorus in steel. The following is the formula and method of preparation:

One hundred grams of molybdic anhydride was thoroughly mixed with 400 cc. of cold distilled water and eighty cc. of ammonia (0.91 sp. gr.) was added. This completely dissolved the molybdic acid. The solution, after filtering to remove any silica or dirt, was poured into a mixture of 300 cc. nitric acid (1.42 sp. gr.) and 700 cc. water. The solution did not become very warm and there was very little tendency on the part of the molybdic acid to separate out during the mixing.

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THE FERRATES.[1]

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"WHO has first seen ferric acid?" This question forms the pertinent title of a controversial article in the *J. Prakt. Chem.*, **32,** 448, and it is there stated that G. E. Stahl discovered that when saltpeter is ignited with iron and the mass is added to water, the caustic alkali resulting from the decomposition of the saltpeter holds a part of the iron in solution and produces an amethyst or purple color. He also stated that if dilute solutions of iron in nitric acid are poured in successive small portions into a strong solution of caustic potash the iron is dissolved on shaking, with a blood-red color.

While verifying the accuracy of the former I have not been able to reproduce the latter of these reactions. On its face it

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[1] Read at the Brooklyn meeting.