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degree of Doctor of Philosophy.

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A STUDY OF
METAL ETHYLENEDIAMMONIUM PHOSPHATES

A dissertation submitted to the

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requirements for the degree of

DOCTOR OF PHILOSOPHY

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by

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CHAPTER I

INTRODUCTION AND OBJECTIVES

The methods now most widely used for the determination of phosphorus leave much to be desired. The familiar gravimetric procedure in which phosphorus is precipitated as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ and subsequently ignited to $\text{Mg}_2\text{P}_2\text{O}_7$ is long and tedious. All of the phosphomolybdate separations involve a critical precipitation step in which a product of somewhat uncertain constitution may be thrown down (1, 2).

Aliphatic diamines react very similarly to ammonia in the formation of both salts and complex-ions. Consequently it appears possible that insoluble compounds, analogous to MgNH_4PO_4 , may be formed, in which the ammonium ion is replaced by ethylenediammonium ion. Incorporation of such salt-forming organic groups frequently improves the physical and crystallographic properties of a compound. Furthermore, ethylenediamine is less volatile than ammonia and the aliphatic mono-amines, and hence may be expected to add desirable drying properties to a precipitate.

A pressing problem in the field of condensed phosphates is the separation and determination of one species of phosphate in mixtures which also contain other phosphate species. Since these materials, without exception, are high valence anions, there is a possibility that a combination of such cations might selectively precipitate one of the condensed phosphate ions. The situation is analogous to one key fitting a particular lock.

Any study whose objective is to learn the possible existence of metal ethylenediammonium phosphates which can precipitate phosphorus quantitatively must necessarily be preceded by an investigation of the chemistry of systems made up of ethylenediamine, phosphate, and a metal ion. The primary objective of this thesis is to explore the chemistry of a series of systems containing ortho- or pyrophosphate, metal ion, and ethylenediamine or ethylenediammonium ion. With triphosphate, trimetaphosphate, and tetrametaphosphate, single experiments were carried out which were designed to learn if a particular system merited further investigation. The work is of a detailed exploratory nature; it includes many single experiments which may point the way to future studies.

CHAPTER II

HISTORICAL

The immediate predecessor of the present investigation was a study by Snook (3) which indicated that a wide variety of double salts containing phosphate and ethylenediamine do exist. However she was unable to identify any of the preparations, nor did she investigate pyrophosphates.

A thorough search of the literature disclosed no other reports of work in this field of metal ion ethylenediammonium phosphates.

Two reports of work with magnesium monoamine orthophosphate were found. Barthe (4) tried without success to prepare a magnesium ethylammonium phosphate. Francois (5) was able to obtain magnesium methylammonium orthophosphate, but did not succeed in preparing the analogous compounds with di- or trimethylamine.

In view of this rather sketchy background, it was necessary to turn to discussions of metal ammonium phosphates for ideas about experimental procedures. Several papers

were helpful here. Travers and Perron (6) present a thorough picture of the chemistry of magnesium ammonium phosphate, which includes both the conditions of precipitation and the effects of temperature. Their paper also describes the preparation of calcium ammonium phosphate. Bassett and Bedwell (7) prepared a wide variety of metal ammonium phosphates. They noted two series of hydrates: hexahydrates and monohydrates. However these workers were more concerned about the glowing phenomenon which accompanies the ignition of these compounds. Auger and Ivanoff (8) prepared a series of metal ammonium phosphates of the alkaline earth metals. They also report a very interesting soluble copper compound, namely $\text{Cu}(\text{NH}_3)_2(\text{NH}_4)_4(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$.

Two other investigations are related to the present study. Basset et al. (9) studied the double salts of some divalent metals with sodium pyrophosphate. They report the preparation of double salts such as $\text{Na}_4\text{P}_2\text{O}_7 \cdot \text{Ni}_2\text{P}_2\text{O}_7 \cdot 12\text{H}_2\text{O}$, $\text{Na}_4\text{P}_2\text{O}_7 \cdot 3\text{Mg}_2\text{P}_2\text{O}_7 \cdot 21\text{H}_2\text{O}$, $7\text{Na}_4\text{P}_2\text{O}_7 \cdot 25\text{Mg}_2\text{P}_2\text{O}_7 \cdot 172\text{H}_2\text{O}$, $\text{Na}_4\text{P}_2\text{O}_7 \cdot 4\text{Cu}_2\text{P}_2\text{O}_7 \cdot 17\text{H}_2\text{O}$, and $8\text{Na}_4\text{P}_2\text{O}_7 \cdot 7\text{Zn}_2\text{P}_2\text{O}_7 \cdot 23\text{H}_2\text{O}$. They also found evidence for the existence of hydrates $\text{Me}_2\text{P}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ (Me = divalent metal) where x may have the value 8.7, 6.5, 6.25, 6.5, 4.2, 3.67, 3.6, 3.25, 2.67, or 2.33. Most of their preparations are only sparingly soluble in water and do not crystallize well.

Such things as intergrown crystals, well formed but extremely minute crystals, and nondescript crystalline fragments were commonplace. When obtainable, optical data are included for the preparations. They believe that there is a marked tendency for the formation of solid solutions containing sodium, and that the sodium pyrophosphate lattice is capable of considerable distortion.

The present writer (10) prepared a series of phosphates of aliphatic diamines. Figure A is the neutralization curve of ethylenediamine vs. orthophosphoric acid. The molar ratio of ethylenediamine to orthophosphoric acid at the inflection point around pH 4 is 1:2. If alcohol is added to the solution at this point, crystals of $\text{enH}_2(\text{H}_2\text{PO}_4)_2$ are obtained (en = ethylenediamine). Figure B applies to pyrophosphoric acid. Here the molar ratio at the inflection point at pH 4 is one ethylenediamine to one pyrophosphoric acid. During the course of that previous investigation, extensive efforts were made to prepare a compound of the composition $(\text{enH}_2)_3(\text{PO}_4)_2$. All such attempts failed. During that work $\text{enH}_2(\text{HPO}_4)$ was invariably the solid phase obtained at very high values of pH, and in strong solutions of ethylenediamine. That product was recovered even when pure $\text{enH}_2(\text{HPO}_4)$ was refluxed for several hours with undiluted ethylenediamine. A compound was never obtained which contained a univalent

ethylenediammonium ion.

FIGURE A

Changes in pH as 0.67 M ethylenediamine is added to 25 ml. of 0.32 M H_3PO_4 .

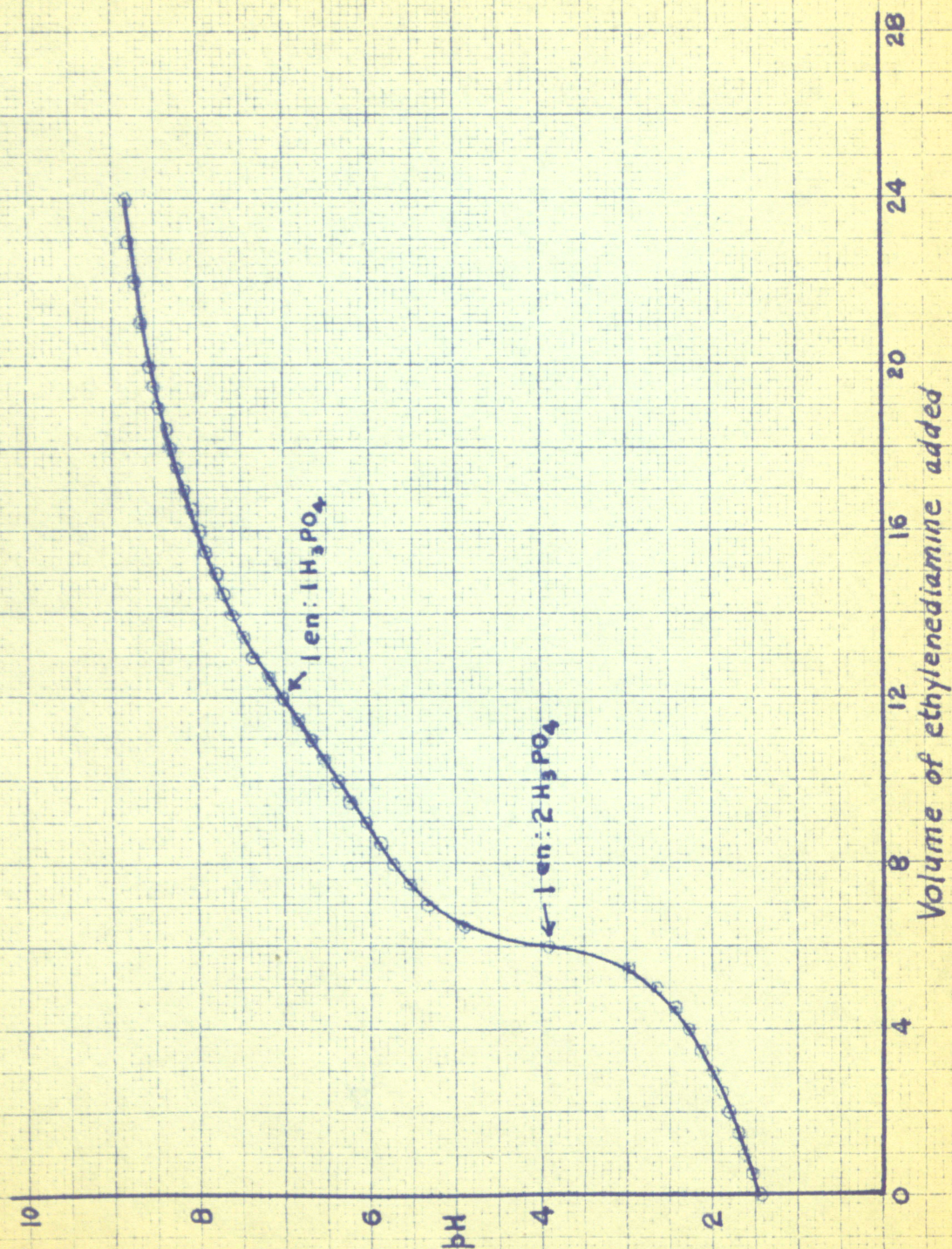
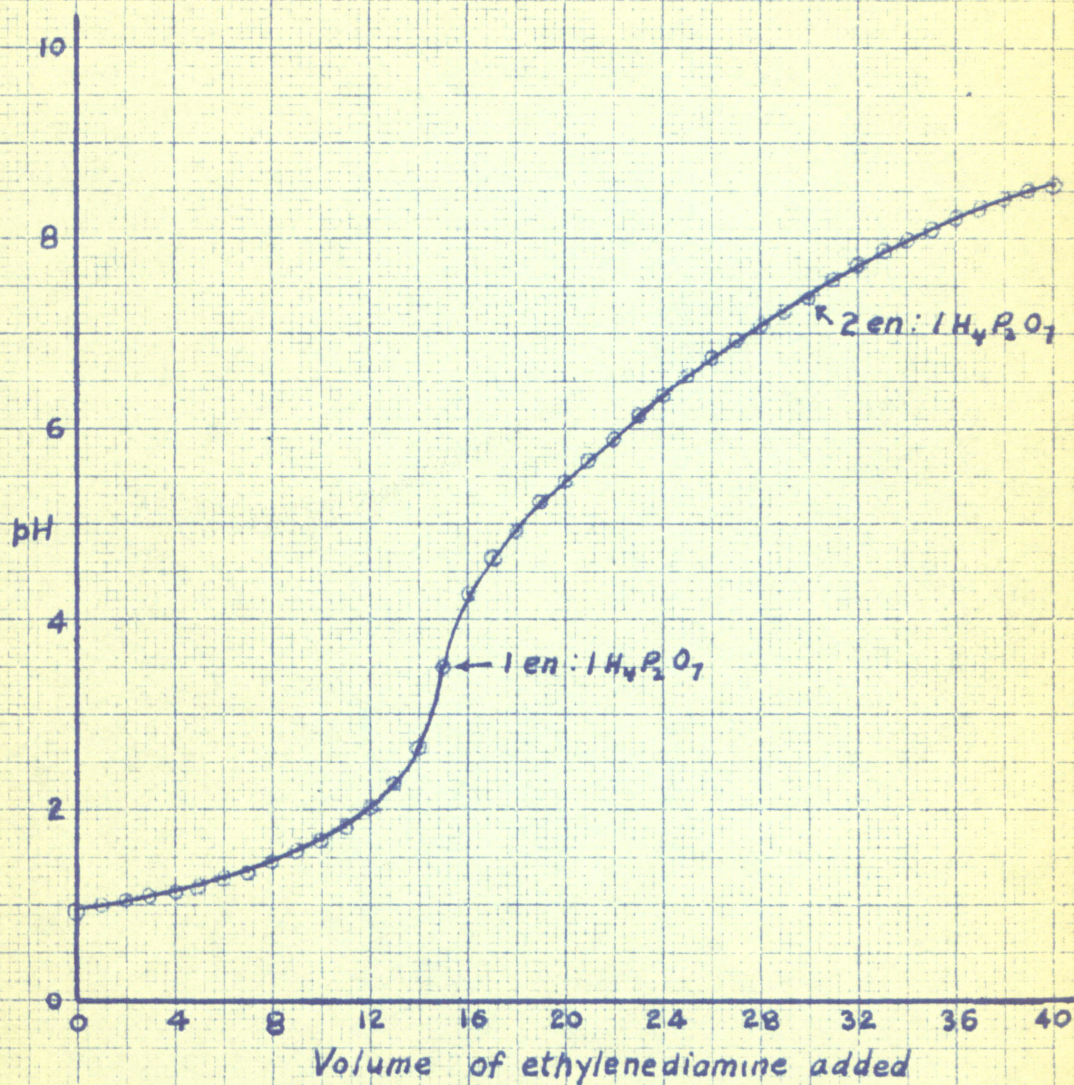


FIGURE B

Changes in pH as 0.75 M ethylenediamine is added to 25 ml. of 0.45 M $\text{H}_4\text{P}_2\text{O}_7$.



CHAPTER III

USE OF X-RAY POWDER PATTERNS*

Theory

Since atoms or molecules in a crystal lattice are arranged in a regular series of space-groups, there are series of parallel planes in the crystal which contain large numbers of atoms. The wave-length of X-ray radiation is of the same magnitude as the distances between these planes of atoms. Therefore, when a beam of monochromatic X-rays is passed through a crystal lattice, the planes of atoms act as a diffraction grating, and the X-rays are diffracted through an angle which partially depends on the distance between the planes. Bragg's law is the mathematical statement which relates these facts:

$$n \lambda = 2d \sin \theta$$

where n is the order of diffraction, λ is the wavelength

* References 11, 12, and 13 are extensive reviews of this subject.

of the X-rays, d is the distance between the planes of atoms, and θ is the angle through which the X-rays are diffracted.

If the crystalline material being irradiated is a powder in which small crystallites are oriented in every conceivable direction, then some crystallites can always be found which fulfill the Bragg condition for every possible interplanar spacing, and a corresponding line will appear on the film. This series of lines of varying intensity is known as the X-ray powder pattern, or the X-ray spectrum.

No two crystalline species have ever been found to give the same X-ray powder pattern in which the lines are identical in both position and intensity. Thus this physical characteristic is a remarkably specific property which has widespread potential applications in chemical research whenever the solid state is involved. Since this diffraction property depends solely on structure, different hydrates give different patterns; even different allotropic forms of the same material give different patterns.

No such orderly arrangement exists in amorphous material, and consequently it gives no X-ray pattern.

There are two methods by which X-ray powder patterns may be used to identify a substance (assuming that no amorphous material is present).

1. The "finger-print" procedure. The X-ray pattern of the unknown is compared with that of a definite chemical entity. If all the lines of the two patterns match in both position and intensity, and there are no additional lines in the unknown or the reference material then the two substances are identical. This method is especially useful when it is desired to learn if the products of two or more different reactions are the same. It was the procedure used most frequently during the present investigation. However, the method becomes impractical whenever the unknown may be any one of a wide number of different materials.

2. Use of the ASTM file (14, 15). It is possible to solve the Bragg equation and thus obtain the interplanar spacing for each line on the X-ray pattern. To do this, n is set equal to unity, and θ is obtained from the geometric relationship of the film to the camera diameter. The interplanar spacings and the relative intensities of the lines for about 5000 different substances are recorded on index cards in the ASTM file. If the identity of the unknown substance is suspected to be one of several probable compounds, the X-ray spectrum recorded on the card is compared with that which has been computed for the unknown material. If the spacings and relative intensities of the lines are the same, the unknown substance has been

identified. There were several instances during the present study when this method proved valuable.

The ASTM file may also be used to identify a completely unknown material. That procedure was not used in this work, and therefore will not be described.

Obviously, the ASTM file is of no value with respect to a substance whose X-ray pattern has not been previously reported.

The powder method has a number of distinct advantages.

1. All the information is permanently recorded at one time on a single film which may be filed and used for future reference or study.

2. The substances at hand reveal their true state of combination. An anhydrous crystalline material gives a powder pattern which differs from that given by a hydrate of the same substance.

3. Components of mixtures give their patterns independent of other substances present. For example, in a mixture of an orthophosphate and a pyrophosphate, the patterns of both substances will appear superimposed on each other. The limitation is that the minimum amount of a component which can be detected in the usual powder pattern is from 3 to 5 %. Accordingly the procedure is not sensitive enough to detect slight impurities.

4. The procedure is a microtechnique; as little as 1 mg. is usually enough to obtain a powder pattern.

5. The procedure is non-destructive. The technique neither requires nor produces any change in the constitution of the sample.

There are two disadvantages which must also be remembered during the use of this procedure.

1. Amorphous materials yield no X-ray pattern, and hence give no indication of their presence in a mixture. Consequently it is profitable to supplement X-ray patterns with microscopic observations whenever possible. This was done in the present investigation.

2. It is usually difficult, if not impossible, to unravel a multicomponent mixture (exceeding three). Here again, the supplemental use of a microscope is sometimes helpful.

Equipment and Techniques

Employed in the Present Investigation

X-Ray Unit: A North American Phillips unit, type number 12033, was used in the present investigation. It is located in the laboratories of the Tanners Research Council on the campus.

X-Ray Tube: All the X-ray patterns reported here were obtained by using CuK_α radiation. This is usually the most

desirable tube for general work because it has a convenient wave length ($1.542 \text{ \AA}$) and sufficient energy so that exposure times do not become prohibitively long. Its longer wave length (as compared with MoK_{α} , $0.711 \text{ \AA}$) has the effect of spreading the pattern over a wider angular interval thereby permitting greater precision in measuring the angles from which spacings are calculated. The disadvantage of using this tube is that samples which contain iron or cobalt fluoresce so strongly when exposed to CuK_{α} radiation that the pattern is completely obliterated. Manganese-containing materials also fluoresce, but in many cases the interference is not enough to obscure the lines of the pattern.

The CuK_{β} radiation was removed with a nickel filter.

Cameras: The conventional DeBye-Scherrer type cameras were used. A strip of 35 mm. film is curved to form a cylinder with the sample mounted in its center. Both film and sample are enclosed in a light-tight case. Holes in the film strip accomodate the pin-hole collimating system and the "beam-catcher."

The diameters of the cameras were 57.3 mm. and 114.6 mm. These dimensions offered the advantage that in the first case 1 mm. measured between corresponding lines represents 1° in 2θ . In the larger camera, 2 mm. represents

1° in 2θ .

The camera of smaller diameter requires a shorter exposure time, whereas spacings are more accurately measured on film exposed in the larger camera. Therefore, the smaller camera was ordinarily used for obtaining the patterns of the large number of products which resulted during the course of the investigation. When it was desired to calculate the spacings of a new compound, the larger camera was used.

Sample Preparation: In order to obtain a satisfactory pattern, the material should be ground until it will pass a 150- or 200-mesh screen. During this investigation, most of the material were obtained directly in a form suitable for X-raying. Usually, no grinding was necessary.

The samples were mounted in glass capillaries whose walls were so thin that they can be crushed by gentle pressure between the thumb and forefinger. These capillaries were 0.5 to 0.8 mm. in diameter and were drawn from Pyrex tubing that was originally one inch in diameter.

Modeling clay was used to mount the filled capillary in the center. Centering screws incorporated in the cameras enable the operator to center the sample accurately. The cameras also have a mechanism for rotating the sample during the exposure in order to smooth out spotty lines.

Exposure Time and Film Treatment: For the small camera, from one to 1-1/2 hours was usually adequate to secure a satisfactory pattern. A minimum of two hours was necessary for the larger camera.

Eastman "no-screen" 35 mm. X-ray film was used in this work. This film is orthochromatic and can be processed under ruby light. Commercial Eastman X-ray film developer was used. The time in the developer was 6 minutes at 68°F. The film was fixed for twice the time to clear, usually from 8 to 12 minutes. After being fixed, the film was washed for one hour, then allowed to dry.

Measurement of the Pattern: For calculating the spacings, the film was viewed on a ground glass viewing screen, the distances between corresponding lines were measured by setting dividers, and transferring the distance to a calibrated metal scale. The spacings were then calculated with the Bragg equation. The relative intensities of the lines must be judged visually, because the best microphotometer will miss lines easily visible to the naked eye. For this same reason, photographic positives do not pick up all of the lines of a pattern. However such prints do show the heavier lines and enable the reader to compare the patterns for himself.

Errors: The usual source of serious error is due to shrinkage of the film during the processing. This fault

was not significant in the present investigation. It was offset in two ways:

1. The film has emulsion on both sides.
2. The diameter of both cameras is fixed so as to compensate for the average film shrinkage.

CHAPTER IV

GENERAL PROCEDURE AND MATERIALS

The three ions involved in these systems may be brought together in a variety of ways. Reactions with both ortho- and pyrophosphate were carried out as follows:

1. Metal ion was added to ethylenediammonium phosphate.
2. Ethylenediammonium phosphate was added to metal ion.
3. Ethylenediamine was added to a solution which contained phosphoric acid and the metal ion in varying initial molar ratios. Four such initial conditions were examined: an equimolar ratio of metal ion to phosphoric acid; metal ion in excess; the phosphoric acid in excess; an excess of ethylenediammonium ion present, the latter being introduced as the hydrochloride.

Standard solutions between 0.5 and 0.8 molar were used in carrying out the reactions. These concentrations were most convenient because they yielded enough precipitate for study without also producing unwieldy volumes of solution.

The reactions were carried out titration style,

with uninterrupted and vigorous mechanical stirring.

The course of each reaction was followed by continuous pH measurement. Since the composition of the phosphate component is closely related to the hydrogen-ion concentration of the solution, changes in pH* during the course of a reaction often provided valuable insight into the changes undergone by the phosphate component.

Specimens of the precipitate were frequently examined under the microscope. Thus phase changes and the existence of mixtures could sometimes be detected visually and at times it was possible to identify products by such observations. No instance was noted in which two products that appeared to be identical under the microscope were later found to be different substances. In several cases crystals appeared to be different, but later they were found to be merely different crystal habits.

Phase changes occurred in nearly all of the reactions. Consequently it became necessary to repeat the operation to isolate each of the different products which formed during a given reaction.

* Most of the pH measurements were made with a Beckman model H-2 line operated pH meter. The remainder were obtained with a Leeds and Northrop model 7668 pH meter. The two meters checked each other to within 0.1 of a pH unit.

The next step was to obtain an X-ray powder pattern for each of the preparations. If two products gave identical X-ray patterns, and each appeared to be homogeneous when examined under the microscope, the two products were established as being chemically identical. The X-ray patterns made it possible to determine the number of different phases which were present in a given system.

The identity of the products was then established by chemical analysis. All determinations were carried out in duplicate. The metal ion, nitrogen, and phosphorus content of each phase was determined, and the atomic ratios of the elements calculated. From these ratios a formula could be deduced which was complete except for the water of hydration. A molecular weight could be estimated, and hence the hydrate number approximated from the formula so obtained and the percentage of one constituent. Only then were any theoretical percentages calculated. The found percentages of all three constituents and the corresponding theoretical percentages had to agree before a compound was accepted as a chemical entity. Finally an attempt was made to dehydrate the compound by heating to confirm, if possible, the bound water content.

