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AN ACCURATE METHOD FOR THE DETERMINATION OF PHOSPHORUS PENTOXIDE AS MAGNESIUM AMMONIUM PHOSPHATE

BY WALLACE MORGAN McNABB¹

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The object of this investigation was to combine the methods of Schmitz and of Brookman for the determination of phosphorus pentoxide as magnesium ammonium phosphate, determine the cause of error and devise a method to eliminate this cause.

In all analyses each filtrate was allowed to stand for not less than 24 hours. Any trace of phosphorus could be recognized by rubbing the bottom of the beaker with a stirring rod. This test was found to be entirely satisfactory.

After completing a number of qualitative experiments according to the method of Schmitz² in boiling hot solution, and also according to another of Schmitz's methods³ in which he uses ammonium acetate, which tends to decrease the solubility of the magnesium ammonium phosphate formed and regulates the precipitation in such a way that secondary products do not form so easily, it was decided to use the ammonium acetate method for the precipitation of magnesium ammonium phosphate. Since the complete removal of precipitates from the beaker is often tedious and uncertain, it was thought desirable to attempt to combine this method of precipitation with the apparently more reliable method of handling the precipitate, consisting in dissolving it off the filter paper and beaker

¹ From a thesis done in coöperation with Doctor Hiram S. Lukens, and submitted by Wallace Morgan McNabb, in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Pennsylvania.

² Schmitz, *Z. anal. Chem.*, **45**, 514 (1906).

³ Schmitz, *ibid.*, **65**, 46 (1924).

walls with dil. nitric acid, collecting in a tared crucible, evaporating the solution to dryness, igniting and weighing.

After precipitating according to the Schmitz method, the solution was filtered, and the method of Brookman⁴ was used to complete the determination. The method as given by Brookman, and used today, recommends that the magnesium ammonium phosphate, after being well washed upon the filter, be dissolved in nitric acid together with the particles clinging to the sides of the beaker, and the solution then be poured directly into a weighed porcelain crucible, evaporated to dryness and ignited. In this manner the loss of precipitate is avoided. It may be mentioned that platinum crucibles are now used in place of porcelain; 1:3 nitric acid was used to dissolve the precipitate.

A number of analyses were made using a solution of disodium hydrogen phosphate. In each filtrate a strong positive test for phosphorus was obtained. It was clearly shown that precipitation was incomplete when using the sodium phosphate, probably due to the presence of sodium chloride which tends to dissolve the magnesium ammonium phosphate.

A series of analyses made from a solution of monopotassium hydrogen phosphate gave negative tests in the filtrate, which indicated that precipitation was apparently complete in each instance but the results were variable.

A series of analyses made from weighed samples of recrystallized monopotassium hydrogen phosphate showed complete precipitation but the results were variable, all below theoretical.

After completing the analyses of the recrystallized salt and finding the discrepancy from calculated results so large, it seemed possible that the loss might be due to the reaction taking place on ignition.

According to Karaoglanow and Dimitrow,⁵ when magnesium pyrophosphate is dissolved in nitric acid, evaporated and ignited, a loss of phosphorus pentoxide occurs. The loss as stated in the reference is probably due to the reaction $Mg_2P_2O_7 + 4HNO_3 = H_4P_2O_7 + 2Mg(NO_3)_2$. Pyrophosphoric acid, $H_4P_2O_7$, in an acid solution changes to the orthophosphoric acid, H_3PO_4 , and this reacting with magnesium nitrate is probably a reversible reaction, $H_3PO_4 + Mg(NO_3)_2 \rightleftharpoons MgHPO_4 + 2HNO_3$, which on ignition gives a loss of phosphorus pentoxide. The same effect would be obtained with magnesium ammonium phosphate as with magnesium pyrophosphate. This was shown by the following qualitative experiments.

A sample of precipitated magnesium ammonium phosphate was dissolved in 1:3 nitric acid and collected in a platinum crucible. The solution was evaporated on a water-bath to a sirupy liquid and then transferred to a sand-bath and heated for about six hours with a low flame. The heat was increased to a full flame, after which the

⁴ Brookman, *Repert. anal. Chem.*, 2, 297 (1882).

⁵ Karaoglanow and Dimitrow, *Z. anal. Chem.*, 57, 353 (1918).

crucible was placed in a porcelain crucible and ignited to red heat. During the operation of heating, a watch crystal was placed over the top of the platinum crucible and a white coating formed on the under surface of the glass. Every 15 minutes this coating was washed off the under surface of the glass into ammonium molybdate solution containing dil. nitric acid and ammonium nitrate. The yellow color appeared in the molybdic acid solution, whereas a blank gave no test. On standing overnight, the yellow color increased in intensity, but the blank remained colorless.

The same operation was repeated with the following variation. After dissolving the precipitate of magnesium ammonium phosphate in 1:3 nitric acid, the solution in the platinum crucible was made alkaline with ammonium hydroxide, then evaporated and ignited. No yellow color was obtained in the molybdic acid solution.