Some of the reactions were followed by conductance titrations in an attempt to detect any complexing.

Several workers (18, 19) have recently described the use of this instrument in the investigation of the formation of complex-ions in solution. The conductance titrations were carried out by adding small increments of a 0.7 or 0.8 molar solution of metal ion to 10 millimoles of ethylenediammonium phosphate in about 650 ml of water. Mechanical stirring was used, and the temperature variation kept within $\pm 0.5^{\circ}$ C. The conductance measurements were made with an Industrial Instruments model RC16 Conductivity bridge.

Exploratory reactions with triphosphate, trimetaphosphate, and tetrametaphosphate were also carried out. Fifteen millimoles of the sodium salt of the condensed phosphate was dissolved in 50-75 ml of water; 1:1 hydrochloric acid was then added until the pH was lowered to 1.00 or less and then 15 millimoles of a solution of metal ion were added. The pH was then gradually raised to 6 or 7 by adding small volumes of ethylenediamine. Phosphorus, nitrogen, and metal ion were determined in any precipitate which formed, and an X-ray diffraction pattern was obtained.

Starting Materials

Ethylenediamine: The commercial grade of ethylenediamine as obtained from Eastman was distilled in an all-

glass apparatus. Not more than 100 ml. were distilled at one time. The purified material was stored in a glass-stoppered Erlenmeyer flask, and was found to remain free of silica. Before use, the ethylenediamine was diluted to about 0.5 molar, and the solution was titrated against standard hydrochloric acid (methyl red end point).

Orthophosphoric Acid: Merck reagent grade 85 per cent orthophosphoric acid was diluted to about 0.5 molar. The diluted acid was standardized by titrating with standard sodium hydroxide to pH 4.3 (pH meter).

Pyrophosphoric Acid: Commercial grade crystalline pyrophosphoric acid was generously provided by the Monsanto Chemical Company. Subsequent work showed that the purity was sufficiently high. The acid was stored under refrigeration. The amount needed for a reaction was dissolved in cold water just prior to being used. The solution was immediately standardized by titrating with standard sodium hydroxide to pH 4.3. The reaction was then carried as rapidly as possible to the point at which precipitation started. Usually no more than 45 minutes elapsed from the time the pyrophosphoric acid was dissolved until precipitation started. Under these circumstances, no serious hydrolysis to orthophosphate occurred.

Ethylenediammonium ortho- and pyrophosphate: These salts were prepared as described by Mast (16, 17); the

preparations were recrystallized twice from water. A 0.3 molar solution of the orthophosphate was prepared and standardized by a Kjeldahl nitrogen determination. The pyrophosphate was weighed and dissolved as needed.

Sodium Triphosphate, Sodium Trimetaphosphate, and Sodium Tetrametaphosphate: These salts were commercial grade products which had been recrystallized at least twice. They were not placed in solution until just prior to being used.

Metal Ions: "Reagent grade" magnesium chloride, zinc sulfate, manganese sulfate, nickel sulfate and copper sulfate were used without further purification. Solutions of these ions were prepared and standardized by the same procedure used to determine the metal ion in the phosphates prepared from them.

Ferrous Sulfate: One hundred grams of "reagent grade" material was dissolved in a mixture of 300 ml of water and 30 ml of sulfuric acid. After solution was complete, iron filings were added, and the mixture stirred vigorously until the sulfocyanate test for ferric iron was negative. The solution was filtered rapidly, and enough alcohol added to produce a permanent cloudiness. The ferrous sulfate precipitated on cooling in an ice bath. The product was separated by suction filtration, pressed between filter paper, allowed to air-dry, and stored in a desiccator over a saturated solution of ammonium chloride. This preparation

was found to contain 20.16 % ferrous iron (theoretical for $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is 20.09 %). The alcohol precipitation avoids the long evaporation step usually associated with this recrystallization, which is quite likely to result in oxidation of part of the iron. The product was placed in solution just prior to being used.

CHAPTER V

ANALYTICAL PROCEDURES

Nitrogen

Nitrogen was determined by the Kjeldahl method (Winkler modification). The sample is digested with concentrated sulfuric acid and potassium sulfate in the presence of mercuric oxide as a catalyst. In this digestion, the nitrogen is converted to an ammonium sulfate. Excess sodium hydroxide is then added, and the liberated ammonia is distilled out and absorbed in boric acid solution. The ammonia is then titrated directly with standard acid.

Procedure (20): Approximately 120 mg. of the unknown was placed in a 500 ml. Kjeldahl flask along with a small piece of analytical filter paper, 0.5 gram of mercuric oxide, and 10 grams of potassium sulfate. Twenty-five ml. of concentrated sulfuric acid was added, and the contents of the flask mixed by swirling. The mixture was digested slowly until the frothing had stopped. Then the heat was increased and the solution boiled briskly until it cleared.

From 30 to 45 minutes heating were usually required to reach this point. The digestion was continued for 2 hours after clearing, the heat being regulated so that no sulfur trioxide now escaped.

When the digestion was completed, the flask and its contents were cooled and 200 ml. of water added cautiously. Several boiling chips were dropped into the flask and 25 ml. of a sodium thiosulfate solution (80 grams of $\text{Na}_2\text{S}_2\text{O}_3$ per liter) added. The function of the latter is to fix the mercury as the sulfide, thus preventing the reaction of mercury with ammonia which would cause incomplete release of the ammonia. Finally 75 ml. of 50 per cent sodium hydroxide was carefully run down the neck of the flask so that the acid and base did not mix immediately. After the apparatus was assembled, the contents of the flask were mixed by gentle swirling, and the distillation started at once. The ammonia-containing distillate was absorbed in 75 ml. of a 3 per cent boric acid solution. The distillation was continued until 150-200 ml. of solution had been collected. A heavy bumping of the flask usually signalled the end of this operation.

When the distillation was completed, 2 drops of methyl red and 3 drops of bromcresol green were added to the distillate. The latter was then titrated directly with standard hydrochloric acid until the mixed indicator had changed

from green through yellow-green to yellow with a faint pink cast.

It was found necessary to run a blank. The blank was found to remain constant, and was equivalent to 0.70 ml. of 0.1 N hydrochloric acid.

The acid which was used in the foregoing Kjeldahl determinations was first standardized with sodium carbonate by the usual procedure.

A new acidimetric standard, tris(hydroxymethyl) aminomethane* $(\text{CH}_2\text{OH})_3\text{CNH}_2$, has become available (21). This substance contains nitrogen which is accessible to Kjeldahl digestion; and therefore, acid to be used for Kjeldahl determinations may be standardized or checked by the very satisfactory method of an actual Kjeldahl procedure. The hydrochloric acid used in the present investigation was checked in this manner.

Phosphorus

In all preparations which contained magnesium as the bivalent metal ion, phosphorus was determined by precipitation as magnesium ammonium phosphate and subsequent ignition to magnesium pyrophosphate.

* Available from the G. Frederick Smith Chemical Co.,
Columbus, Ohio.

When the preparations contained divalent metal ions other than magnesium, those ions form metal ammonium phosphates which are less soluble than magnesium ammonium phosphate, and mixtures result. Many of the preparations themselves were soluble only in acidic solutions. It was therefore desirable to select a procedure by which the phosphorus can be precipitated from strongly acidic solution. The phosphomolybdate separation meets these requirements. The phosphorus is thrown down as the yellow ammonium phosphomolybdate, $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 3\text{HNO}_3 \cdot \text{H}_2\text{O}$, and subsequently ignited to "phosphomolybdic oxide," $\text{P}_2\text{O}_5 \cdot 24\text{MoO}_3$.

Magnesium Ammonium Phosphate Procedure (22): A solution of "magnesia reagent" was prepared as follows: 400 grams of magnesium chloride hexahydrate and 300 grams of ammonium chloride were dissolved in 1500 ml. of warm water, and the resulting solution made alkaline to litmus. After standing one hour, any precipitate which had formed was filtered off, and the solution acidified with hydrochloric acid.

A sample of the unknown orthophosphate preparation which weighed 150 mg. was placed in a 250 ml. Erlenmeyer flask, and dissolved in 5 ml. of 1:1 hydrochloric acid. The resulting solution was diluted with 50 ml. of water, then 60 ml. of "magnesia reagent" and one drop of methyl red were added. The solution was then made basic to methyl red by dropwise addition of ammonium hydroxide (sp. g. 0.90).

At this point, precipitation started and an excess of 2 ml. of the ammonia was added. The suspension was diluted to 150 ml. with water, shaken at intervals for an hour, and then allowed to stand overnight.

The precipitate was filtered through close-textured paper, and washed once with a small volume of 1:20 ammonium hydroxide. The filtrate was discarded. The precipitate was dissolved in about 40 ml. of 1:4 hydrochloric acid by swirling the acid in the original flask, then pouring it through the filter paper into a 250 ml. beaker. The flask and paper were washed with more of the same acid until a total of 75 ml. of solution was obtained. After adding 1 ml. of "magnesia reagent" to the solution, concentrated ammonium hydroxide was added slowly and with stirring until the solution was alkaline to litmus, then an excess of 5 ml. of the ammonia was added. The suspension which resulted was stirred occasionally during an hour, then aged overnight.

The precipitate was collected on a Sela porcelain filter crucible, washed with cold 1:20 ammonium hydroxide, and then ignited to constant weight at 1050°C (muffle furnace).

It was necessary to hydrolyze pyrophosphate and other condensed phosphates to orthophosphate before making the initial precipitation of magnesium ammonium phosphate.

To accomplish this the sample was diluted to 75 ml., 25 ml. of hydrochloric acid added, followed by boiling for 30 minutes. The solution was then cooled, the "magnesia reagent" added. The subsequent procedure was that given for orthophosphates.

Phosphomolybdate Procedure (23): The ammonium molybdate reagent was freshly prepared by mixing two solutions:

- (a) 100 grams of ammonium molybdate was dissolved in 400 ml. of water and 80 ml. of ammonium hydroxide. This solution was stored in a polyethylene bottle to avoid any troublesome dissolved silica.
- (b) 400 ml. of nitric acid was diluted with 600 ml. of water.

Immediately before use, the ammonium molybdate reagent was prepared by pouring a suitable volume of solution (a) into twice its volume of solution (b).

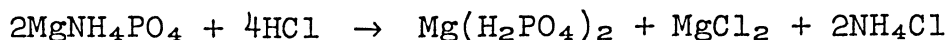
Approximately 100 mg. of sample was dissolved in 5 ml. of 6 N nitric acid and diluted with 75 ml. of water. The solution was then adjusted approximately to pH 2 by addition of 2:3 ammonia (pH meter), warmed to 40-45°C, and 60 ml. of the freshly mixed molybdate reagent was added. The yellow precipitate was allowed to age overnight.

The product was collected in a Selas porcelain filtering crucible, and washed thoroughly with a 5 per cent solution of ammonium nitrate. The precipitate was ignited in an electric furnace at 450° C for one hour. The composition of the bluish-black product is usually given as $P_2O_5 \cdot 24MoO_3$.

Pyrophosphates and other condensed phosphates were hydrolyzed to orthophosphate before forming the yellow precipitate. The sample was diluted to 75 ml., 25 ml. of nitric acid added, and the solution boiled for 30 minutes. From this point, the procedure for orthophosphate was followed.

Acidimetric Titrations

Instead of igniting magnesium ammonium phosphate in the determination of phosphorus, the precipitate may be dissolved in an excess of standard acid, and the excess acid titrated with standard base to the methyl orange end point (30, 31). The reaction may be written:



Thus a tertiary orthophosphate has reacted with two equivalents of standard acid when the methyl orange endpoint is reached; the equivalent weight of phosphorus is therefore $31/2$ or 15.5. Under the same conditions, a secondary orthophosphate reacts with only one equivalent of acid, and its

equivalent weight is therefore 31. If the percentage of phosphorus in the sample is known, the above reaction may be used to determine the equivalent weight of the phosphorus. An equivalent weight of 15.5 signifies that the unknown material is a tertiary orthophosphate. If 31, the preparation is a secondary orthophosphate. Should the equivalent weight fall between 15.5 and 31, the material being studied is a mixture of secondary and tertiary orthophosphates.

In the orthophosphate preparations which were analyzed during this investigation, the percentage of phosphorus was determined gravimetrically. Then the acidimetric titration just described was used to determine whether the orthophosphate was secondary or tertiary.

Magnesium

Magnesium was determined by precipitation as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ and subsequent ignition to $\text{Mg}_2\text{P}_2\text{O}_7$. This long and rather tedious procedure was selected because of its accuracy, and also because a magnesium determination could be carried through the same steps as the phosphorus determination thus effecting a considerable saving in time.

Procedure (24): Approximately 150 mg. of the unknown preparation was dissolved in 5 ml. of concentrated HCl, then

diluted to 150 ml. Ten ml. of a freshly prepared diammonium orthophosphate solution (2.5 grams $(\text{NH}_4)_2\text{HPO}_4$ in 10 ml. of H_2O) was added along with 2 drops of methyl red. The precipitation of magnesium ammonium phosphate by addition of ammonium hydroxide, the period of aging, the filtration, and the solution in 1:4 hydrochloric acid were carried out in exactly the same manner as in the phosphorus determination. After the magnesium ammonium phosphate was dissolved in acid, 1 ml. of the ammonium phosphate solution was added. The re-precipitation, filtration, and ignition duplicated the procedure for phosphorus.

Zinc

The precipitation of zinc as zinc ammonium phosphate and subsequent ignition to zinc pyrophosphate was the first method attempted. Accurate results were obtained with chemically pure zinc oxide and zinc phosphate. However, the method failed with zinc ethylenediammonium phosphates. The results were uniformly low (found 33.10 per cent, calculation 34.26 per cent). Since satisfactory determinations could be obtained when the ethylenediammonium ion was absent, the interference may be due to some coprecipitation phenomenon induced by the presence of the ethylenediammonium ion.

Precipitation of zinc by 8-hydroxyquinoline (oxine) proved satisfactory.

Procedure (25): Approximately 100 mg. of the unknown was dissolved in 5 ml. of 1:1 hydrochloric acid, and the solution then diluted to 100 ml. with water. Three grams of sodium acetate was added and the pH adjusted to 4.8-5.0 (pH meter) with 2:3 ammonium hydroxide. The solution was heated to 60° C and a 3 per cent alcoholic solution of oxine added dropwise until the supernatant liquid was canary-yellow. From 4 to 8 ml. of the oxine solution was usually sufficient. The precipitate was digested for 30 minutes between 60 and 80°C. The product was filtered hot through a sintered glass crucible and washed well with hot water. The zinc oxinate was dried to constant weight at 130°C, being weighed as the anhydrous material, $\text{Zn}(\text{C}_9\text{H}_6\text{ON})_2$. This proved to be a most satisfactory procedure; it was never necessary to repeat a pair of zinc determinations when this method was used.

Manganese

Manganese was successfully determined by precipitation as manganese ammonium phosphate, and subsequent ignition to manganese pyrophosphate.

Procedure (26): Approximately 150 mg. of the unknown was dissolved in 5 ml. of 1:1 hydrochloric acid, then diluted to 150 ml. with water. 20 grams of ammonium chloride

and 2 grams of diammonium orthophosphate were added, and the solution heated to boiling. Dilute ammonium hydroxide (2:3) was added drop by drop and with constant stirring until a precipitate appeared. The addition of ammonium hydroxide was stopped and the suspension stirred until the precipitate became crystalline. Another drop of ammonium hydroxide was added, the suspension stirred, and this routine continued until no more precipitate was produced and its silky appearance remained unchanged. The boiling temperature was maintained throughout the precipitation step. Finally an excess of 0.5 ml. of the ammonium hydroxide was added, and the solution allowed to cool, and stand for at least 2 or 3 hours. The precipitate was filtered in a Sela's porcelain filter crucible, washed with water, then ignited at 950-1000°C to manganese pyrophosphate.

Nickel

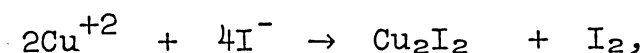
Nickel was determined by precipitation with dimethylglyoxime, and drying as nickel dimethylglyoxime, $\text{Ni}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2$.

Procedure (27): Approximately 130 mg. of the unknown was dissolved in 5 ml. of 1:1 hydrochloric acid, and diluted to 200 ml. with water. The solution was heated to 80°C,

and 20 ml. of a 1 per cent alcoholic solution of dimethylglyoxime was added. Ammonium hydroxide was then added until the liquid was slightly ammoniacal (odor) and the suspension digested on a hot plate for 30 to 60 minutes. The precipitate was filtered through a sintered glass crucible, and washed with hot water until the washings gave no reaction for chloride when tested with nitric acid and silver nitrate. The filtrate was tested for complete precipitation by adding a little dimethylglyoxime solution. The precipitate was dried in an oven at 110°C to constant weight.

Copper

The iodometric method was used to determine copper. The copper is precipitated as cuprous iodide:



and the free iodine is titrated with sodium thiosulfate solution. The latter was standardized with pure copper.

Procedure (28): A sample (approximately 200 mg.) was dissolved in 5 ml. of 6 N nitric acid, then diluted with 35 ml. of water. Dilute (2:3) ammonium hydroxide was added until the solution became deep blue in color, then 20 ml. of 6 N acetic acid and 1 ml. of 0.1 N silver nitrate were added. At this point, the pH of the solution was

checked (pH meter) to be certain it was approximately 3.7. Then three grams of potassium iodide in 15 ml. of water was added to the copper solution. The iodine liberated was titrated immediately with the standard (0.1 N) thiosulfate solution until the muddy brown color faded to pale yellow. Then 5 ml. of starch solution was added and the titration completed.

Ferrous Iron

This ion was determined by simply dissolving the unknown preparation in acid and titrating with standard potassium dichromate in the presence of H_3PO_4 . The indicator was a 0.2 per cent aqueous solution of sodium diphenylamine sulfonate.

Procedure (29): A sample weighing about 200 mg. was dissolved in a solution which contained 100 ml. of water, 5 ml. of 1:5 sulfuric acid, 3 ml. of 85 per cent ortho-phosphoric acid and 6 to 8 drops of indicator. The standard (0.1 N) potassium dichromate solution was added slowly and with constant stirring until the color changes from light green to violet.

CHAPTER VI

MAGNESIUM ETHYLENEDIAMMONIUM PHOSPHATES

Since the compounds which were expected to be included in the present investigation are somewhat analogous to magnesium ammonium phosphate, magnesium was the first cation selected for study.

All of the reactions in this system with both ortho- and pyrophosphate were carried out between 25 and 30°C.

Orthophosphate Studies

The most direct method of bringing together magnesium, ethylenediammonium, and orthophosphate ions is to add a solution of magnesium ion to a solution of ethylenediammonium orthophosphate, $\text{enH}_2(\text{HPO}_4)$. Figure 1 shows the variation in pH accompanying the addition of magnesium chloride to ethylenediammonium orthophosphate solution. No further precipitation could be detected after the molar ratio of $1\text{MgCl}_2:2\text{enH}_2(\text{HPO}_4)$ was passed. Microscopic examination showed the crystals to be perfect rectangular prisms, and relatively large as compared with

FIGURE 1

Variation of pH as a 0.38 M MgCl_2 solution is added to 35 ml. of 0.38 M $\text{enH}_2(\text{HPO}_4)$ solution.

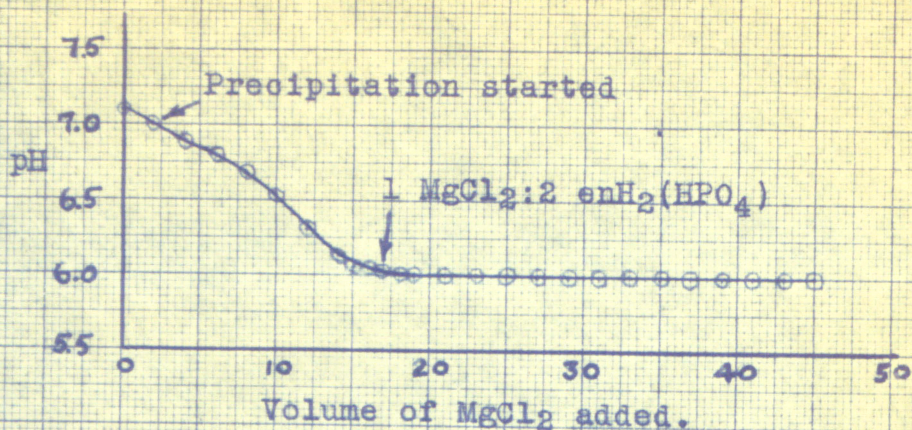
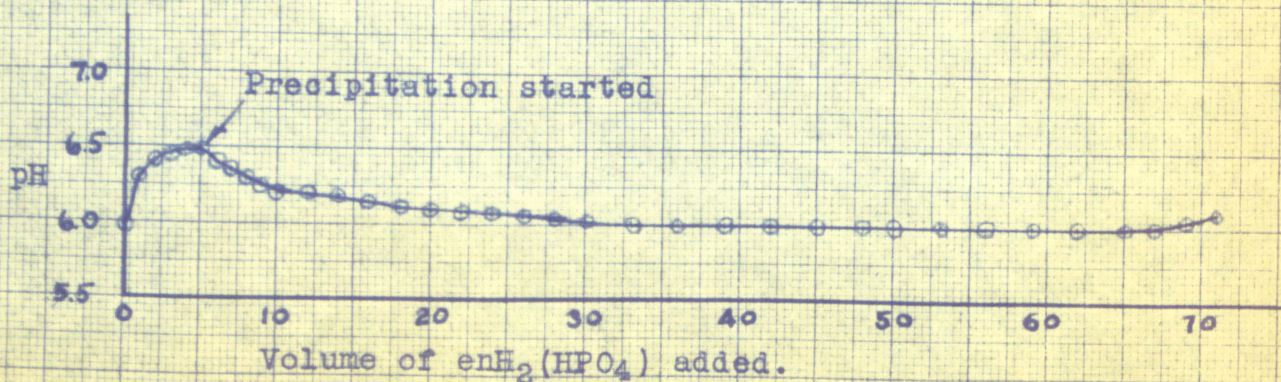


FIGURE 2

Variation of pH as a 0.38 M $\text{enH}_2(\text{HPO}_4)$ solution is added to 35 ml. of 0.38 M MgCl_2 .



subsequent products of other metal ions. No change was observed in the physical appearance of the precipitate during the course of the reaction. The product was stored in a desiccator over calcium chloride and sodium hydroxide.

The analytical findings on the preparation may be summarized as follows:

Constituent	PerCent Found	Gram-atoms	Atomic Ratio	Calculated PerCent for $\text{Mg(enH}_2\text{)}(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$
Mg	6.33	0.261	1	6.25
N	7.28	0.519	2	7.25
P	15.92	0.514	2	15.97
$\text{H}_2\text{O}(125^\circ\text{C})$	27.75	1.54	5.9	27.95

The equivalent weight of phosphorus, as determined by the acidimetric titration, was 30.9, indicating secondary orthophosphate. This deduction combined with the analytical results established the identity of the compound as $\text{Mg(enH}_2\text{)}(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$. Plate IA shows the X-ray powder pattern of the preparation.

Consequently, the following reaction occurs when magnesium chloride is added to ethylenediammonium orthophosphate:

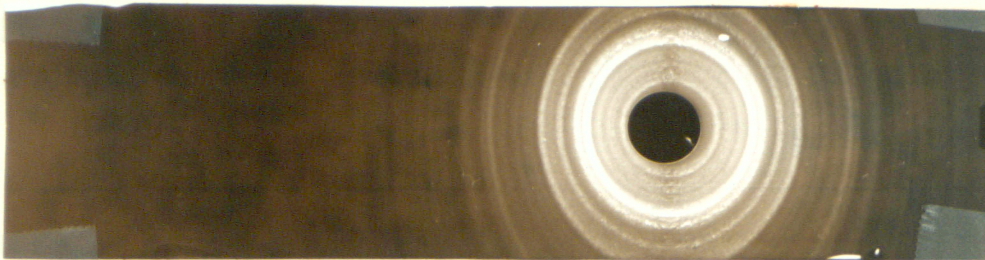


Figure 3 shows the change in conductance as the above reaction is carried out. These data give no evidence

PLATE I



A



B



C



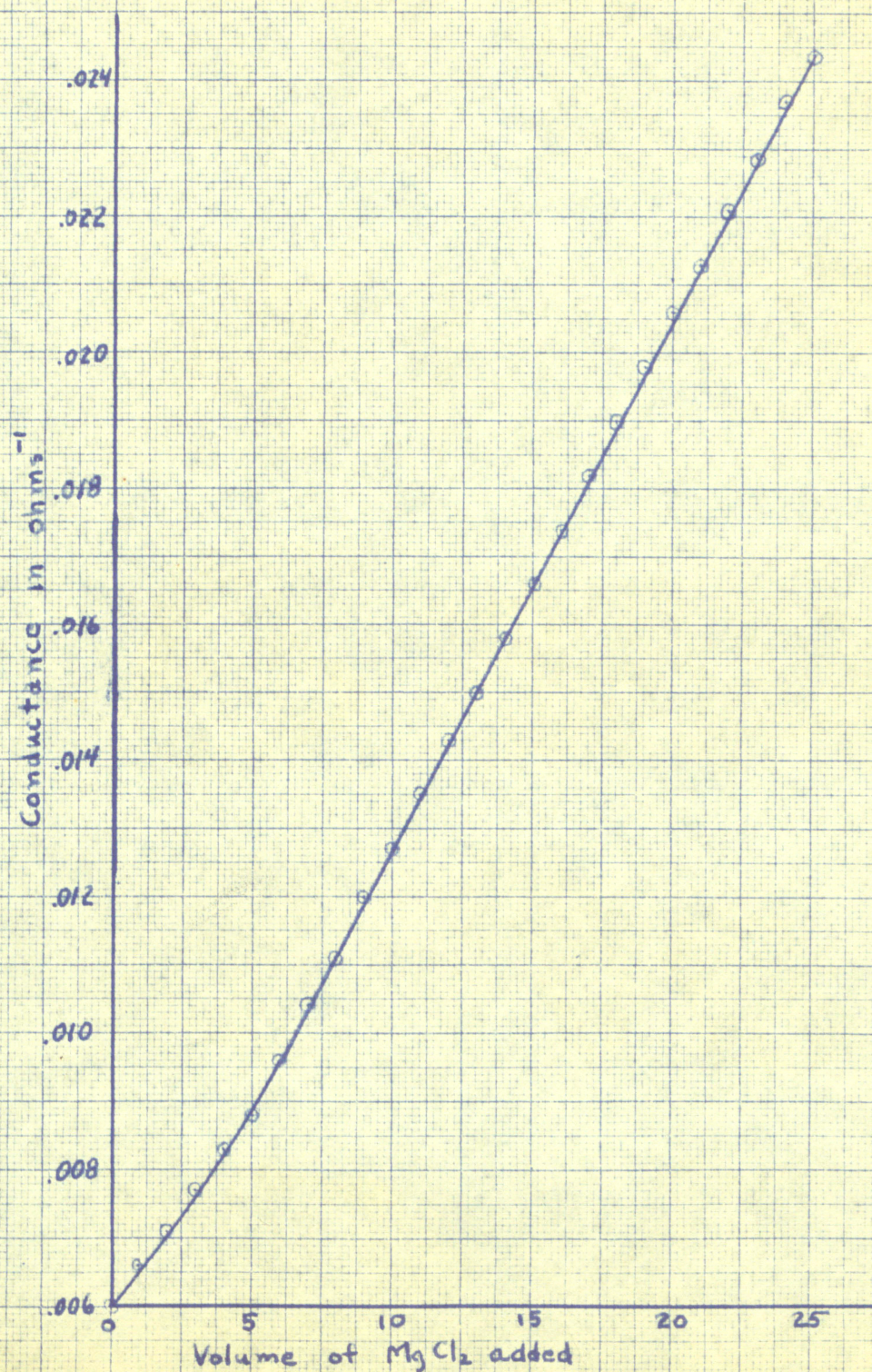
D



E

FIGURE 3

Change in conductance as 0.38 M MgCl_2 solution is added to a solution which contains 25 ml. of 0.38 M $\text{enH}_2(\text{HPO}_4)$ diluted with 600 ml. of H_2O .



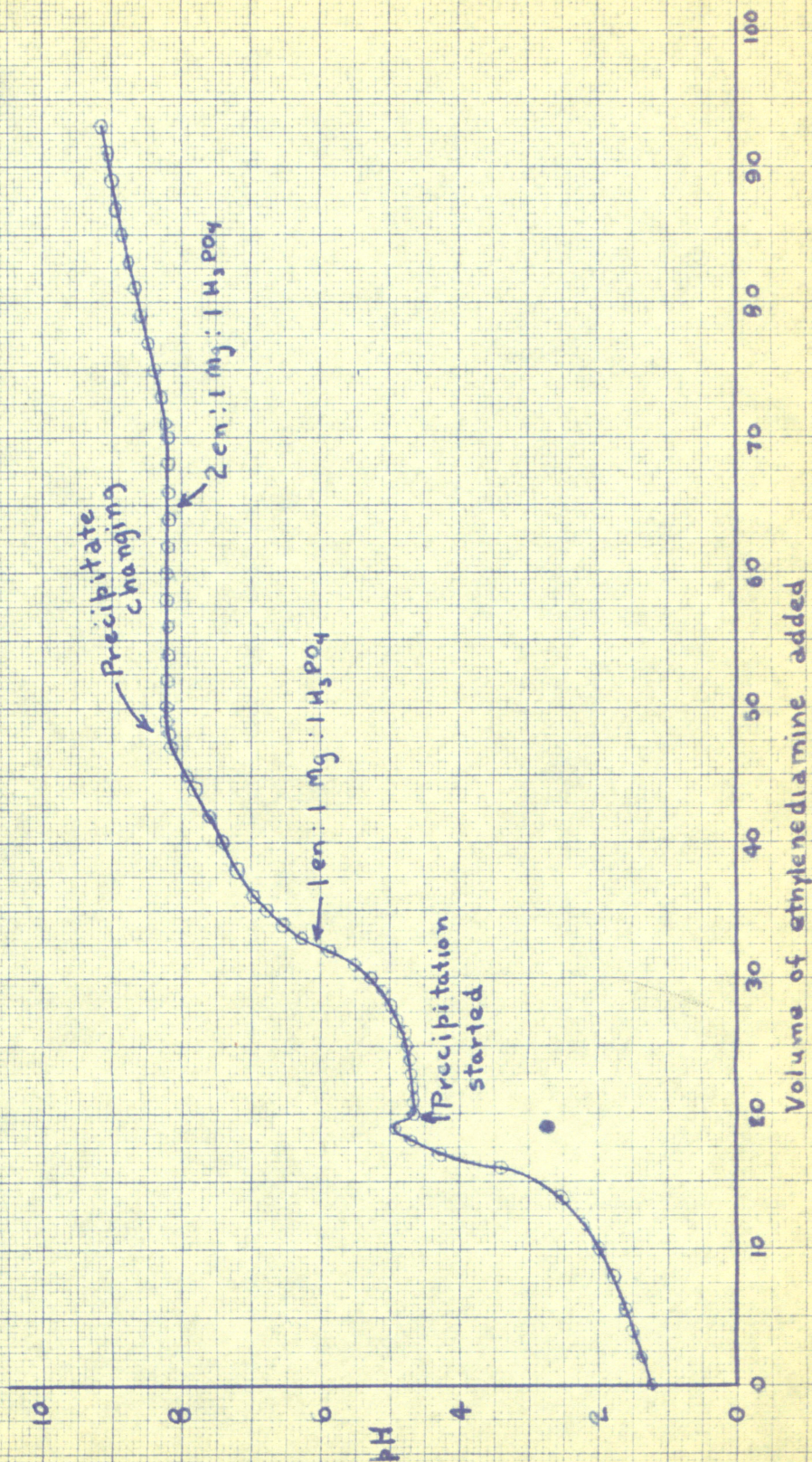
of complexing. A possible explanation of the straight line (conductance curve) is that the same number of ions are produced by the precipitation as are being added, and furthermore that both the ions produced and those being added have the about same ionic mobility.

When the ethylenediammonium phosphate solution is added to the magnesium chloride, i.e. reversing the previous order of addition (Figure 2), the same product is obtained. It was identified by the X-ray powder pattern (Plate IB) and also by microscopic observation. Again, the change in pH during the reaction is very slight. The only difference between this reaction and the one represented in Figure 1 is the period of supersaturation which occurs early in present reaction.

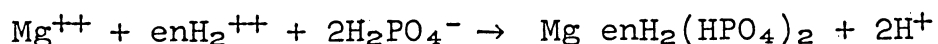
These reactions served as an introduction to the system. A more comprehensive picture was obtained by adding ethylenediamine to solutions containing phosphoric acid and magnesium ion in varying initial molar ratios. Figure 4 records the changes in pH which occur in that reaction when the initial molar ratio of magnesium chloride to orthophosphoric acid is 1:1. The initial part of the curve represents simply the neutralization curve of ethylenediamine and orthophosphoric acid. Precipitation begins at pH 4.9, and the pH drops to 4.6 as the solid appears. The product is $\text{Mg enH}_2(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ (microscopic

FIGURE 4

Change in pH as 0.41 M en is added to a solution prepared from 35 ml. of 0.38 M MgCl_2 and 26 ml. of 0.51 M H_3PO_4 . The initial molar ratio of $\text{MgCl}_2:\text{H}_3\text{PO}_4$ is 1:1.



observation). Since at this pH the prevailing phosphate species in the solution is the $(\text{H}_2\text{PO}_4)^{-1}$ ion, hydrogen ions are liberated as the precipitate forms, and accounts for the observed fall in pH.



When further addition of ethylenediamine produces no more precipitate, the pH of the solution rises.

When pH 8.2 is reached, the precipitate begins to change and hydrogen ions are found. This solid phase transformation is relatively slow; at least 30 minutes being required for the pH reading to reach a constant value, i.e. after 2 additional milliliters of ethylenediamine has been introduced the pH rises as the ethylenediamine is added, then slowly falls until a constant value is attained. The new product is flocculent, and does not settle. It shows no crystallinity under the microscope. No further changes were observed in the precipitate, and the addition of ethylenediamine was discontinued at pH 8.6. The entire reaction period was 6-9 hours. All of the long, comprehensive reactions required similar periods.

The flocculent precipitate was filtered off and air-dried. It yielded the X-ray powder pattern shown in Plate IC, which proves that the product is not amorphous. Chemical analysis gave:

Constituent	PerCent Found	Gram-Atoms	Atomic Ratio	Calculated Per Cent for $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$
Mg	17.47	0.721	1.49	17.93
N	0.37	-----	----	0
P	15.06	0.485	1.00	15.10

The product loses only 0.3 per cent of its weight at 105°C ; this hydrated magnesium phosphate is known to lose no weight at this temperature (32).

The table on the following page gives a comparison of the X-ray pattern of the product and that of $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (14).

The discrepancies between the present observed values of the spacings and those reported in the ASTM file can be explained either by the original author using an X-ray tube with a different target, or by errors* in the two sets of observations**. The number of lines in the observed pattern and their intensity are in satisfactory agreement with the pattern for $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ reported in the ASTM file.

* See p. 149 for a check on the accuracy of the present author's calculations.

** In their use of the file, workers in Proctor and Gamble laboratories have noted occasional patterns which are erroneous, e.g. $\text{Zn}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$.

Comparison of X-Ray Pattern for $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$
with that of Unknown Preparation

<u>d(observed)</u>	<u>d(literature)</u>	<u>I/I₀(observed)</u>	<u>I/I₀(literature)</u>
8.03	7.7	m	m
7.02	6.7	vs	vs
4.31*		m	-
3.86*		m	-
3.29	3.19	w	w
3.21	2.94	s	s
3.06	2.69	s	s
2.44	2.51	m	m
2.31	2.40	m	m
2.15	2.20	w	w
2.06	2.05	w	w
1.67	1.66	w	w
1.59	1.57	w	w

d = spacing calculated from the Bragg equation.
I/I₀ = relative intensity of the lines.

vs = very strong
s = strong
m = moderate
w = weak

* These lines are due to the presence of $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$.

The differences in spacings could also be accounted for by the occurrence of solid solution in the material at hand. This proposal however seems doubtful in view of the fact that the lines due to $\text{Mg}(\text{enH}_2)(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ are not shifted at all.

The evidence presented, indicates that the material which is filtered off at the end of this reaction is a mixture of $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and $\text{Mg}(\text{enH}_2)(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$. The presence of about 5 per cent of the latter would account for the slight loss of weight on heating, and the shift in the analytical results.

When a 2:1 molar ratio of magnesium chloride to phosphoric acid is treated with ethylenediamine, the reaction occurs as indicated by Figure 5. Precipitation of $\text{Mg}(\text{enH}_2)(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ (microscopic observation) again begins at pH 4.9. The change to $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ plus $\text{Mg}(\text{enH}_2)(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ mixture (X-ray pattern, plate ID) occurs at pH 7.9. The product from this reaction was filtered and air-dried in the same manner as was that from the previous reaction.

A different final product is obtained from a reaction containing magnesium ion and excess orthophosphoric acid. When ethylenediamine is added to a solution which contains magnesium chloride and orthophosphoric acid in an initial 1:2 molar ratio (Figure 6) $\text{Mg}(\text{enH}_2)(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ is again the initial precipitate (identified by its characteristic

FIGURE 5

Change in pH as 0.41 M en is added to a solution prepared from 70 ml. of 0.38 M MgCl_2 and 26 ml. of 0.51 M H_3PO_4 . The initial molar ratio of $\text{MgCl}_2:\text{H}_3\text{PO}_4$ is 2:1.

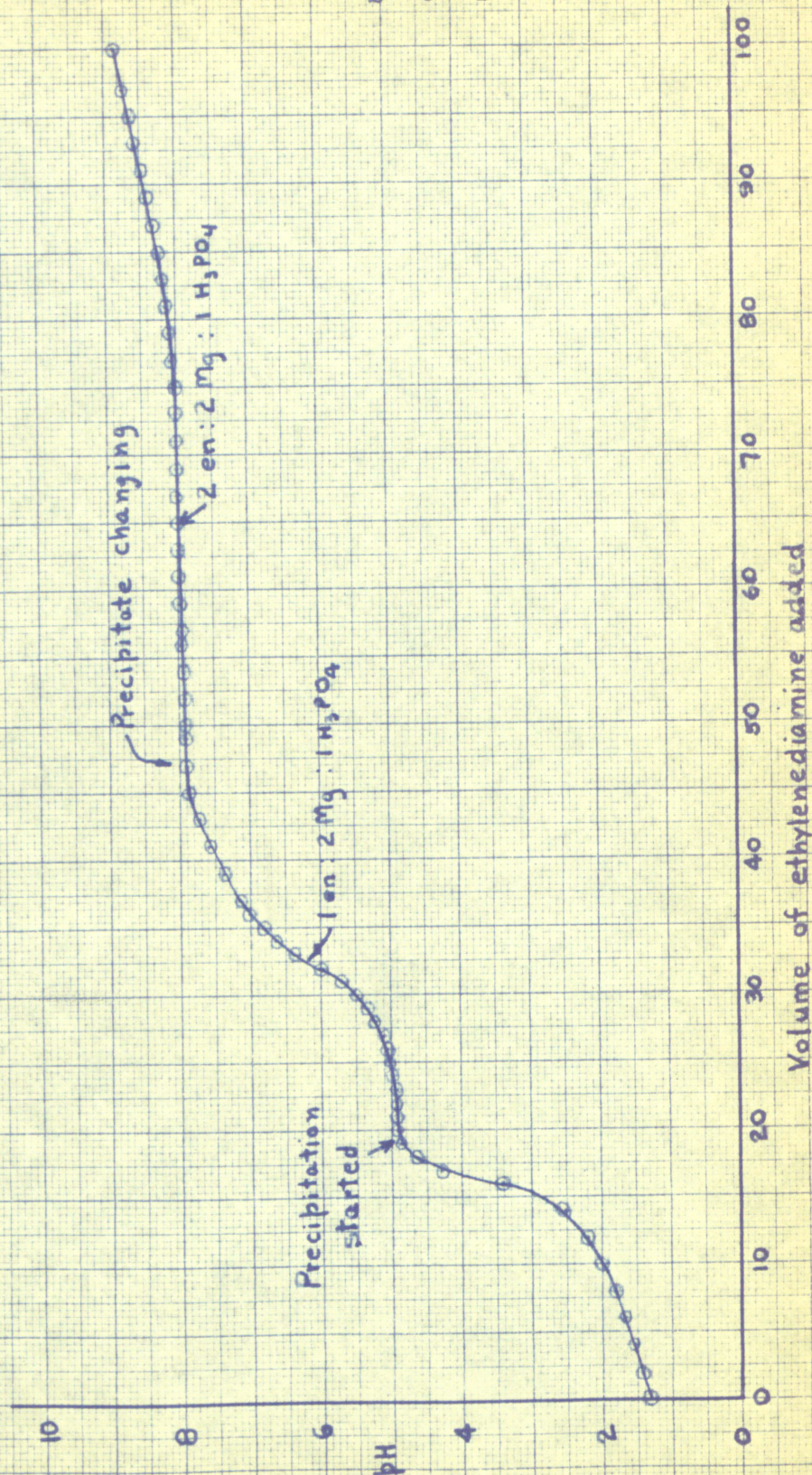
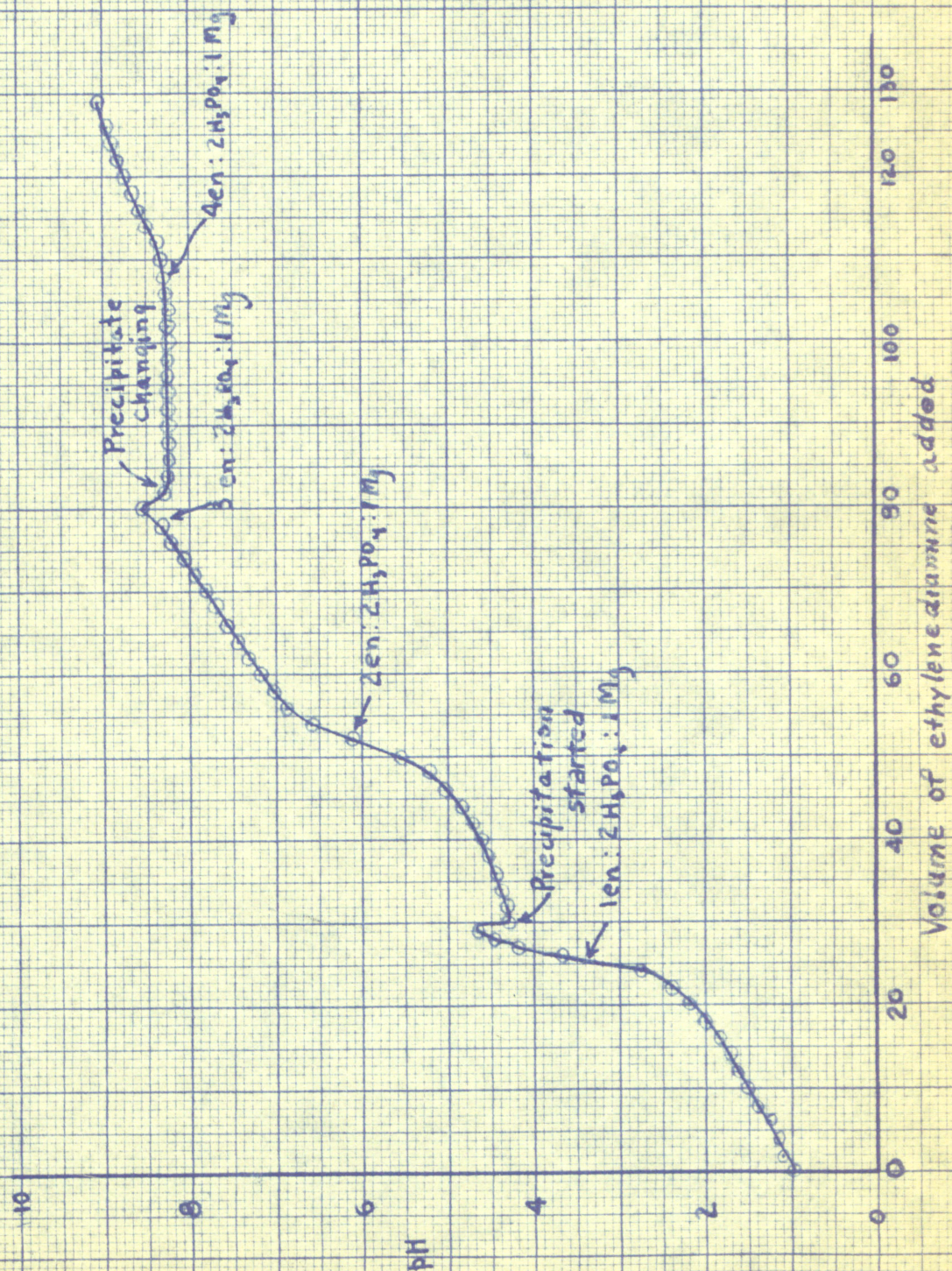


FIGURE 6

Change in pH as 0.51 M en is added to a solution prepared from 52.5 ml. of 0.51M H_3PO_4 and 14.5 ml. of 0.90 M $MgCl_2$. The initial molar ratio of $MgCl_2:H_3PO_4$ is 1:2.



appearance under the microscope). At pH 8.5, $\text{Mg(enH}_2\text{)(HPO}_4\text{)}_2 \cdot 6\text{H}_2\text{O}$ changes to a new and completely different phase (Plate I-E). The new product is complex in nature and will be discussed in detail later (p. 52).

When ethylenediamine is added to a solution containing excess ethylenediammonium ion (added as the hydrochloride) plus magnesium and orthophosphoric acid, the only precipitate is $\text{Mg(enH}_2\text{)(HPO}_4\text{)}_2 \cdot 6\text{H}_2\text{O}$ (Figure 7, Plate II-A). The initial molar ratios of magnesium chloride to phosphoric acid to ethylenediammonium hydrochloride were 1:1:2. Extensive buffering occurs in the system between pH 7 and 8. Because of this effect, a titration-type reaction becomes impractical above pH 8.

The following attempts were made to prepare a double salt which contains magnesium, ethylenediammonium ion, and a tertiary orthophosphate.

A. About 1.5 grams of $\text{Mg(enH}_2\text{)(HPO}_4\text{)}_2 \cdot 6\text{H}_2\text{O}$ was placed in suspension with 20 ml. of water, and the pH adjusted to 10.3 with 0.6 M ethylenediamine. The mixture was allowed to stand at room temperature for one week. During this period, the suspension was stirred thoroughly about 3 or 4 times daily. The product was filtered and dried in a desiccator over calcium chloride. It gave the X-ray pattern shown in Plate II-B.

B. Preparation A was repeated with the exception that

FIGURE 7

Change in pH as 0.41 M en is added to a solution which contains 30 ml. of 0.51 M H_3PO_4 , 17 ml. of 0.90 M MgCl_2 , and 8.16 gm. of enH_2Cl_2 . The initial molar ratios are 1 H_3PO_4 :1 MgCl_2 :4 enH_2Cl_2 .