After having discovered through qualitative tests that a loss of phosphorus pentoxide takes place in dissolving magnesium ammonium phosphate in nitric acid, evaporating and igniting; likewise, having found that the addition of ammonium hydroxide to the dissolved magnesium phosphate prevents the volatilization of phosphorus pentoxide on ignition, the quantitative experiments were resumed.

In dissolving magnesium pyrophosphate in nitric acid, it changes to orthophosphoric acid, according to the reactions $Mg_2P_2O_7 + 5HNO_3 = H_4P_2O_7 + 2Mg(NO_3)_2 + HNO_3$ and $H_4P_2O_7 + H_2O = 2H_3PO_4$, so that the only difference between dissolving the pyrophosphate and magnesium ammonium phosphate, after the addition of ammonium hydroxide, is that the latter solution would contain more ammonium nitrate than the former.

Pure magnesium ammonium phosphate was prepared, transferred to a weighed platinum crucible and ignited between 900° and 1000° to constant weight. This ignited product, magnesium pyrophosphate, was then dissolved in 1:3 nitric acid, made alkaline with ammonium hydroxide, evaporated and ignited to constant weight.

It is to be noted in Table I that when the evaporation is carried out, after making the solution alkaline with ammonium hydroxide, there is no marked change in weight; when, however, the solution is not made alkaline before evaporation, but allowed to remain acid, there is a marked loss after evaporation and ignition.

TABLE I

COMPARATIVE ANALYSES, SHOWING LOSS OF P₂O₅ BY VOLATILIZATION WHEN THE PRECIPITATE IS DISSOLVED IN HNO₃, BUT THAT ADDITION OF NH₄OH PREVENTS THIS LOSS

MgNH ₄ PO ₄ , ignited to Mg ₂ P ₂ O ₇ , g.	0.1805	0.1897	0.2606	0.3719
Mg ₂ P ₂ O ₇ , dissolved in 1:3 HNO ₃ , NH ₄ OH added, evaporated and ignited, g.1805	.1898	.2606	.3719
Mg ₂ P ₂ O ₇ , dissolved in 1:3 HNO ₃ , evaporated and ignited, g.1718	.1873

After having shown in the preceding qualitative and quantitative experiments that there is a loss when magnesium ammonium phosphate

is dissolved in nitric acid, evaporated and ignited, and that there is no loss when the solution is made alkaline with ammonium hydroxide before evaporating and igniting, a number of comparative analyses by the author's method and the nitric acid method were made, showing the errors as calculated against theoretical. The results are given in Tables II and III, respectively.

The following procedure was used for the rapid and complete precipitation of the phosphate in a pure, crystalline state.

The weighed samples of monopotassium hydrogen phosphate were transferred to a small beaker and dissolved in a small amount of water. To this solution was added several drops of dil. 1:10 hydrochloric acid, then 25 cc. of a 20% solution of ammonium acetate and 30 cc. of magnesia mixture. After heating the solution almost to boiling, several drops of phenolphthalein indicator were added, and 2.5% ammonium hydroxide was added drop by drop, with constant stirring, until a red color appeared. (If a faint turbidity appears at the beginning of the precipitation, the addition of ammonium hydroxide is discontinued and the solution vigorously stirred, until the turbidity disappears and the precipitate becomes crystalline. This should result in about half a minute.)

The solution was allowed to stand until cold, then about one-fifth of its volume of concd. ammonium hydroxide was added; it was stirred vigorously, allowed to stand a few minutes and then filtered. The precipitate was well washed in the beaker with 2.5% ammonium hydroxide and poured onto the filter paper. After drawing out the excess

TABLE II
ANALYSES MADE BY THE AUTHOR'S METHOD (NH_4OH ADDED TO THE CONTENTS OF THE CRUCIBLE BEFORE EVAPORATING AND IGNITING)

KH_2PO_4 , g.	$\text{Mg}_2\text{P}_2\text{O}_7$, g.	P_2O_5 , g.	P_2O_5 calcd., g.	P_2O_5 difference, g.
0.2000	0.1637	0.1044	0.1043	+0.0001
	.1633	.1042		- .0001
	.1635	.1043		.0000
	.1635	.1043		.0000
	Av. .1635	.1043	.1043	.0000
Av. % deviation from that calcd. = 0.00				
0.5000	0.4088	0.2607	0.2609	-0.0002
	.4094	.2611		+ .0002
	.4087	.2607		- .0002
	.4084	.2605		- .0004
	.4089	.2608		.0000
Av. .4088	.2608	.2609	.2609	- .0001
Av. % deviation from that calcd. = -0.03				
1.0000	0.8172	0.5213	0.5217	-0.0004
	.8182	.5219		+ .0002
	.8185	.5221		+ .0004
	.8180	.5218		+ .0001
	.8184	.5220		+ .0003
	.8192	.5225		+ .0008
Av. .8182	.5219	.5217	.5217	+ .0002
Av. % deviation from that calcd. = +0.04				