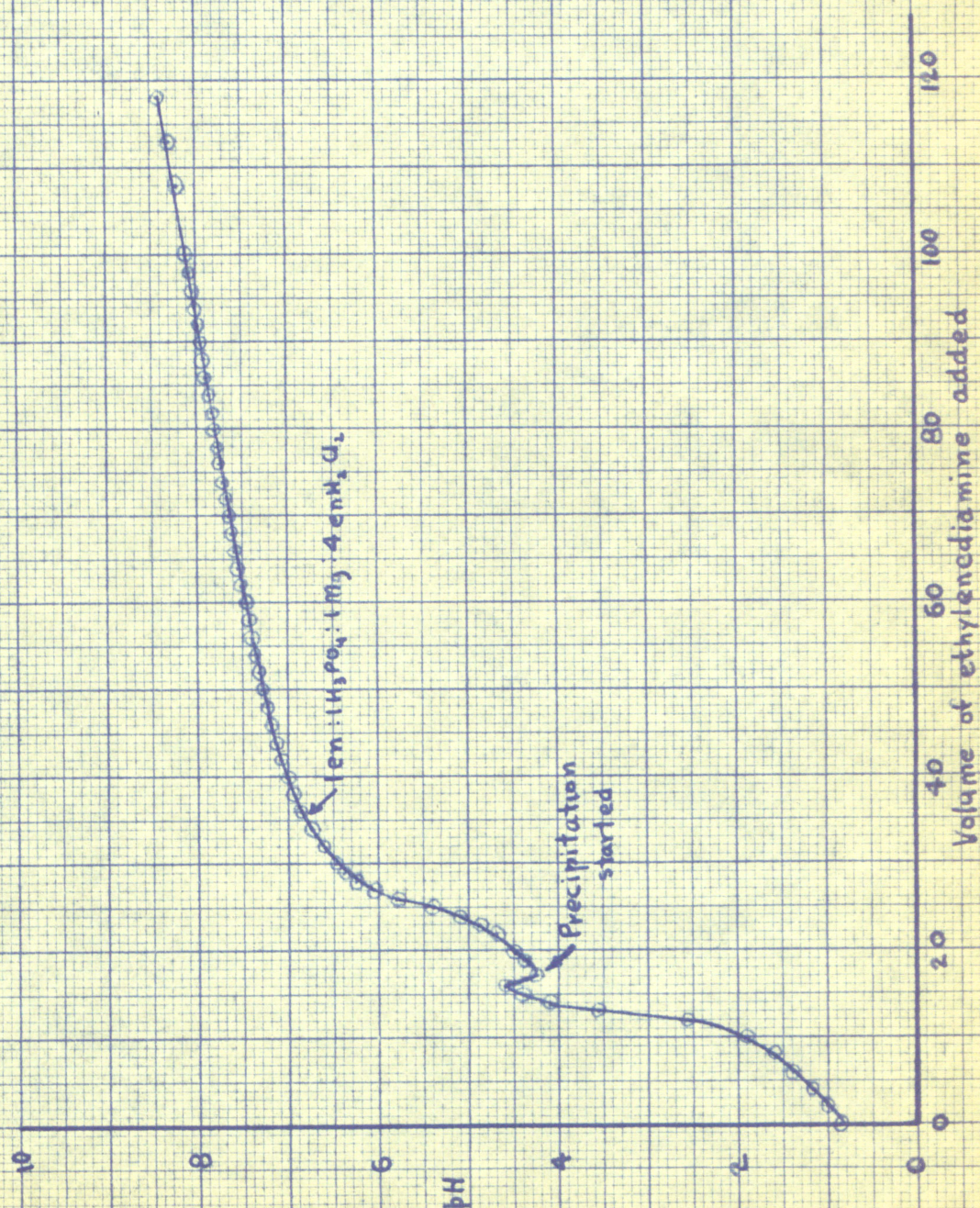


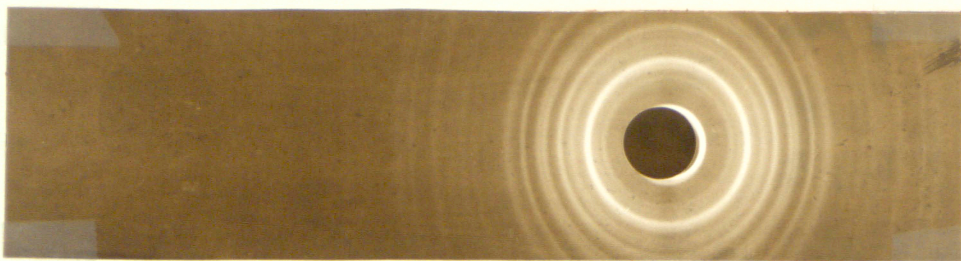
PLATE II



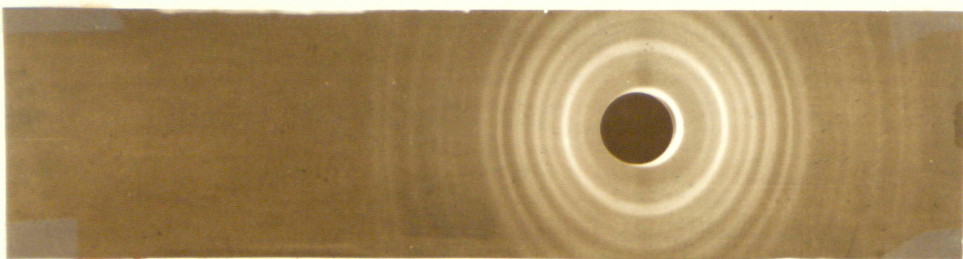
A



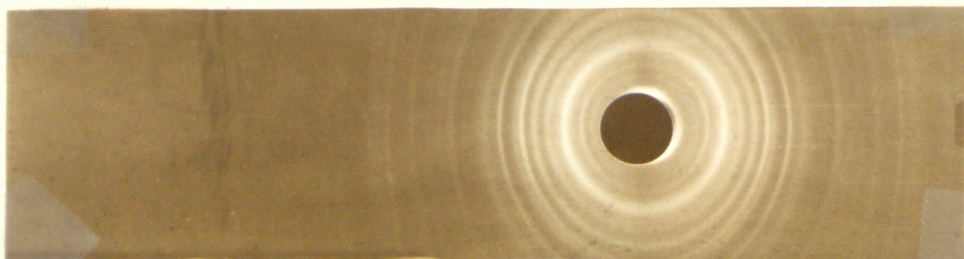
B



C



D



E

1.6 grams of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was also present. The starting molar ratio of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ to $\text{MgenH}_2(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ was 2:1. Plate II-C is the X-ray pattern of the product.

C. Preparation A was repeated once more, this time 1.6 grams of ethylenediammonium hydrochloride was also present. The initial molar ratio of $(\text{enH}_2)\text{Cl}_2$ to $\text{MgenH}_2(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ was 2:1. The X-ray pattern of the product is given in Plate II-D.

D. Approximately 3.8 grams of $\text{MgenH}_2(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ were refluxed with 75 ml. of 1.8 M aqueous ethylenediamine solution for 3 hours. The product was filtered hot, then washed once with 50 ml. of ethyl alcohol to remove ethylenediamine adhering to the precipitate. It was then stored in a desiccator over calcium chloride. Plate II-E is the X-ray pattern of the product.

E. The precipitate which was filtered off at the end of the reaction depicted in Figure 6 (p. 50) has the same X-ray pattern (Plate I-E) as the foregoing four preparations, and will accordingly be discussed here.

The following table summarizes the analytical data on this series of preparations. Where incomplete analytical data are given, not enough of that particular product was obtained to carry out further determinations.

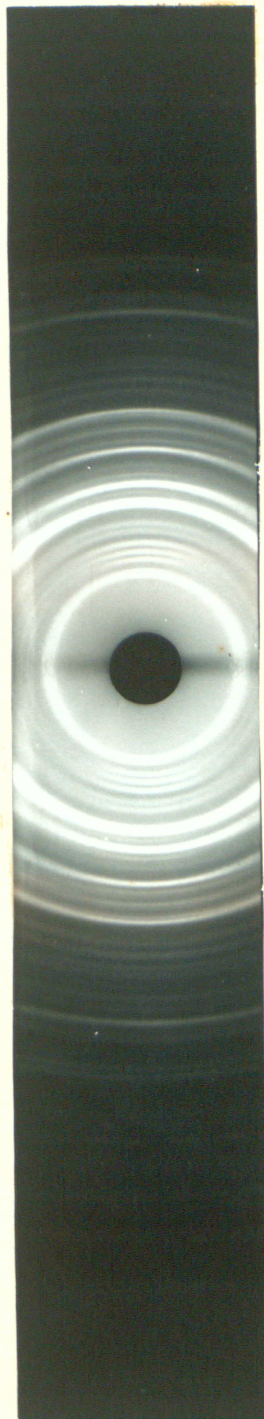
Constituent Determined	A	B	C	D	E
N	-----	6.97	-----	7.02	6.95
P	17.75	-----	17.76	17.75	17.66
Mg	14.43	14.36	14.41	14.38	14.46

The first facts to be noted are that these foregoing preparations have a constant composition and that all give the same X-ray diffraction pattern. The gram atoms of the constituents are 0.594 Mg, 0.573 P, and 0.499 N. The corresponding ratios are 1.19 Mg: 1.00 N: 1.15P, - which obviously are non-integral numbers. An acidimetric titration which was carried out on preparation D showed that the equivalent weight of phosphorus was 15.6, indicating a tertiary orthophosphate. One more point should be noted, namely that the gram-atoms of magnesium plus the moles of ethylenediamine are in a 1:1.47 ratio with the gram atoms of phosphorus ($0.593 + 0.249 = 0.842$; $0.842 \div 0.573 = 1.47$). Thus the total cation charge ($2 \times 0.594 + 2 \times 0.249 = 1.69$) equals the total anion charge ($3 \times 0.573 = 1.72$). This fact establishes the validity of the analytical data.

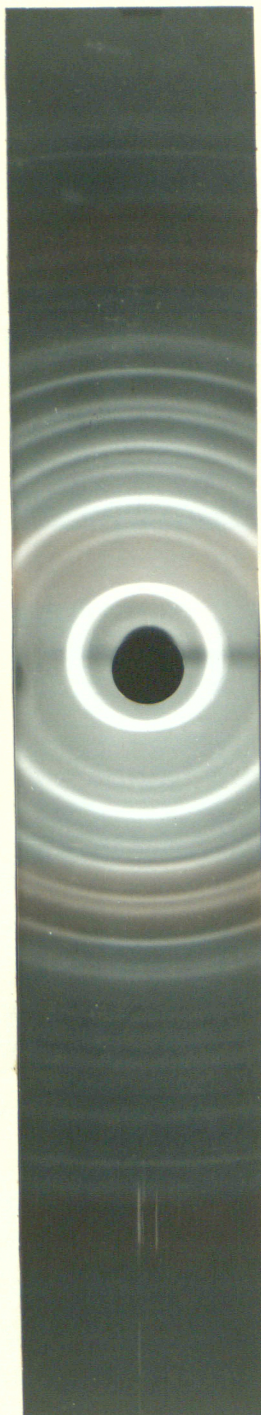
Plates III-A and III-B are the large X-ray patterns for $\text{Mg}(\text{enH}_2)(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ and this latter phase respectively.

Some calculated percentages for some hydrates of a compound having the composition $\text{Mg}_2(\text{enH}_2)(\text{PO}_4)_2$ are as follows:

PLATE III



A



B

<u>Constituent</u>	<u>Per Cent in Dihydrate</u>	<u>Per Cent in Trihydrate</u>
Mg	14.43	13.68
N	8.32	7.89
P	18.37	17.45

In the analytical data of the phase being discussed, the magnesium content agrees with the dihydrate, while both the phosphorus and the nitrogen agree with the trihydrate.

These data seem to indicate that the preparation, if a compound, has non-integral quantities of the constituents. It may be pictured as a crystal lattice which accommodates more magnesium ions than ethylenediammonium ions.

The high pH region of this system is one which merits further investigation. A phase study might shed more light on the peculiar phase under discussion.

An exploratory reaction was carried out to learn if the formation of $\text{Mg}(\text{NH}_2\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ as an analytical precipitate would merit further study. Reagent grade disodium orthophosphate (Na_2HPO_4) which had been recrystallized twice and dehydrated at 105°C , was used as the reference material. A sample weighing 200 mg. was dissolved in 5 ml. of 1:1 hydrochloric acid, then diluted to 100 ml. with water. Six grams of ethylenediammonium hydrochloride and 3 grams of magnesium chloride hexahydrate were dissolved in this solution. When the pH was raised to 7 with a 2:3 solution of ethylenediamine, no precipitation occurred. It

therefore appears that $\text{Mg enH}_2(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ is too soluble to precipitate under analytical conditions. This exploratory reaction was not carried to higher pH ranges, but it is quite likely that magnesium phosphate would precipitate under more basic conditions.

Pyrophosphate Studies

The most direct combination of the ions involved can be effected by adding magnesium chloride to a solution of ethylenediammonium pyrophosphate. Figure 8 shows the pH changes accompanying this addition. After a few milliliters of magnesium chloride are added, the whole system assumes the consistency of hand lotion. Aging overnight brings about no improvement in the nature of the product. However, it is filterable. When dried in a desiccator over calcium chloride and sodium hydroxide, the product becomes very hard and vitreous. The X-ray pattern is diffuse and indicates some crystallinity (Plate IV-A). Its composition is: magnesium 7.84 per cent, nitrogen 8.43 per cent, phosphorus 14.95 per cent. These figures correspond to gram-atoms of 0.32 magnesium, 0.60 nitrogen, and 0.48 phosphorus. They are not easily resolved into a simple numerical ratio which is compatible with the ions which may be present. The X-ray pattern, the general appearance of the product, and the analytical data indicate that the

FIGURE 8

Variation in pH as 0.90 M MgCl_2 is added to a suspension of 0.01 mole of $(\text{enH}_2)_2\text{P}_2\text{O}_7$ in 60 ml. of water.

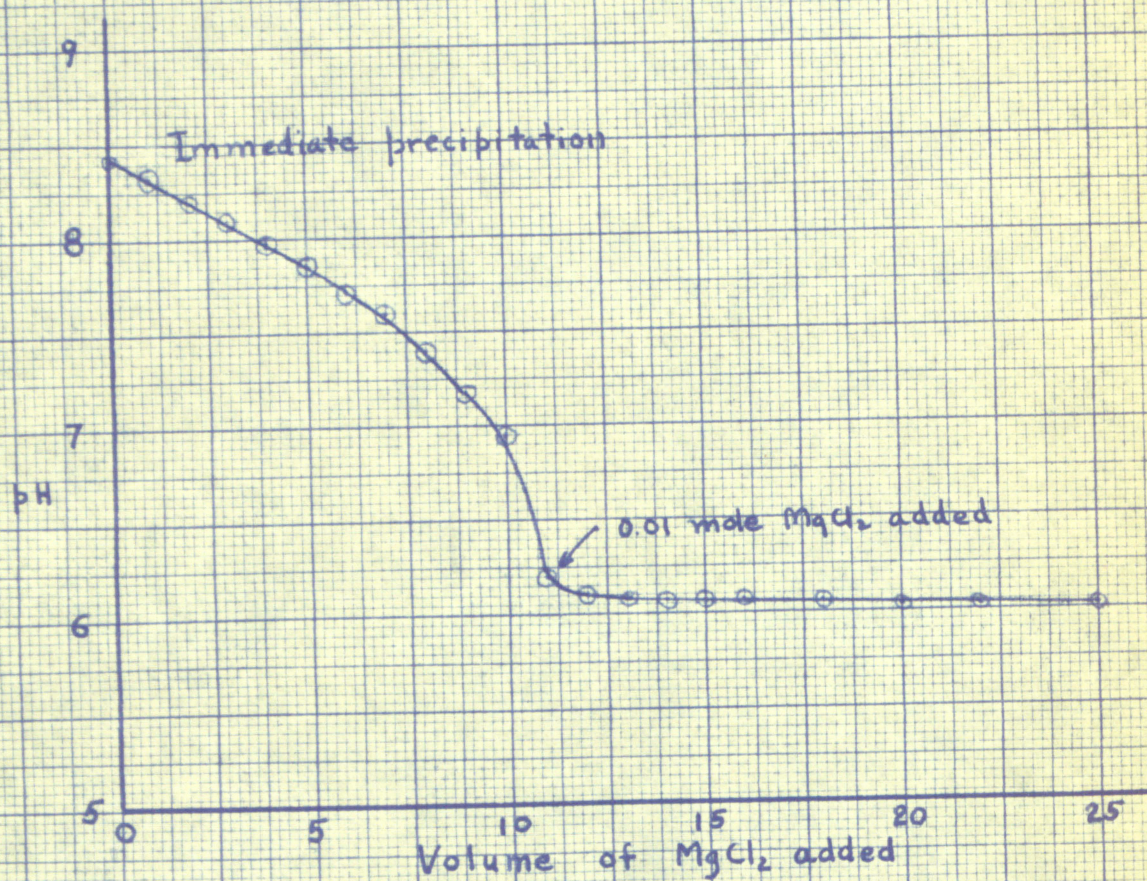


FIGURE 9

Change in conductance as 0.90 M MgCl_2 solution is added to a solution which contains 0.01 mole of $(\text{enH}_2)\text{P}_2\text{O}_7$ dissolved in 600 ml. of H_2O .

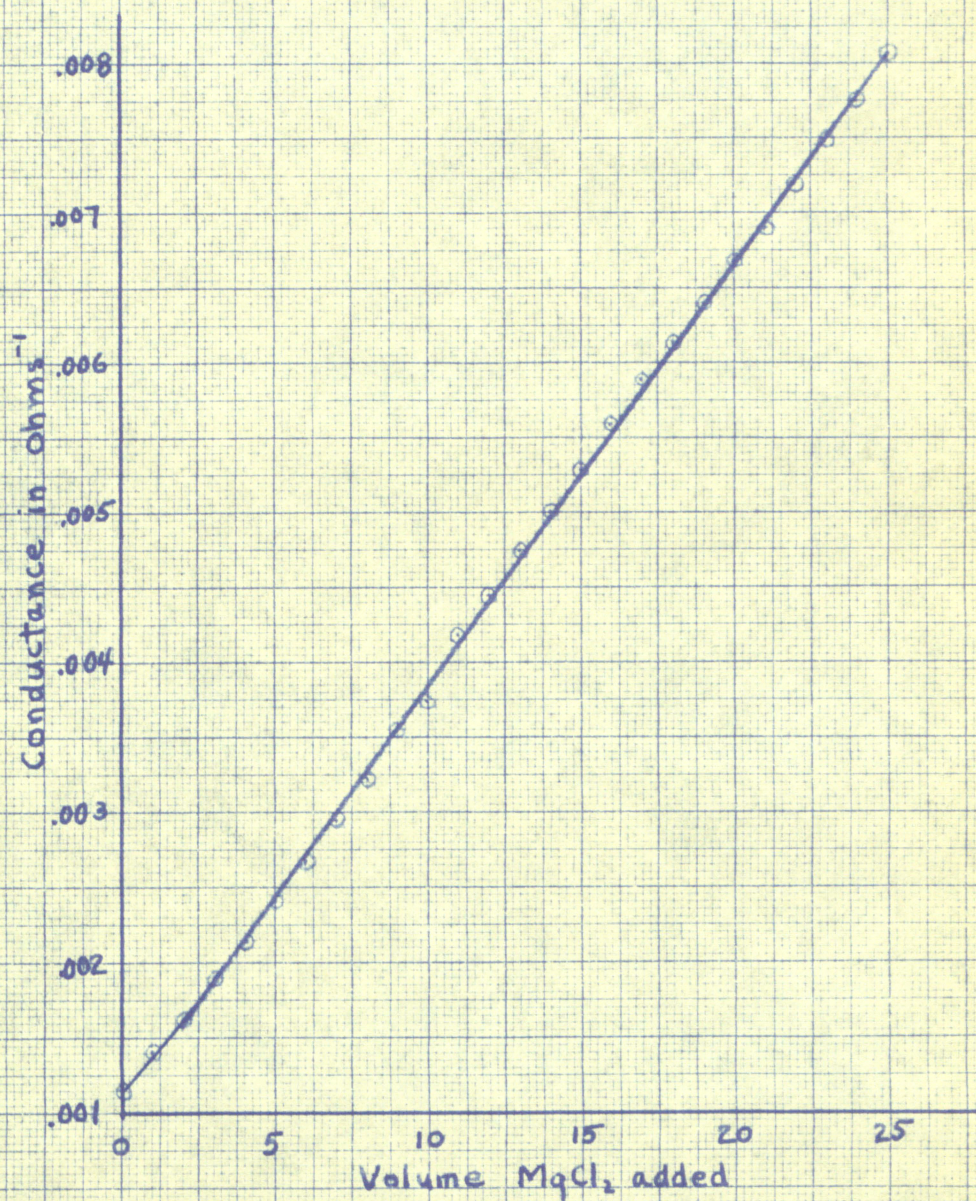
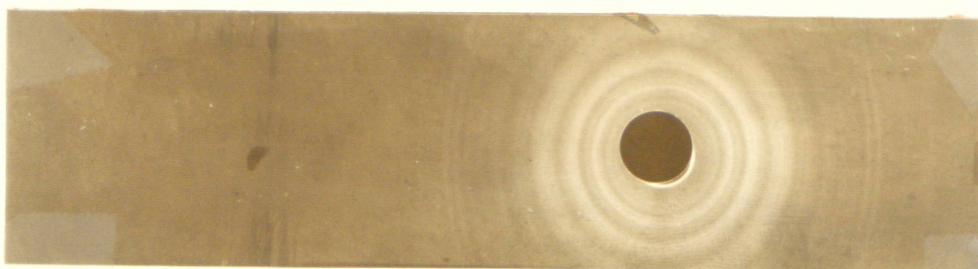
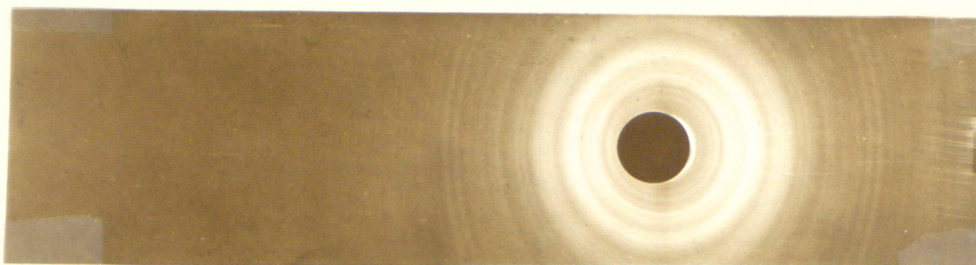


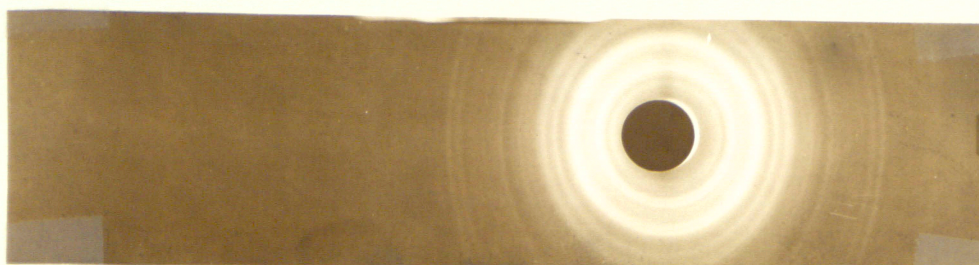
PLATE IV



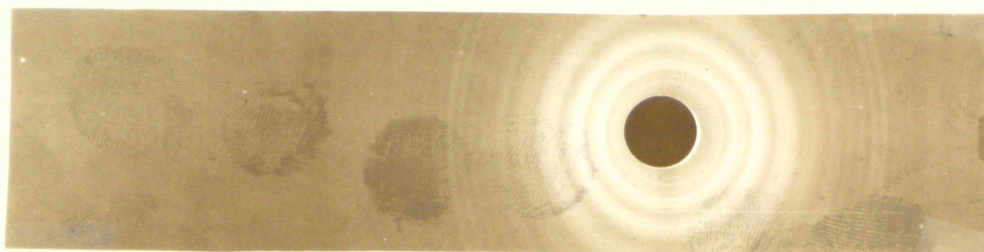
A



B



C



D



E

product is a mixture.

Figure 9 is a conductance titration for the same system. It gives no additional information.

When ethylenediamine is added to a solution which contains magnesium chloride and pyrophosphoric acid in an initial 1:1 molar ratio (Figure 10), precipitation begins at pH 3.5. The crystals under X450 magnification appear as very small, closely-packed spherulites. They settle rapidly leaving the supernatant liquor clear. The product obtained at this pH was dried over calcium chloride and sodium hydroxide. Plate IV-B is the X-ray pattern of the preparation.

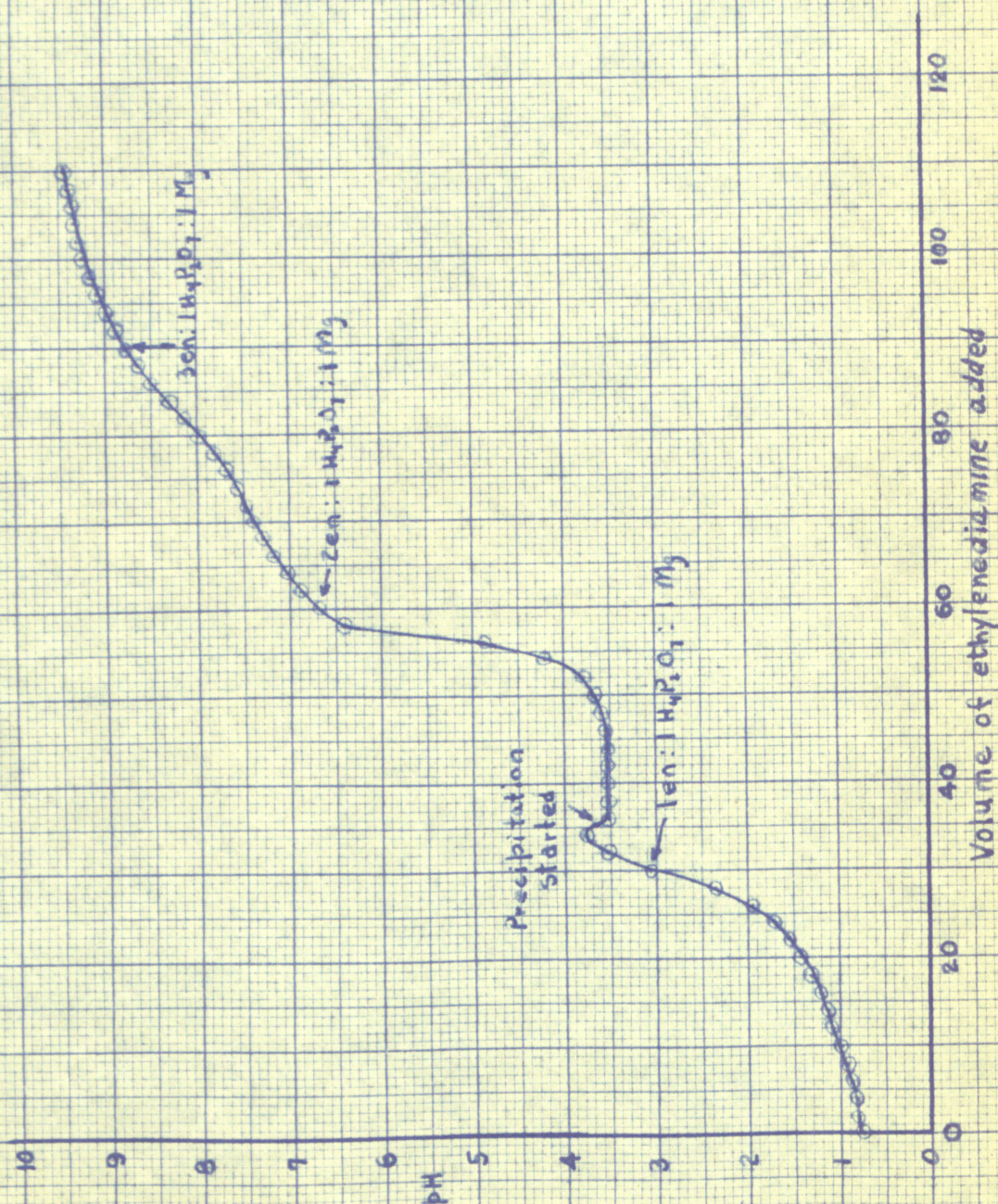
The following table gives the results of the chemical analysis of the product.

Constituent	PerCent Found	Gram-Atoms	Atomic Ratio	Calculated Per Cent for $\text{MgenH}_2(\text{P}_2\text{O}_7) \cdot 4.5\text{H}_2\text{O}$
Mg	7.10	0.292	1.00	7.14
N	8.08	0.578	1.98	8.21
P	18.15	0.585	2.01	18.13
$\text{H}_2\text{O}(115^\circ\text{C})$	23.92	1.33	4.52	23.81

A phosphorus determination showed that anhydrous magnesium ethylenediammonium pyrophosphate was obtained by dehydration of the foregoing preparation. (Phosphorus found: 23.91 per cent, theoretical phosphorus content for $\text{MgenH}_2(\text{P}_2\text{O}_7)$: 23.80 per cent). The evidence presented identifies the

FIGURE 10

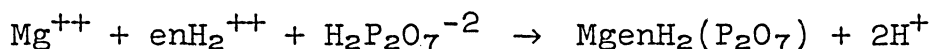
Change in pH as 0.51 M en is added to a solution which contains 19.6 ml. of 0.77 M $\text{H}_4\text{P}_2\text{O}_7$ and 16.6 ml. of 0.90 M MgCl_2 . The initial molar ratio of MgCl_2 to $\text{H}_4\text{P}_2\text{O}_7$ is 1:1.



original preparation as $\text{MgenH}_2(\text{P}_2\text{O}_7) \cdot 4.5\text{H}_2\text{O}$.

When the reaction (Figure 10) is continued, no further change is observed in the nature of the precipitate. Plate IV-C is the X-ray pattern of the final product. The lines toward the center are not as well defined as those given by the initial product, but it is still definitely the same compound. The slight differences in the intensities of some of the lines can be explained as orientation effects.

A straightforward reaction occurs when excess pyrophosphoric acid is present. Figure 11 shows the pH changes as ethylenediamine is added to a solution which contains magnesium chloride and pyrophosphoric acid in an initial 1:2 ratio. Precipitation begins at pH 3.9 and a drop in pH occurs as the product forms. Since $\text{H}_2\text{P}_2\text{O}_7^{-2}$ is the prevailing pyrophosphate species at this pH, the fall in pH can be attributed to the following reaction:



There is no apparent change in the product as the reaction is continued. Plate IV-D is the X-ray pattern of the precipitate which was filtered off at the end of the reaction.

On the basis of the pattern, the product can be taken to be $\text{MgenH}_2(\text{P}_2\text{O}_7) \cdot 4.5\text{H}_2\text{O}$.

Figure 12 depicts the changes in pH when ethylene-

FIGURE 11

Change in pH as 0.52 M en is added to a solution which contains 20 ml. of 0.62 M $\text{H}_4\text{P}_2\text{O}_7$ and 7.5 ml. of 0.83 M MgCl_2 . The initial molar ratio of $\text{MgCl}_2:\text{H}_4\text{P}_2\text{O}_7$ is 1:2.

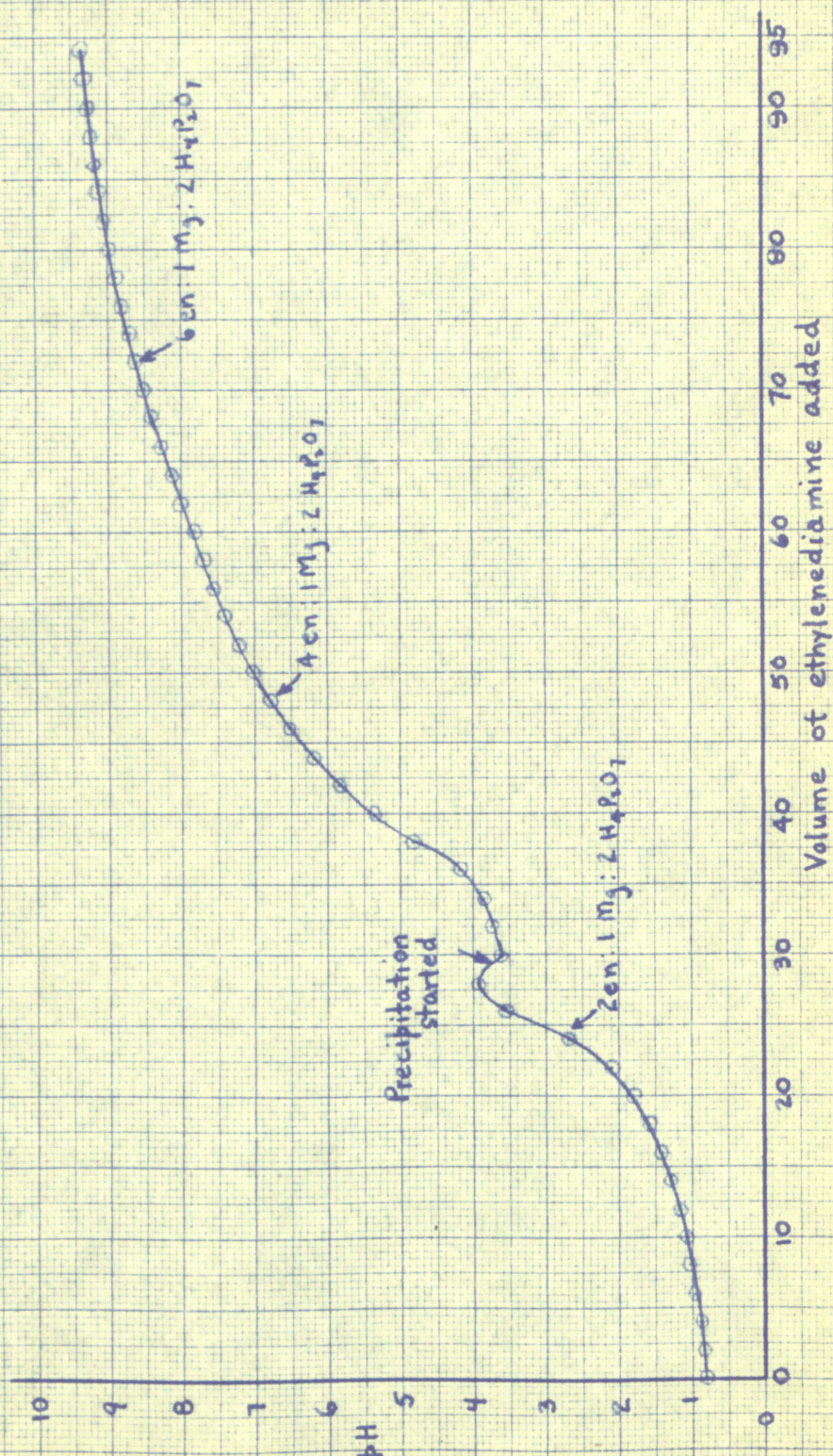
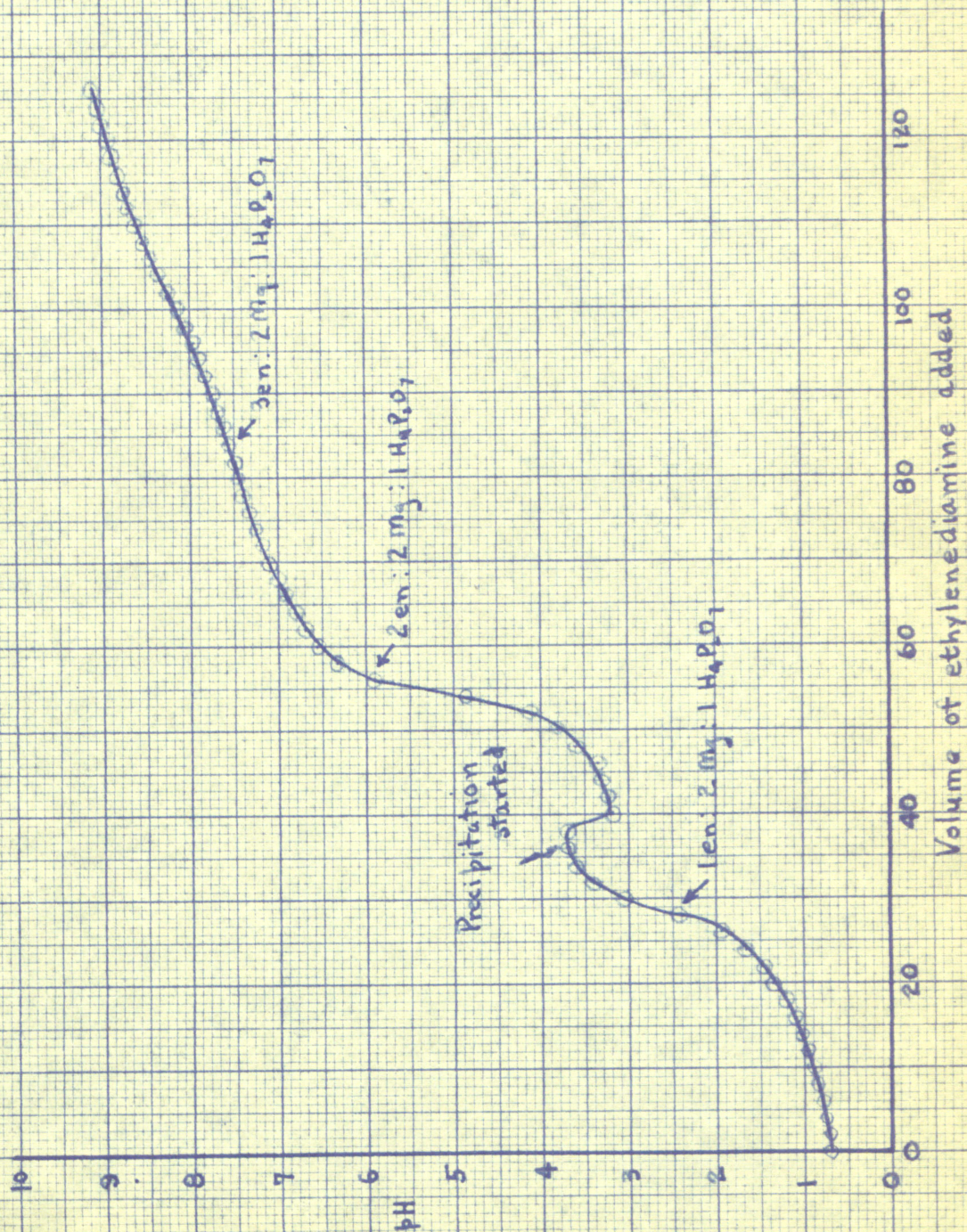


FIGURE 12

Change in pH as 0.51 M en is added to a solution which contains 19 ml. of 0.76 M $\text{H}_4\text{P}_2\text{O}_7$ and 33 ml. of 0.90M MgCl_2 . The initial molar ratio of $\text{MgCl}_2:\text{H}_4\text{P}_2\text{O}_7$ is 2:1.

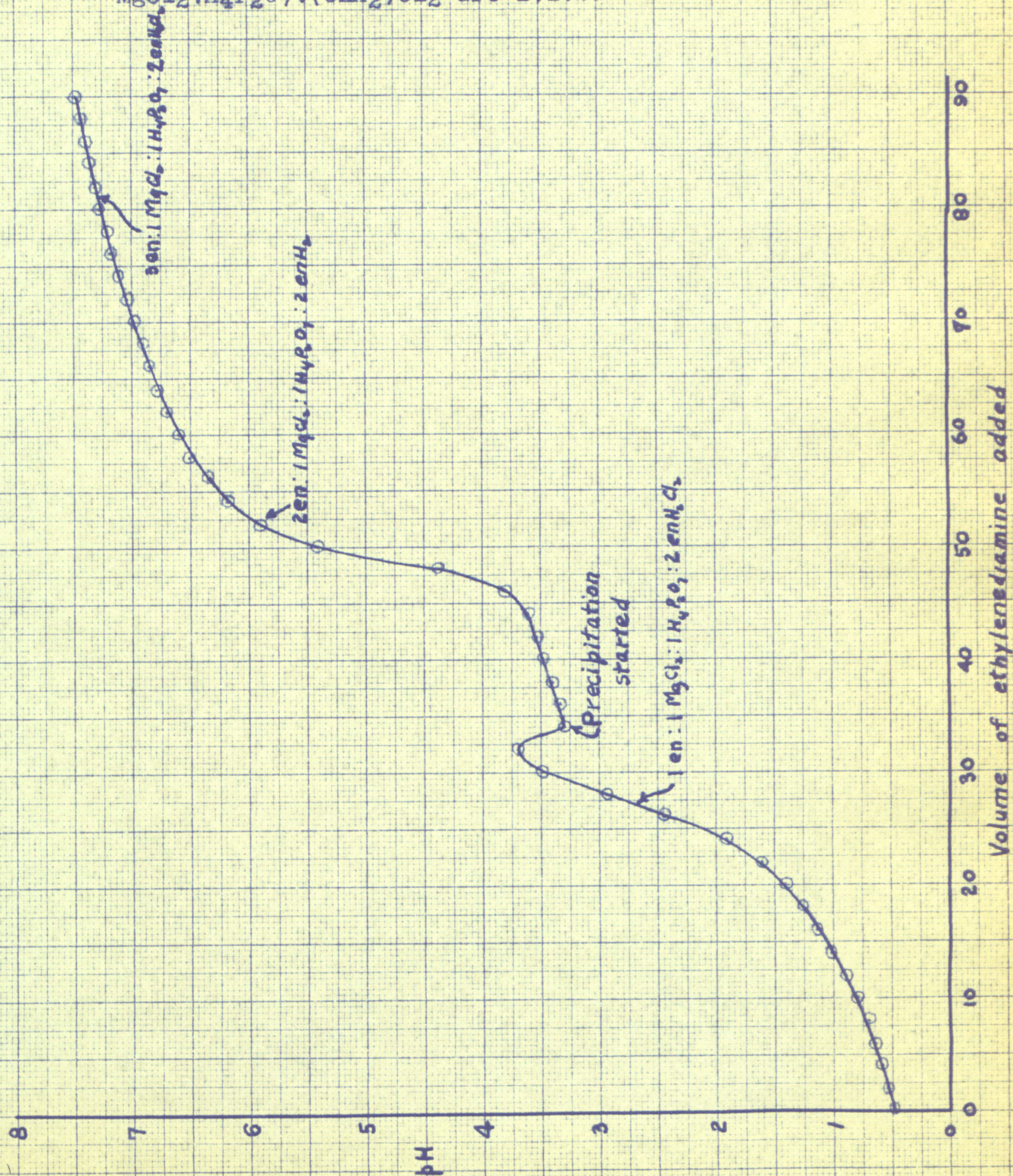


diamine is added to a solution which contains pyrophosphate and excess magnesium ion. The initial molar ratio of magnesium chloride to pyrophosphoric acid is 2:1. The appearance of the curve is much the same as Figure 11, however the product is quite different. Precipitation begins at pH 3.6. The solid is very finely divided, and does not settle. When the final product is filtered, some passes through a "medium" sintered glass filter crucible, and the whole filtering operation is very tedious. After drying over calcium chloride and sodium hydroxide, the product can be crushed into a very fine powder. Plate IV-E gives the X-ray pattern of the product. There are many diffuse regions, and the few lines are weak and poorly defined. The preparation was found to contain 3.06 per cent nitrogen, 14.68 per cent magnesium, and 19.85 per cent phosphorus. These percentages correspond to 0.219 nitrogen, 0.604 magnesium, and 0.641 phosphorus; which correspond to ratios of 1.00 nitrogen to 2.75 magnesium to 2.93 phosphorus. The analytical results indicate that the preparation is a mixture, possibly containing a large percentage of some form of magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$).

The reaction which was carried out with magnesium, pyrophosphate, and excess ethylenediammonium ion is shown in Figure 12a. It is straightforward. The final product settled rapidly, and filtered well. To check the possibility that storing previous products over calcium chloride and

FIGURE 12a

Change in pH as 0.56 M en is added to a solution which contains 18 ml. of 0.83 M MgCl_2 , 22 ml. of 0.68 M $\text{H}_4\text{P}_2\text{O}_7$, and 4 gm. of $(\text{enH}_2)\text{Cl}_2$. The initial molar ratios of $\text{MgCl}_2:\text{H}_4\text{P}_2\text{O}_7:(\text{enH}_2)\text{Cl}_2$ are 1:1:2.

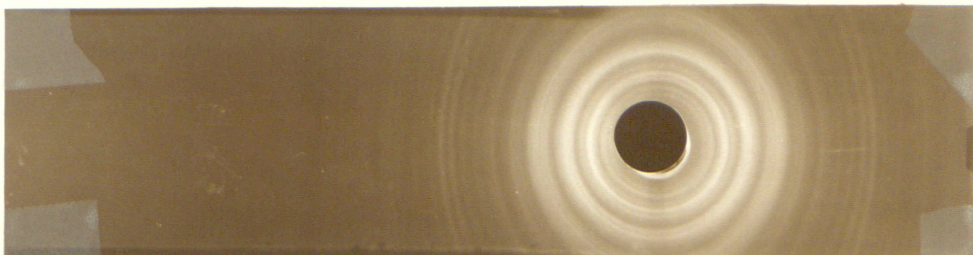


sodium hydroxide was partially dehydrating them, this preparation was washed with two 25 ml. portions of alcohol, two 25 ml. portions of ether, then air-dried. The X-ray pattern was exactly the same (Plate V-A); and the phosphorus content of the product was found to be 18.07 per cent, as compared with 18.13 per cent calculated for $\text{Mg}_2\text{H}_2(\text{P}_2\text{O}_7) \cdot 4.5\text{H}_2\text{O}$.

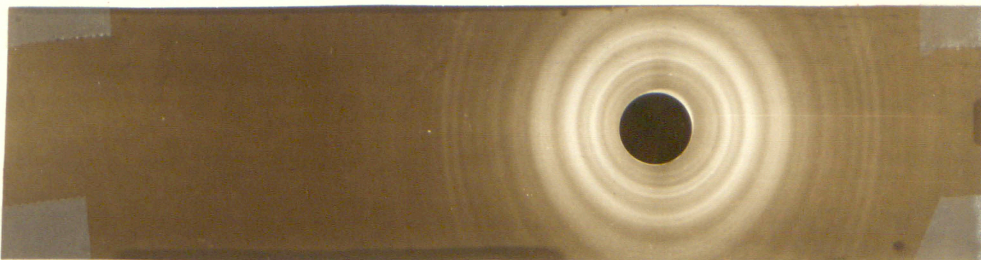
It is possible to recrystallize the magnesium ethylenediammonium phosphate by dissolving a small amount in dilute (1:1) hydrochloric acid, then adding 3:2 ethylenediamine until precipitation begins. This recrystallized product gives the same X-ray pattern as the previous preparations (Plate V-B).