TABLE III
ANALYSES MADE DISSOLVING THE PRECIPITATE OFF THE FILTER WITH 1:3 NITRIC ACID
BEFORE EVAPORATING AND IGNITING

KH ₂ PO ₄ , g.	Mg ₂ P ₂ O ₇ , g.	P ₂ O ₅ , g.	P ₂ O ₅ calcd., g.	P ₂ O ₅ difference, g.
0.2000	0.1622	0.1035	0.1043	-0.0008
	.1629	.1040		-.0003
	.1575	.1005		-.0040
	.1613	.1029		-.0014
	Av. .1610	.1027	.1043	-.0016
Av. % deviation from that calcd. = -1.55				
0.5000	0.4008	0.2556	0.2609	-0.0053
	.4013	.2560		-.0049
	.4051	.2594		-.0015
	.4054	.2586		-.0023
	.4029	.2570		-.0039
	Av. .4031	.2573	.2609	-.0036
Av. % deviation from that calcd. = -1.39				

of ammonium hydroxide from the precipitate by means of suction, a weighed platinum crucible was placed under the filter and a hole punched in the filter paper. Several drops of warm 1:3 nitric acid in a few cubic centimeters of water were used to dissolve the precipitate clinging to the sides of the beaker, and this was used to wash down most of the precipitate on the filter paper into the crucible. The remaining part on the filter can easily be washed into the crucible by means of a wash bottle throwing a fine stream. If any particles persist in clinging to the paper, a drop or two of nitric acid may be used. (It was found best to use as small an amount of nitric acid as possible, as this prevents the formation of an excess of ammonium nitrate, making the final heating much easier to carry out.)

Ammonium hydroxide was then added to the contents of the platinum crucible, until a strong odor of ammonia was obtained, and the crucible placed in a porcelain crucible standing on a steam-bath and protected from dust by means of an inverted funnel with a test-tube over the top. After evaporating to dryness, the precipitate was first heated gently on a ring burner, and finally to red heat. The crucible was transferred to a porcelain crucible containing platinum foil in the bottom, and heated for 15 minutes with a Meker burner at about 900°. All ignitions were conducted for 15 minutes, followed by ignitions for 20-minute periods, until constant weight was attained.

Conclusions

1. More accurate results can be obtained in the determination of phosphorus pentoxide as magnesium ammonium phosphate, precipitating from a solution of monopotassium hydrogen phosphate, than from a solution of disodium hydrogen phosphate.

2. Although check results may be obtained by dissolving magnesium ammonium phosphate in nitric acid, evaporating and igniting, it is definitely shown that there is a loss of phosphorus pentoxide by volatilization.

3. Accurate determinations of quantities of phosphorus pentoxide ranging from 0.1 g. to 0.5 g. can be made by washing the precipitate of magnesium ammonium phosphate off the filter paper into a weighed platinum crucible and dissolving the small particles clinging to the walls

of the beaker and remaining on the filter paper with warm dil. nitric acid. After being made alkaline with ammonium hydroxide, the solution is evaporated to dryness and ignited to constant weight.

4. The method developed yields results deviating from the calculated values by from -0.03 to $+0.04\%$, depending upon the amount being estimated, whereas a deviation of from -1.39 to -1.55% was obtained, using the method commonly employed.

PHILADELPHIA, PENNSYLVANIA

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THE ADEQUACY OF THE ASSUMPTION OF MOLECULAR AGGREGATION IN ACCOUNTING FOR CERTAIN OF THE PHYSICAL PROPERTIES OF GASEOUS NITROGEN

BY FREDERICK G. KEYES AND ROBERT S. TAYLOR

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Introduction

At the present time direct proof of molecular aggregation is not generally possible. Indeed, there exist no tests for conceived varieties of molecular species, particularly in the gaseous phase, when only small numbers of the polymerized molecules exist. It is of course well known that nitrogen dioxide polymerizes or associates chemically to a double species, N_2O_4 , but in this instance a change in color attends the shift in species; moreover, the numbers of the doubled molecules are so considerable at a pressure of one atmosphere and less, that the departure from the perfect gas laws of either species is not sufficient to prevent detection of the polymerization by means of density measurements.

Acetic acid furnishes an example of a gas or vapor which presents no change in color on shift of species to double molecules, and here again the large changes in density at low pressures are satisfactorily explained on the assumption that a doubling of species exists. It is quite possible, perhaps even certain, that acetic acid vapor and other associating gases would show a change in the absorption spectrum in regions other than the visible, but investigations to determine this important fact are lacking as far as known.

The detection, in gases under considerable pressure, of small amounts of associated or aggregated molecules either double or of higher order, presents a problem of great difficulty when the attempt is made to detect the polymerized species by means of an examination of the pressure-volume-temperature data. Obviously even at atmospheric pressure, if the fraction of double molecules is small enough, the presence of the latter may be masked because of the normal departure of the simpler species from