An experiment was carried out to learn if the formation of $\text{Mg}_2\text{H}_2(\text{P}_2\text{O}_7) \cdot 4.5\text{H}_2\text{O}$ is quantitative for phosphorus. "Reagent grade" tetrasodium pyrophosphate which had been recrystallized twice and dehydrated at 105°C was the reference material. About 200 mg. of $\text{Na}_4\text{P}_2\text{O}_7$ was dissolved in 50 ml. of water and 5 ml. of 1:1 hydrochloric acid. Six grams of ethylenediammonium hydrochloride and 3 grams of magnesium chloride hexahydrate were added to the solution. The pH of the solution was then raised to 6 by dropwise addition of 2:3 diethylenediamine. Precipitation occurred, and the product appeared to be a mixture. Some of it was flocculent and did not settle, while the remainder

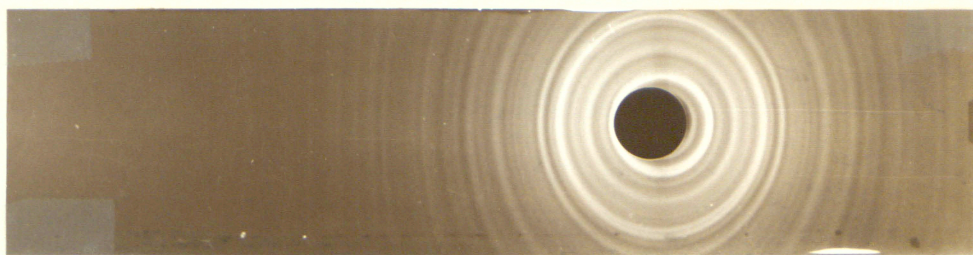
PLATE V



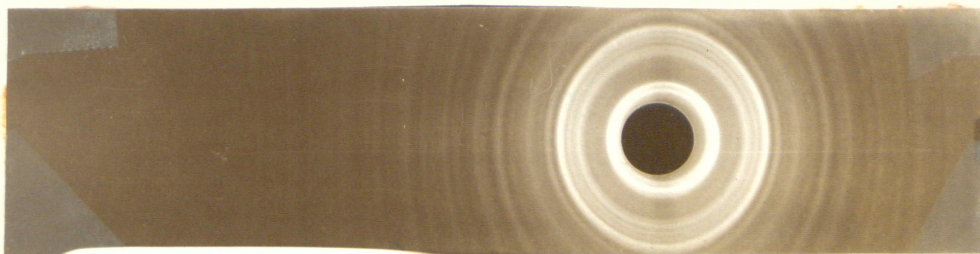
A



B

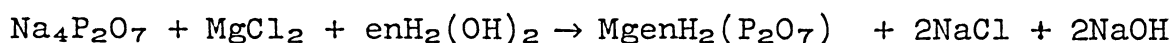


C



D

settled well. The product was aged overnight. No change in the appearance of the precipitate occurred during the aging. All the foregoing operations were carried out at room temperature. The material was dried to constant weight at 115°C. If all of the sample had been converted to $\text{MgenH}_2(\text{P}_2\text{O}_7)$,



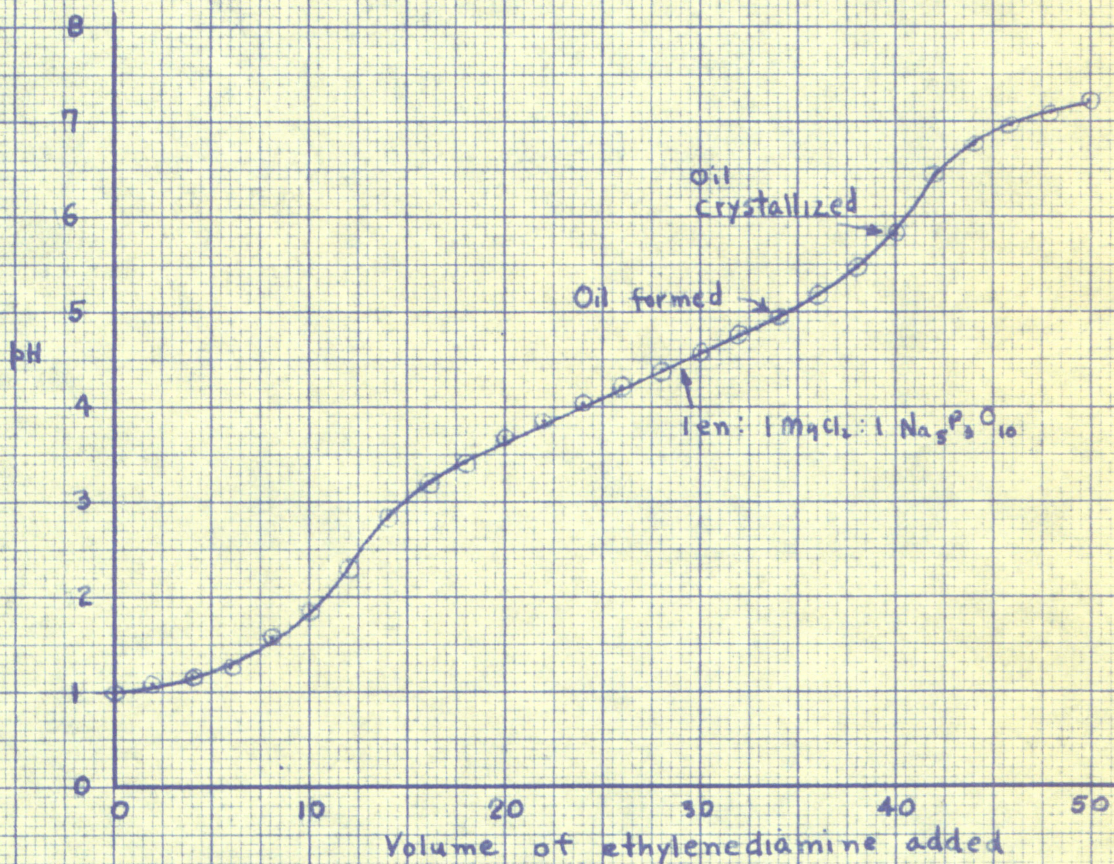
0.196 grams would have resulted. Only 0.148 grams was recovered.

Exploratory Reactions

Sodium Triphosphate: A solution which contained 7.14 grams $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ in 50 ml. of water was treated with enough 1:1 hydrochloric acid to lower the pH to 1.00. Magnesium chloride solution was added until the molar ratio of sodium triphosphate to magnesium chloride was 1:1. The pH was slowly raised by adding ethylenediamine (Figure 13). At pH 5 an oil separated, which crystallized at pH 5.8. The product consisted of prisms. The reaction was stopped at pH 7 since the acid regions seem to give the most clearly defined reactions, and are therefore more interesting from the analytical viewpoint. The product was filtered, washed with two 25 ml. portions of alcohol, followed by a like treatment with ether, and air-dried. Plate V-C is the

FIGURE 13

Variation in pH as 0.52 M en is added to a solution which contains 7.14 gm. of $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$, 18 ml. of 0.83 M MgCl_2 , and enough 6 M HCl to lower the pH to 1.00. The initial molar ratio of $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}:\text{MgCl}_2$ is 1:1.



X-ray pattern of the precipitate. Analysis of the preparation disclosed no nitrogen , 4.57 per cent magnesium, 9.5 per cent sodium* and 16.62 per cent phosphorus. The foregoing percentages correspond to gram-atoms of 0.188 magnesium, 0.413 sodium, and 0.537 phosphorus, or ratios of 1Mg:2.2Na:2.8P. The results of the analysis indicate that the product is probably a mixture.

Sodium Trimetaphosphate: Dilute hydrochloric acid (1:1) was added to a solution of 4.6 grams of $\text{Na}_3\text{P}_3\text{O}_4$ in 50 ml. of water until the pH was lowered to 1.00. After adding 18 ml. of 0.83 M magnesium chloride, the molar ratio of $\text{MgCl}_2:\text{Na}_3\text{P}_3\text{O}_9$ was 1:1. When small amounts of 0.52 M ethylenediamine were added, no precipitation occurred below pH 7.

Sodium Tetrametaphosphate: Fifteen millimoles of $\text{Na}_4\text{P}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$ (7.2 grams) were dissolved in 50 ml. of water and enough 1:1 hydrochloric acid added to lower the pH to 0.9. Fifteen millimoles of magnesium chloride were added (18 ml. of 0.83 M MgCl_2), and then the pH was raised by adding 0.52 M ethylenediamine: Precipitation (prisms) started at pH 1.1, after which the pH rose abruptly to

* This value was obtained by Beckman Flamephotometer at Proctor and Gamble by courtesy of Dr. O.T. Quimby.

above 7. The product was filtered, washed with two 25 ml. portions of alcohol then with ether, and air-dried. The preparation (plate V-D) was found to contain 6.04 per cent nitrogen, no magnesium, and 27.07 per cent phosphorus. Those percentages correspond to gram-atoms of 0.432 nitrogen and 0.875 phosphorus; a ratio of 1.00 nitrogen: 2.03 phosphorus. The foregoing results suggest a compound $\text{Me}_2^{\text{I}}(\text{enH}_2)(\text{P}_4\text{O}_{12}) \cdot x\text{H}_2\text{O}$ (Me = cation). One possibility is $\text{Na}_2(\text{enH}_2)(\text{P}_4\text{O}_{12}) \cdot 2\text{H}_2\text{O}$ which would contain 27.10 per cent phosphorus and 6.09 per cent nitrogen. The product loses no weight at 105°C. Dehydrations of condensed phosphates by heat above this temperature are of doubtful value because of the danger of hydrolysis of the phosphate by the water of hydration.

CHAPTER VII

ZINC ETHYLENEDIAMMONIUM PHOSPHATES

The reactions discussed in this section were carried out at 30-35°C, i.e. prevailing room temperatures plus the heating effect from the magnetic stirrer. After filtering all the products were washed with two 25 ml. portions of alcohol followed by a like treatment with ether, and then air-dried.

Orthophosphate Studies

The ions may be combined directly by adding a solution of zinc sulfate to ethylenediammonium phosphate. Figure 14 shows the accompanying pH changes when such a reaction is carried out. If this figure is compared with the one showing the corresponding magnesium reaction (Figure 1, p. 39), a much greater fall in pH is observed in the zinc reaction (see below). This is the first clue indicating that hydrogen-ions are liberated during this reaction. Precipitation begins with the first addition of zinc sulfate. Under the microscope, the crystals are very small tablets (X450); they are relatively dense and set-

FIGURE 14

Variation of pH as a 0.83 M ZnSO_4 solution is added to 50 ml. of 0.29 M $\text{enH}_2(\text{HPO}_4)$ solution.

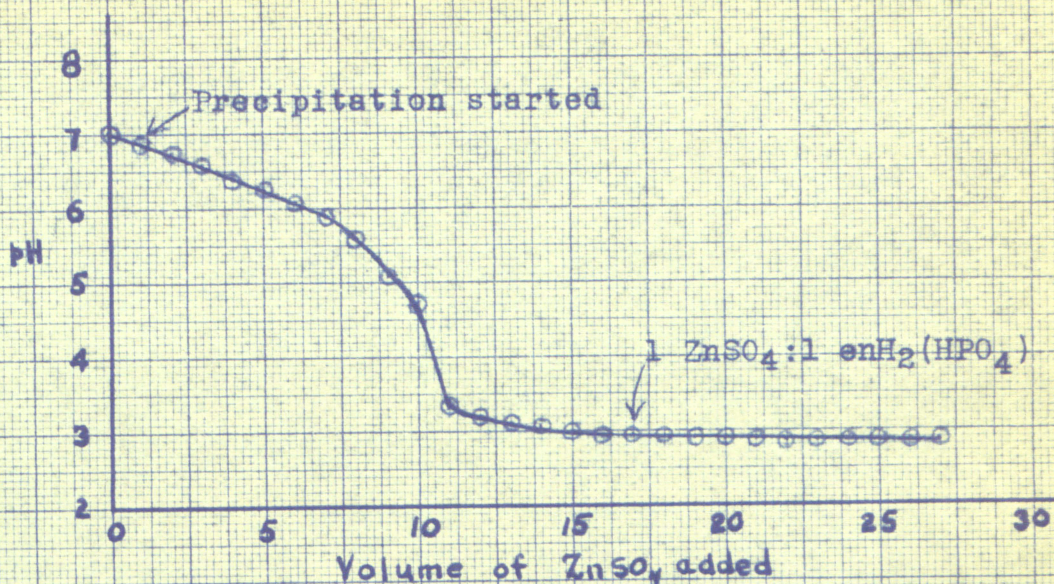
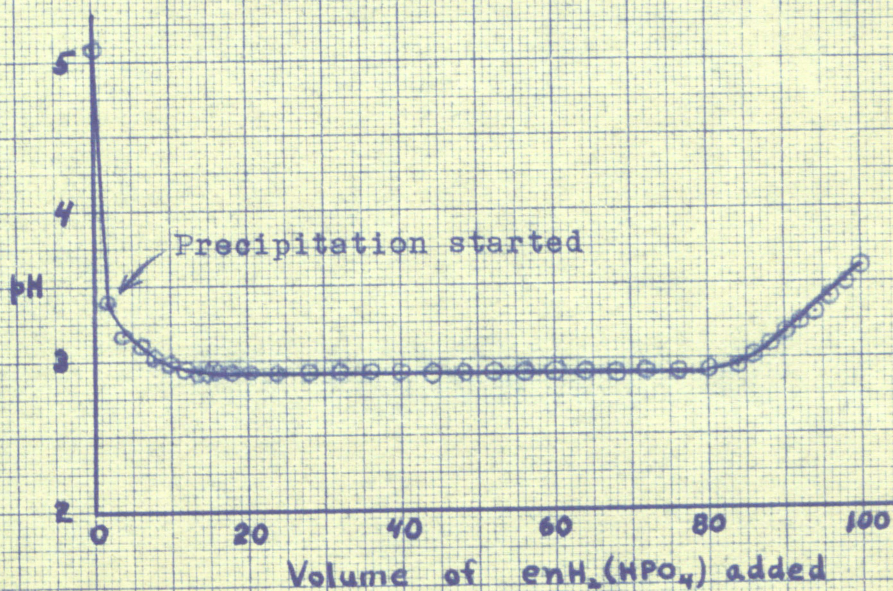


FIGURE 15

Variation of pH as a 0.29 M $\text{enH}_2(\text{HPO}_4)$ solution is added to 20 ml. of 0.83 M ZnSO_4 solution.



tle rapidly. Plate VI-A is the X-ray pattern of the product.

The analytical findings are as follows:

Constituent	PerCent Found	Gram-Atoms	Atomic Ratio	Calculated Per Cent for $\text{Zn}_2\text{enH}_2(\text{PO}_4)_2$
Zn	34.26	0.525	1.01	34.18
N	7.38	0.527	1.02	7.31
P	16.06	0.519	1.00	16.15

The product loses no weight at 160°C . The equivalent weight of phosphorus, determined by an acidimetric titration, is 15.5, thus confirming the tertiary orthophosphate structure. The identity of the preparation is thereby established as $\text{Zn}_2\text{enH}_2(\text{PO}_4)_2$. The ionic equation of its formation may be written:

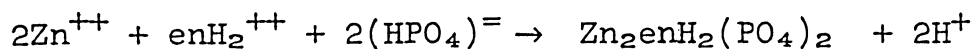
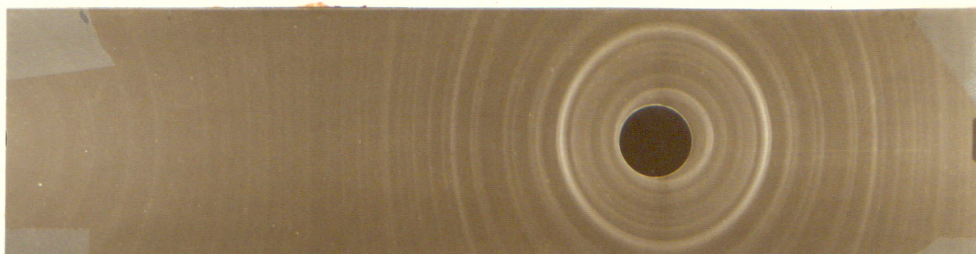


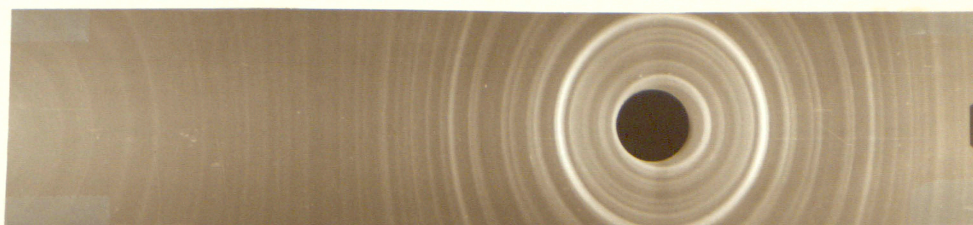
Figure 16 is the conductance curve of this reaction. A possible explanation for the straight line is that the high ionic mobility of the hydrogen ion released during the precipitation of $\text{Zn}_2\text{enH}_2(\text{PO}_4)_2$ causes an increase in conductance which is equal to that due to the simple addition of zinc sulfate after the precipitation stops.

Figure 15 follows the changes in pH when the zinc sulfate and ethylenediammonium orthophosphate are brought together in the reverse order, i.e. adding the $\text{enH}_2(\text{HPO}_4)$

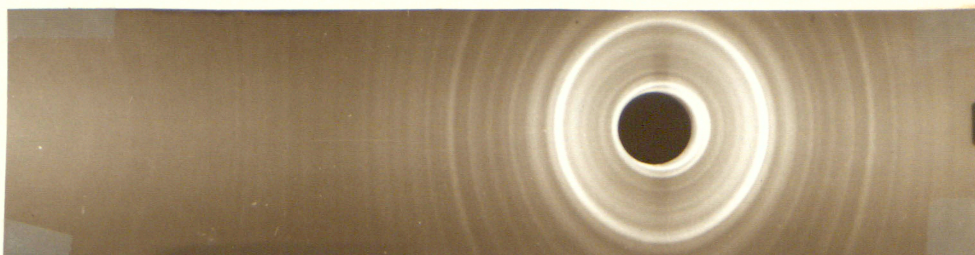
PLATE VI



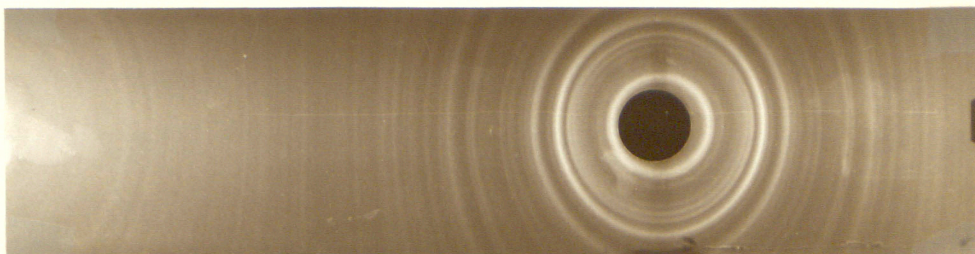
A



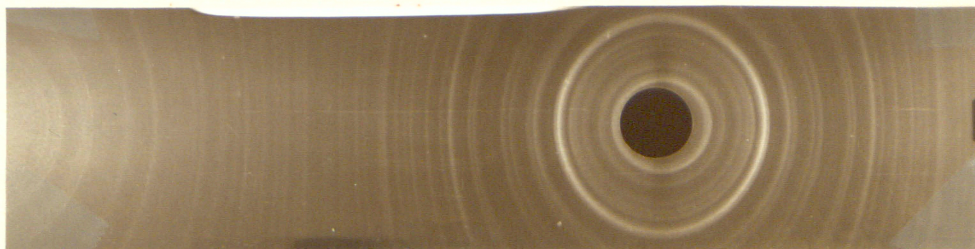
B



C



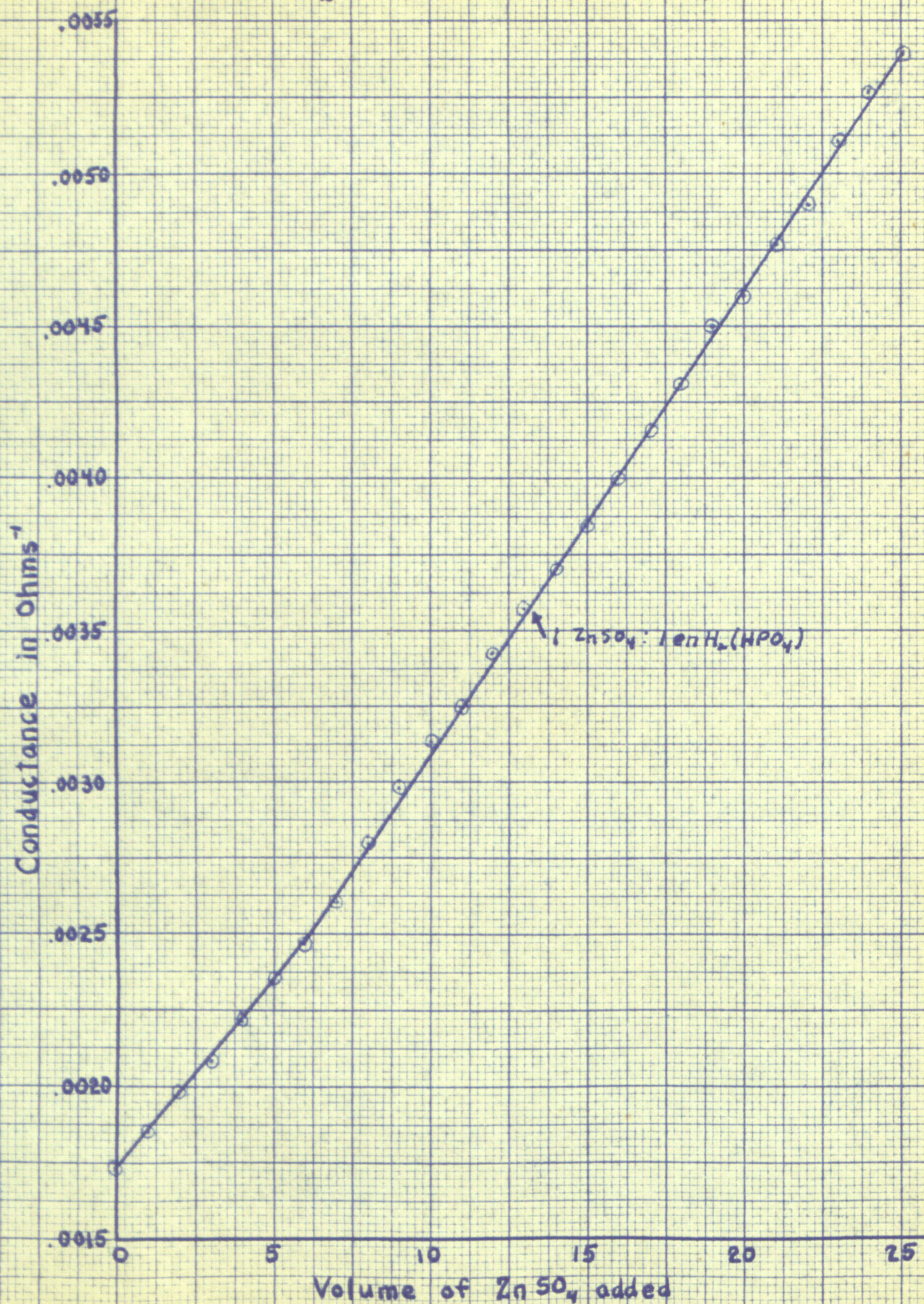
D



E

FIGURE 16

Variation in conductance as 0.78 M ZnSO_4 solution is added to a solution which contains 35 ml. of 0.29 M $\text{enH}_2(\text{HPO}_4)$ and 600 ml. of H_2O .



to the ZnSO_4 . Plate VI-B is the X-ray pattern of the product, and a comparison with the pattern of the previous preparation shows that they are identical, i.e. they both refer to $\text{Zn}_2\text{enH}_2(\text{PO}_4)_2$.

In the first of the more comprehensive reactions, ethylenediamine was added to a solution containing orthophosphoric acid and zinc sulfate in an initial 1:1 molar ratio (Figure 17). Precipitation starts at pH 2.7, and the section of the curve which follows indicates that hydrogen ions are released. Microscopic examination showed that the product was in the form of needles, occurring singly, in clusters, and in spherulites. This first product proved to be quite complex and will be discussed in detail later (p. 79). Plate VI-C is its X-ray pattern. When pH 4.3 is reached, the precipitate changes to $\text{Zn}_2\text{enH}_2(\text{PO}_4)_2$, and more hydrogen ions are liberated. From 30 to 45 minutes is required for the complete transformation. No further changes in the precipitate occurred. The final product was identified by its X-ray pattern (Plate VI-D and by its characteristic appearance under the microscope.

When the initial molar ratios of zinc and orthophosphoric acid are altered, a considerable change in the course of the reaction results. Figure 18 shows the variation in pH as ethylenediamine is added to a solution which contains zinc sulfate and orthophosphoric acid in a

FIGURE 17

Change in pH as 0.52 M en is added to a solution prepared from 18 ml. of 0.83 M ZnSO_4 and 29.5 ml. of 0.51 M H_3PO_4 . The initial molar ratio of $\text{ZnSO}_4:\text{H}_3\text{PO}_4$ is 1:1.

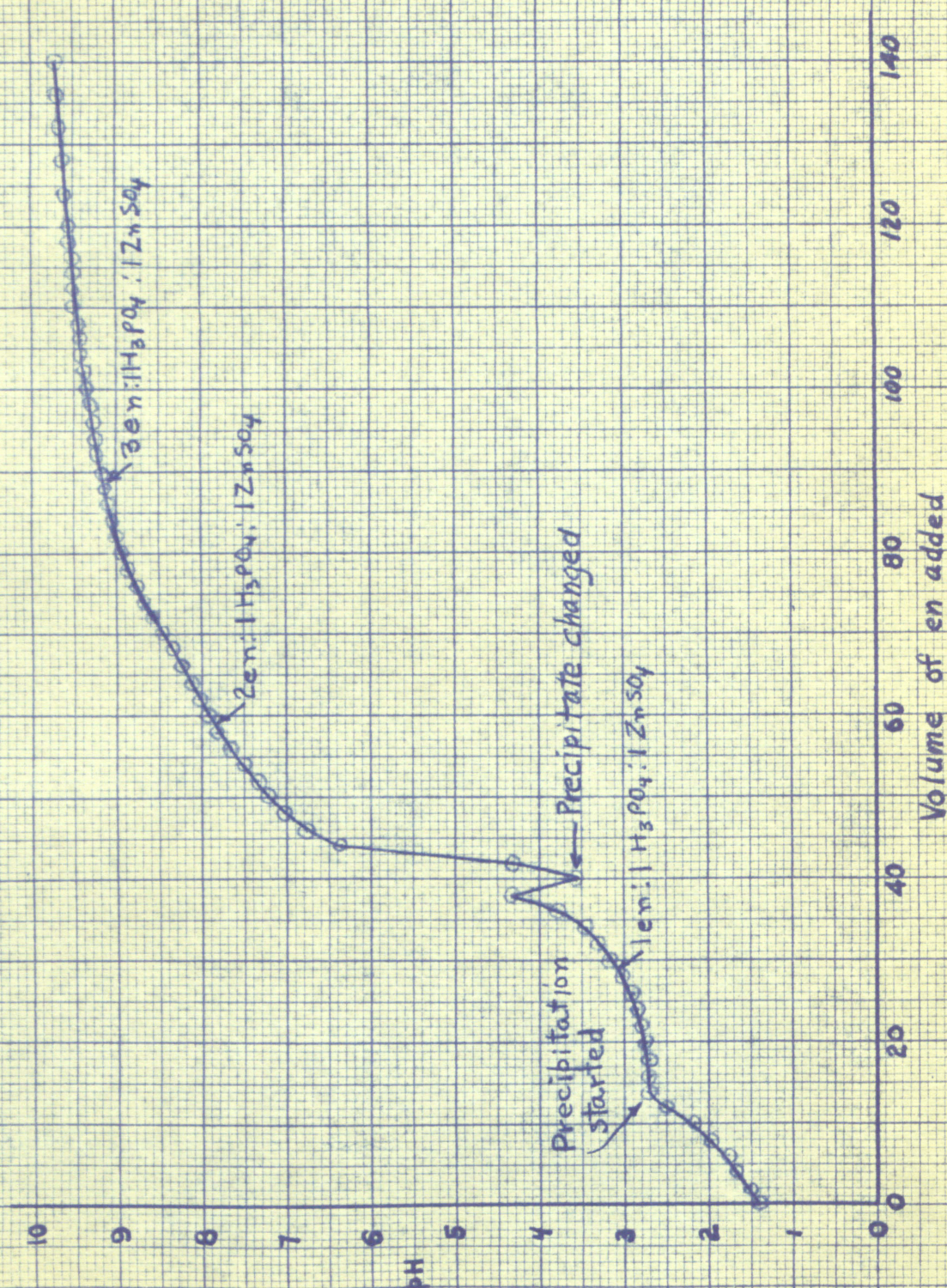
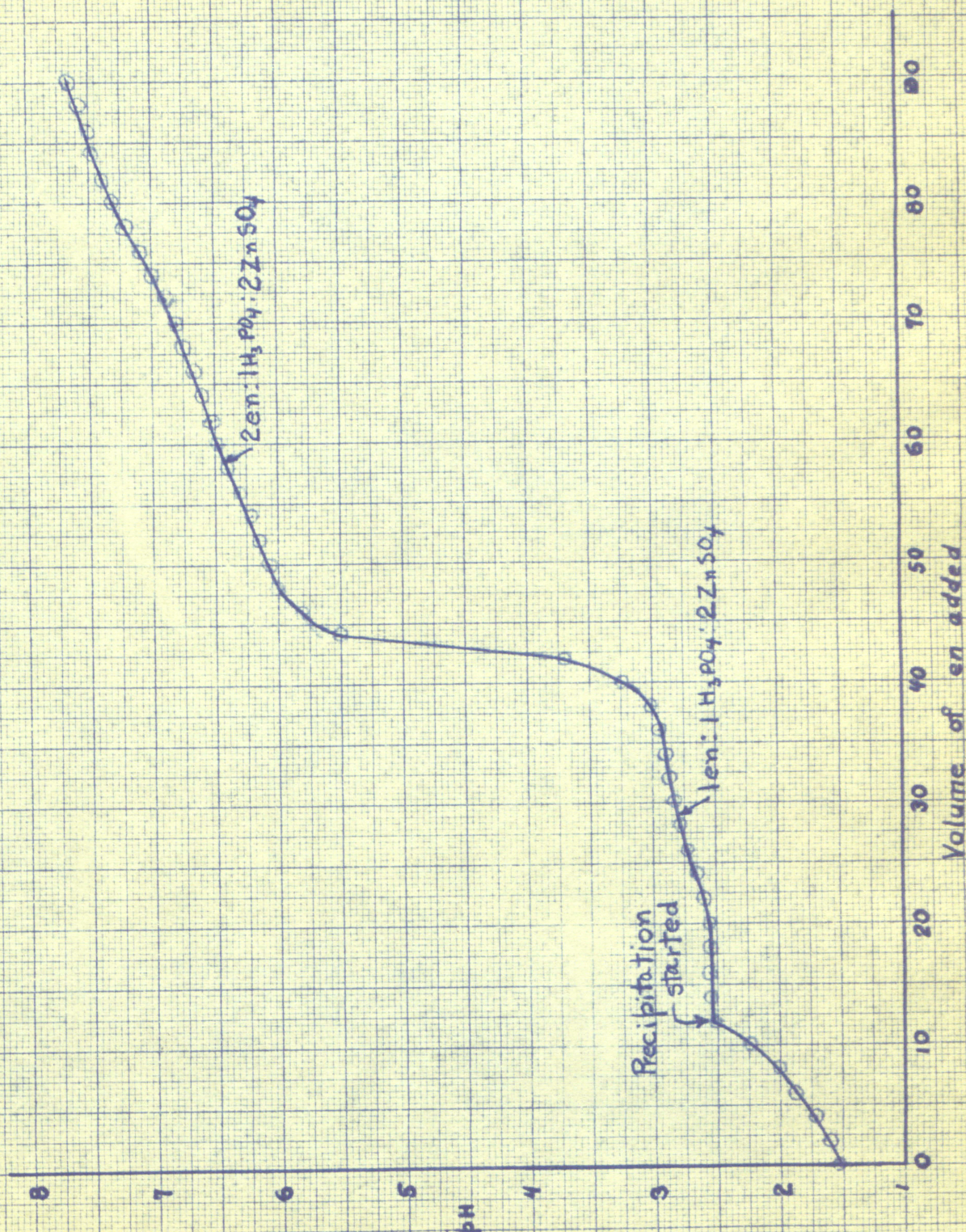


FIGURE 18

Change in pH as 0.51 M en is added to a solution prepared from 36 ml. of 0.83 M ZnSO_4 and 29.5 ml. of 0.51 M H_3PO_4 . The initial molar ratio of $\text{ZnSO}_4:\text{H}_3\text{PO}_4$ is 2:1.



2:1 initial molar ratio. The material which precipitates at pH is the third different product to appear in this system. When the pH reaches 7.5, the new phase begins slowly to change to $\text{Zn}_2\text{enH}_2(\text{PO}_4)_2$. The pH of the solution remains constant while the transformation occurs. After three days, the precipitate is homogeneous; it is $\text{Zn}_2\text{enH}_2(\text{PO}_4)_2$ as proved by its X-ray pattern (Plate VI-E) and microscopic observation.

The preceding reaction was repeated and the first phase which precipitates was isolated. The following table summarizes the chemical analysis of the material:

Constituent	PerCent Found	Gram-Atoms	Atomic Ratio	Calculated Per Cent for $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$
Zn	42.69	0.654	1.50	42.80
N	0	-----	-----	-----
P	13.48	0.435	1.00	13.55

Plate VII-A is the X-ray pattern of the product. Plate VII-B is the X-ray pattern given by a sample of pure $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ *. The identity of the material as $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ is established by either the fact that these two patterns are identical or the analytical data.

When ethylenediamine is added to a solution containing zinc sulfate and an excess of orthophosphoric acid (Figure 19), precipitation begins at pH 2.3. Micro-

* Furnished by the Proctor and Gamble Company.

FIGURE 19

Change in pH as 0.54 M en is added to a solution prepared from 50 ml. of 0.51 M H_3PO_4 and 15.5 ml. of 0.83 M ZnSO_4 . The initial molar ratio of H_3PO_4 : ZnSO_4 is 2:1.

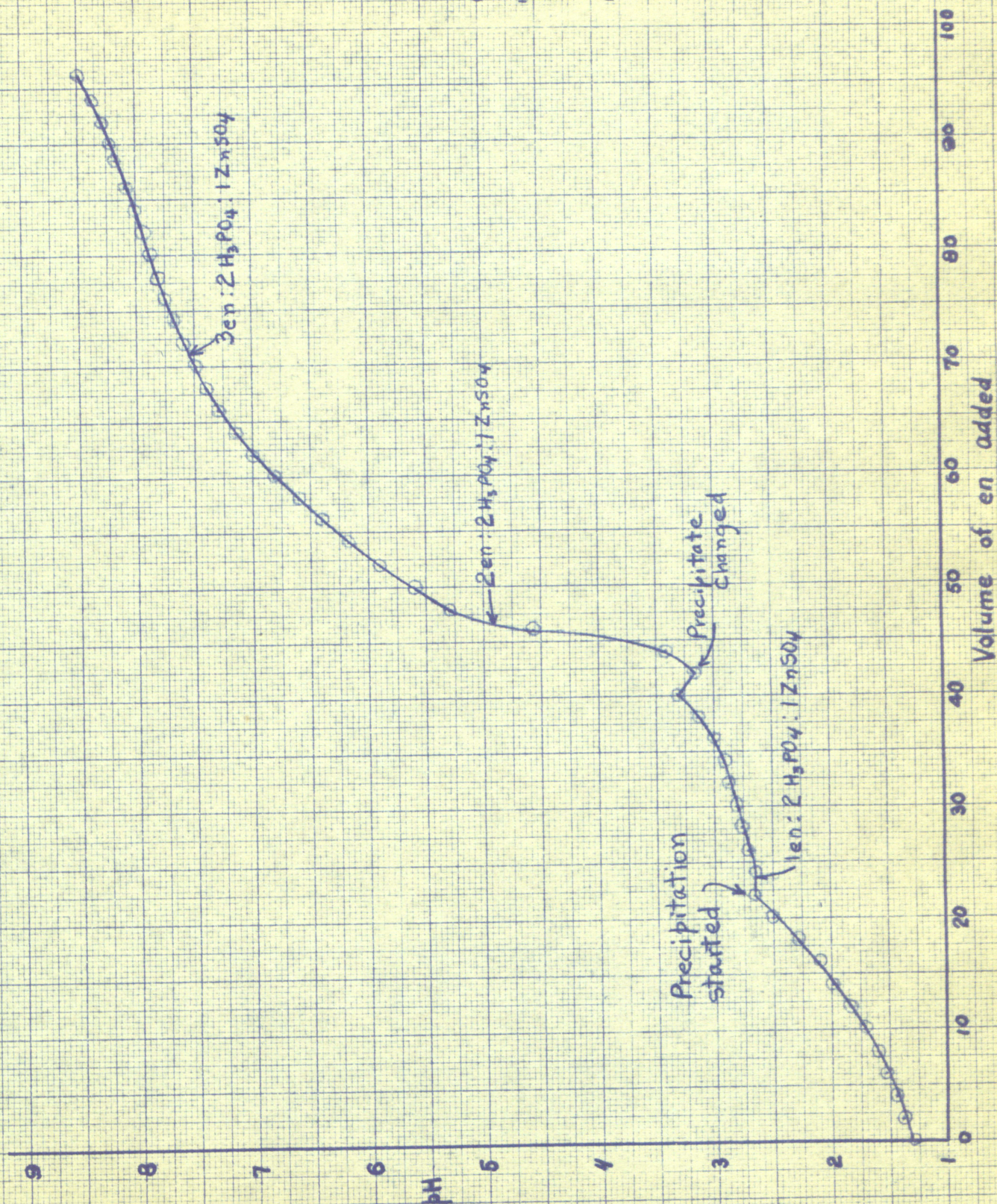
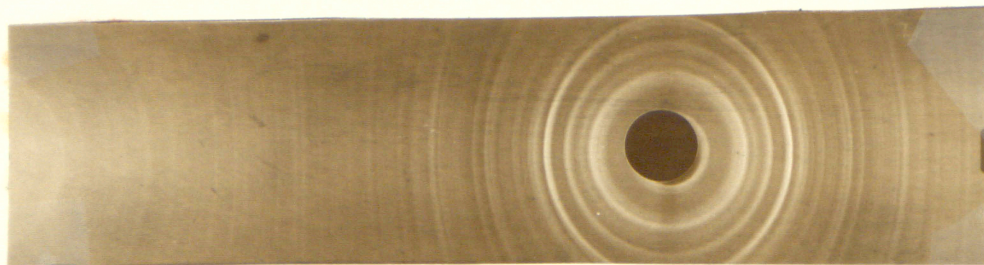
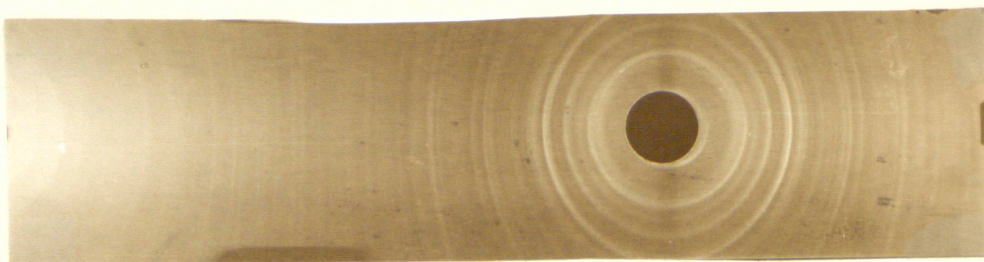


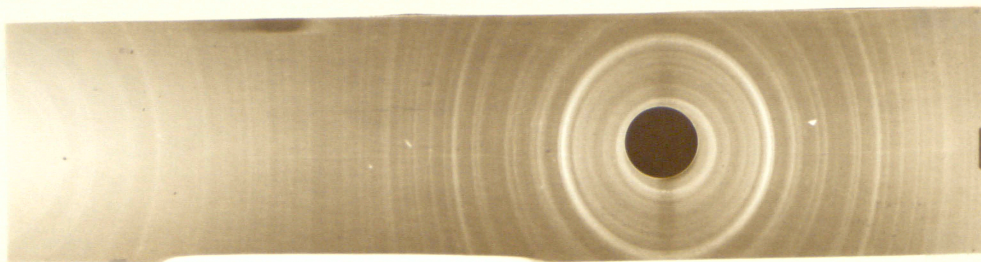
PLATE VII



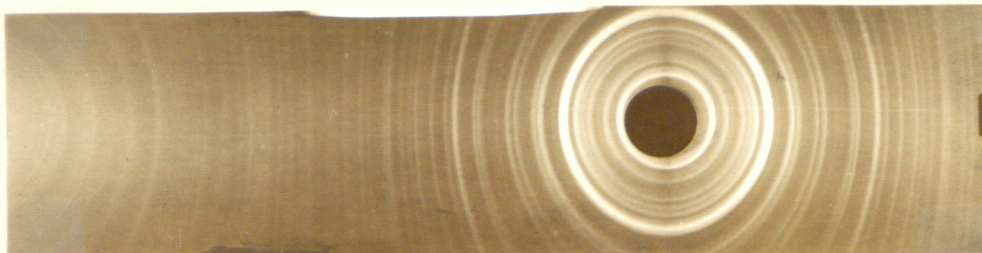
A



B



C



D



E

scopic examination disclosed that this material is a mixture in which $\text{Zn}_2\text{enH}_2(\text{PO}_4)_2$ predominates. When pH 3.6 is reached, the product becomes homogeneous $\text{Zn}_2\text{enH}_2(\text{PO}_4)_2$ and undergoes no further changes during the course of the reaction. Plate VII-C is the X-ray pattern given by the final product.

The most straightforward reaction in this series occurs when ethylenediamine is added to a phosphoric acid solution which also contains zinc sulfate and excess ethylenediammonium ions (Figure 20). $\text{Zn}_2\text{enH}_2(\text{PO}_4)_2$ begins to precipitate at pH 2.4, and it undergoes no further change as the reaction progresses. The identity of the product was established by the X-ray powder pattern (Plate VII-D).

A rather complex material forms under certain conditions in the acid pH region. Three preparations of this product were obtained as follows:

A. It is the initial precipitate when ethylenediamine is added to a solution containing zinc sulfate and phosphoric acid in a 1:1 molar ratio (Figure 17, Plates VI-C and VIII-A). The crystals are needle-shaped and also form cactus-like spherulites. This product was obtained from the reaction mixture at pH 2.8.

B. When $\text{Zn}_2(\text{enH}_2)(\text{PO}_4)_2$ is dissolved in dilute hydrochloric acid(1:20) and the solution made basic by dropwise addition of ethylenediamine (2:3), crystals of this material

FIGURE 20

Change in pH as 0.54 M en is added to a solution which contains 19 ml. of 0.78 M ZnSO_4 , 29.5 ml. of 0.51 M H_3PO_4 , and 4 gm. of $(\text{enH}_2)\text{Cl}_2$. The initial molar ratios of $\text{ZnSO}_4:\text{H}_3\text{PO}_4:(\text{enH}_2)\text{Cl}_2$ are 1:1:2.

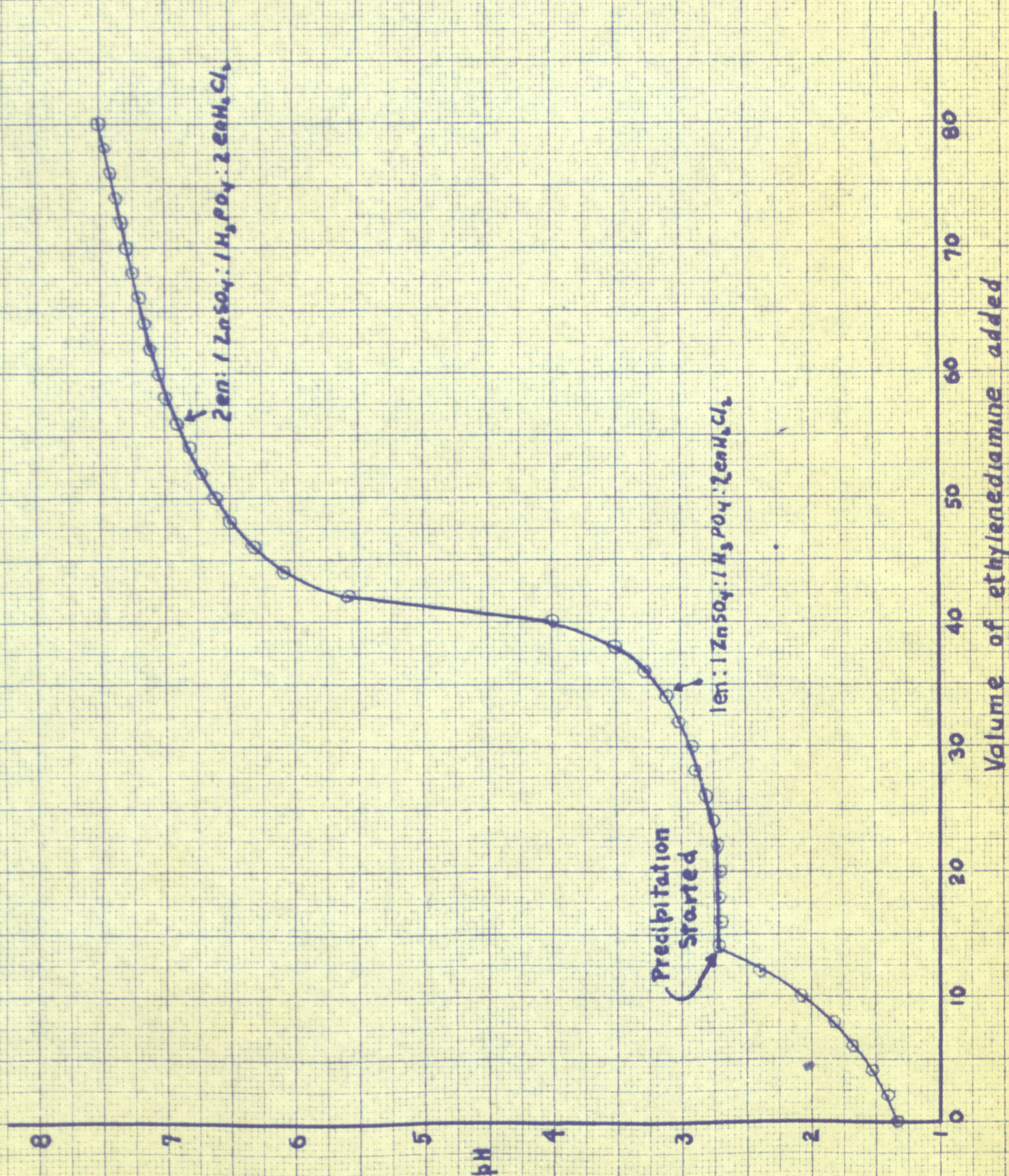
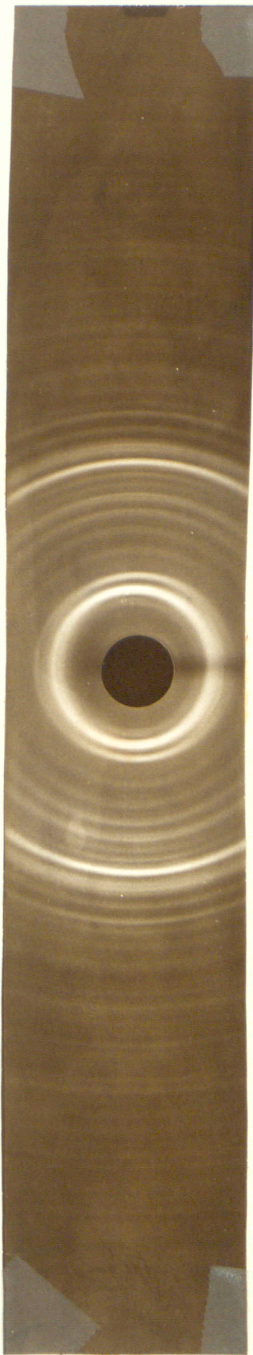
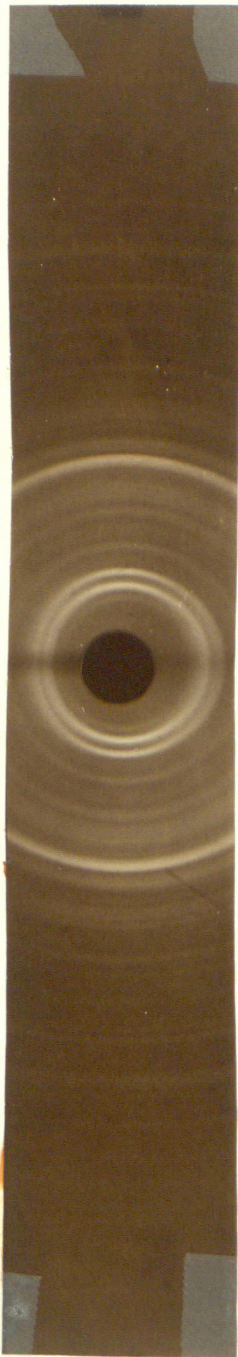


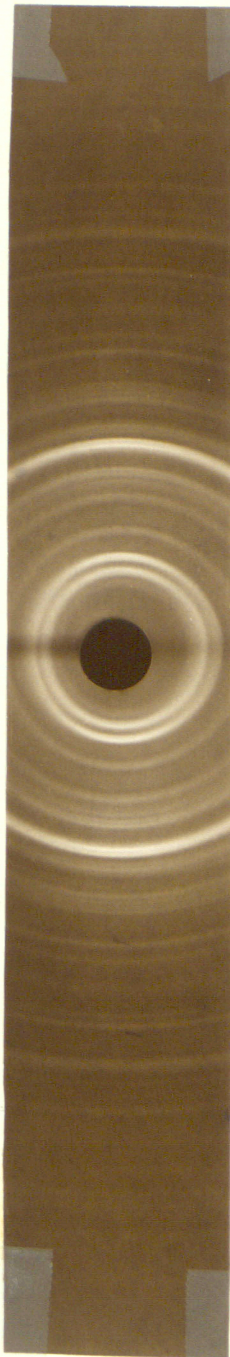
PLATE VIII



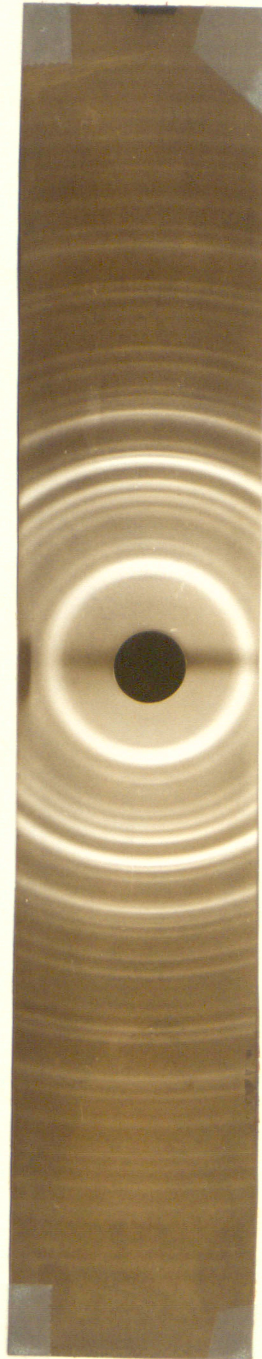
A



B



C



D

are the first solid to separate (Plate VIII-B). This product (at pH 3.1) was again in the form of needles and spherulites.

C. It is the first precipitate to appear when ethylenediamine is added to a solution which contains zinc sulfate, orthophosphoric acid, and ethylenediammonium hydrochloride in an 2:1:2 molar ratio. These crystals (at pH 2.7) were uniformly acicular, no spherulites were present (Plate VIII-C).

These products were found to have the following compositions:

	A		B		C	
	PerCent	Gram Atom	PerCent	Gram Atom	PerCent	Gram Atom
P	15.31	0.494	16.37	0.528	15.66	0.505
Zn	31.84	0.487	32.24	0.523	33.20	0.508
N	5.54	0.395	5.66	0.404	5.60	0.401

The corresponding atom ratios are:

- A. 1.23 zinc : 1.00 nitrogen : 1.25 phosphorus
- B. 1.30 zinc : 1.00 nitrogen : 1.31 phosphorus
- C. 1.26 zinc : 1.00 nitrogen : 1.26 phosphorus

Preparations A and C are easily resolved into whole number ratios namely 5 zinc : 4 nitrogen : 5 phosphorus.

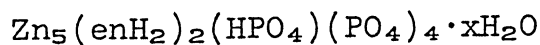
In overall appearance, the X-ray patterns given by these three preparations are quite similar. All are shown on Plate VIII; Plate VIII-D is $\text{Zn}_2\text{enH}_2(\text{PO}_4)_2$ included here for purposes of comparison. However, closer examination

discloses minute differences in the patterns, the one for preparation B differing the most.

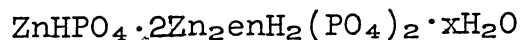
An acidimetric titration on three preparations gave the following equivalent weight for phosphorus: A - 18.8; B - 18.2; and C - 18.7. These figures indicate that the preparation is a mixture of secondary and tertiary orthophosphates. If it is assumed that those two species of orthophosphate are the only phosphate ions in the preparation, and the standard analytical mixture treatment is applied, the calculations yield:

	<u>PerCent Tertiary Orthophosphate</u>	<u>PerCent Secondary Orthophosphate</u>
A	78.8	21.2
B	82.7	17.3
C	79.5	20.5

The figures for preparations A and C are very near a 4:1 ratio of PO_4^{-3} to HPO_4^{-2} . Furthermore, a ratio of 4PO_4^{-3} and 1HPO_4^{-2} balance the cations which would be required by the preceding atomic ratios. In other words, the following formula fits the findings:



or



Some calculated percentages for pertinent hydrates of such a double salt are:

Constituent	Pentahydrate	Tetrahydrate	Found	
			Prep.A	Prep.C
Zn	32.15	32.80	31.84	33.20
N	5.51	5.61	5.54	5.60
P	15.30	15.56	15.31	15.66

The percentages of constituents found for Preparation A fit the data for the pentahydrate; while those for Preparation C agree with the tetrahydrate.

A close comparison of the X-ray patterns of the foregoing preparations and $\text{Zn}_2\text{enH}_2(\text{PO}_4)_2$ (Plate VIII-D) shows that the possibilities of a mechanical mixture of the two salts is slight. One very prominent line on the pattern for $\text{Zn}_2\text{enH}_2(\text{PO}_4)_2$ (marked by arrow) does not appear on any of the other patterns.

If preparation A and C are a compound having the formula $\text{ZnHPO}_4 \cdot 2\text{Zn}_2\text{enH}_2(\text{PO}_4)_2 \cdot 4.5\text{H}_2\text{O}$, there are analogies for such double phosphates in the literature. Berg and Bokil (33) reported the following: $5\text{K}_2\text{HPO}_4 \cdot \text{KH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, $3\text{K}_2\text{HPO}_4 \cdot \text{KH}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$, $2\text{K}_2\text{HPO}_4 \cdot \text{KH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, and $\text{K}_2\text{HPO}_4 \cdot \text{KH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$. In the sodium system, $\text{Na}_2\text{HPO}_4 \cdot \text{NaH}_2\text{PO}_4$ and $\text{Na}_2\text{HPO}_4 \cdot 2\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ have been described recently (34).

An unexpected transformation occurs when 2.9 grams of $\text{Zn}_2\text{enH}_2(\text{PO}_4)_2$ is mixed with 50 ml. of 2:3 ethylenediamine. The starting material does not dissolve as might be predicted. Instead, the original tablets are $\text{Zn}_2\text{enH}_2(\text{PO}_4)_2$; they change to rather short prisms (X450)

after the mixture is stirred for 15 minutes. The product gives an X-ray pattern which differs from that of the $\text{Zn}_2\text{enH}_2\text{PO}_4)_2$ (Plate VII-E). The analytical results are:

Constituent	PerCent Found	Gram-Atoms	Atomic Ratio	Calculated Per Cent For $\text{Zn}(\text{enH}_2)_2(\text{PO}_4)_2$
Zn	17.22	0.263	1.00	17.22
N	14.59	1.04	3.97	14.75
P	16.17	0.523	1.99	16.32

The equivalent weight of phosphorus is 15.2, indicating tertiary orthophosphate. The preparation loses no weight at 160°C . The foregoing evidence indicates that $\text{Zn}(\text{enH}_2)_2(\text{PO}_4)_2$ is formed in this reaction.

An exploratory experiment was carried out to learn if the formation of $\text{Zn}_2(\text{enH}_2)(\text{PO}_4)_2$ as an analytical precipitate for phosphorus merits further investigation. "Reagent grade" disodium orthophosphate which had been dehydrated at 105°C was the reference material. A sample weighing 124 mg. was dissolved in 100 ml. of water. Four grams of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 5 ml. of 1:1 hydrochloric acid, and 6 grams of ethylenediammonium hydrochloride were added. When all the solids were completely dissolved, the pH was raised to 6.5 by dropwise addition of 2:3 ethylenediamine. A flocculent precipitate formed; its appearance was unchanged by digestion at 70°C for 30 minutes. The product was filtered, washed with water, and dried to constant weight.

at 105°C. If $\text{Zn}_2(\text{enH}_2)(\text{PO}_4)_2$ had been formed, the precipitate would have weighed 100 mg. If $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ had been the product, 184 mg. would have been formed. The product actually weighed 180 mg. Therefore it appears likely that the product was a mixture of zinc phosphate and a little of the desired $\text{Zn}_2\text{enH}_2(\text{PO}_4)_2$.

Pyrophosphate Studies

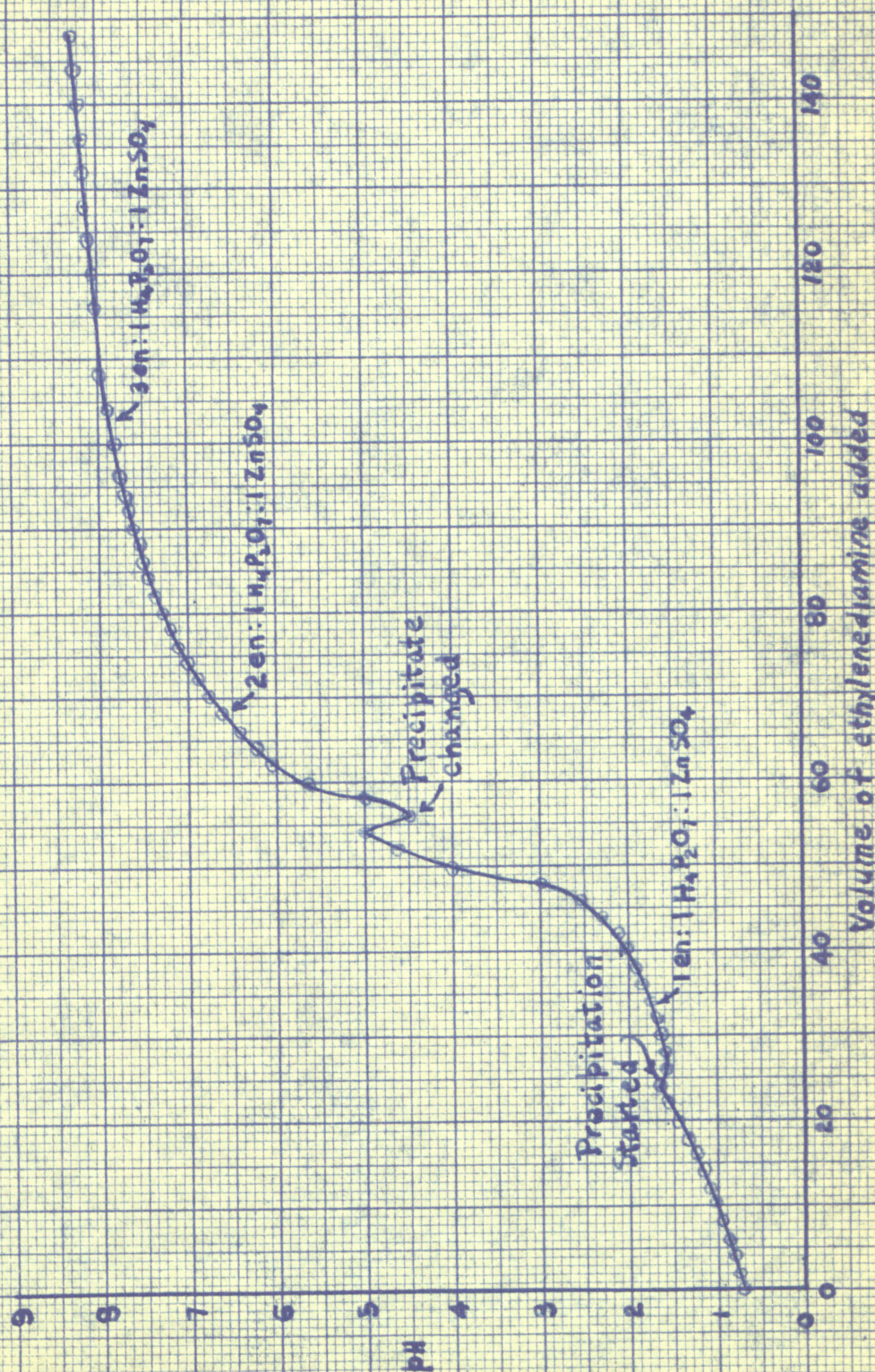
No pure zinc ethylenediammonium pyrophosphate was isolated. The following reactions were carried out and the products analyzed.

A. A solution of zinc sulfate was added to a solution of ethylenediammonium pyrophosphate; a sticky gum separated which adhered tenaciously to glass. This characteristic makes it impossible to read pH or conductance values in solution. If the reaction mixture is stirred for about one hour, most of the gum crystallizes but remains at its original site of precipitation. It gives the X-ray pattern on Plate IX-C.

B,C,D. The addition of ethylenediamine to a solution containing zinc sulfate and pyrophosphoric acid in an initial 1:1 molar ratio was the first lengthy reaction carried out over an extended pH range. Figure 21 shows the changes in pH as the ethylenediamine is added. Precipitation begins at pH 1.7. Under the microscope the

FIGURE 21

Change in pH as 0.54 M en is added to a solution prepared from 35.5 ml. of 0.82 M $H_4P_2O_7$ and 22 ml. of 0.82 M $ZnSO_4$. The initial molar ratio of $ZnSO_4:H_4P_2O_7$ is 1:1.



solid product is a nondescript crystalline material. Preparation B was filtered from this reaction at pH 2.1 (Plate IX-D). When the operation is carried out above this pH, the precipitate changes at pH 5. The solid is now in the form of spherulites. Preparation C is the product isolated at pH 5.8 (Plate X-A). Preparation D is the material which was obtained from an identical reaction at pH 6.4 (Plate X-B). When the reaction is not interrupted, the solid begins to dissolve about pH 7, and solution is complete about pH 8.2.

E,F. When the initial molar ratio of zinc sulfate to pyrophosphoric acid is changed to 2:1 and ethylenediamine added to this solution, solid first appears at pH 1.6 (Figure 22). A break in the pH curve indicates a change in the precipitate at pH 4.0. At pH 7, the solid becomes increasingly amorphous in appearance. Preparation E (Plate X-C) is the product isolated from the early part of this reaction, at pH 3.2, and preparation F (Plate X-D) is the solid which was obtained at the completion of the operation.

G,H. If the starting molar ratio of zinc sulfate to pyrophosphoric acid is 1:2 and ethylenediamine is added, the pH changes as recorded in Figure 23. Again nondescript crystalline fragments form in the acidic pH regions (Preparation G, Plate XI-A). This solid changes to spherulites at pH 6.3. The product obtained at the end of the

FIGURE 22

Change in pH as 0.54 M en is added to a solution prepared from 19.5 ml. of 0.77 M $H_4P_2O_7$ and 38 ml. of 0.78 M $ZnSO_4$. The initial molar ratio of $ZnSO_4:H_4P_2O_7$ is 2:1.

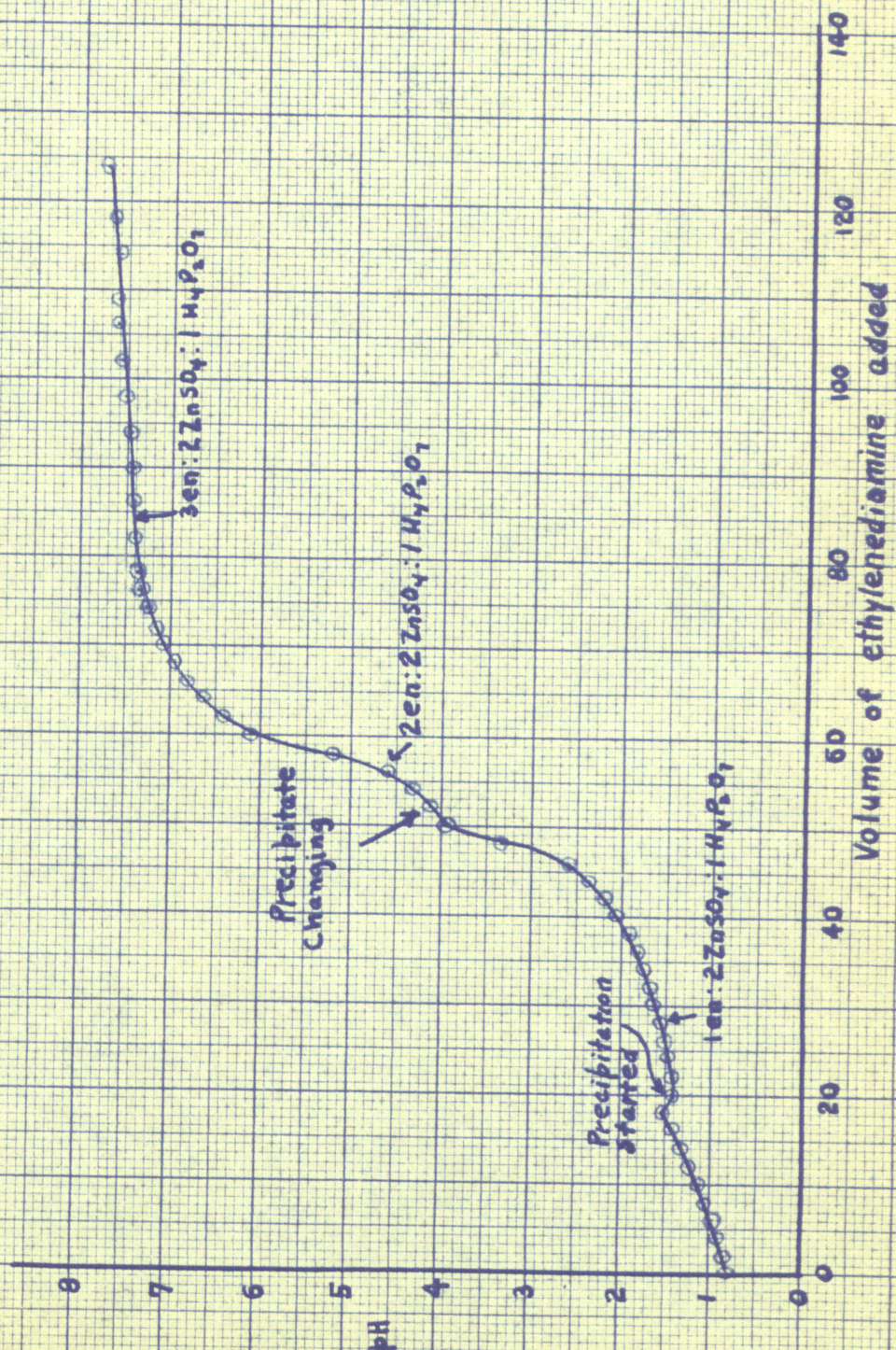
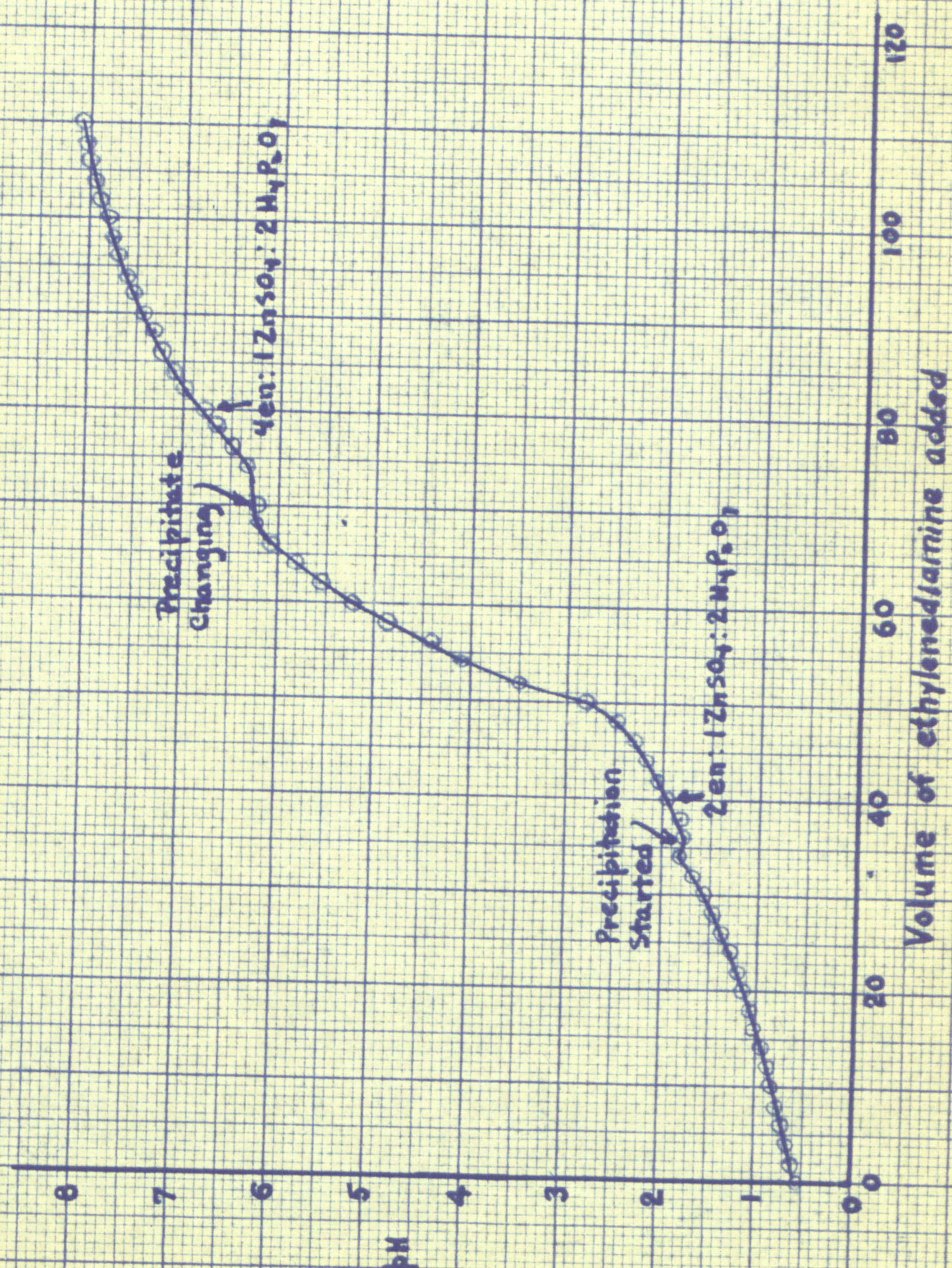


FIGURE 23

Variation in pH as 0.54 M en is added to a solution which contains 43 ml. of 0.50 M $\text{H}_4\text{P}_2\text{O}_7$ and 13.9 ml. of 0.78 M ZnSO_4 . The initial molar ratio of $\text{ZnSO}_4:\text{H}_4\text{P}_2\text{O}_7$ is 1:2.



reaction (pH 8) is preparation H; it gives the X-ray pattern shown in Plate XI-B.

I. A similar reaction occurs if ethylenediamine is added to a solution of ethylenediammonium hydrochloride, pyrophosphoric acid, and zinc sulfate in an initial 2:1:1 molar ratio. Figure 24 shows the changes in pH which occur as the reaction proceeds. Preparation I (Plate XI-C) is the solid isolated at the conclusion of the operation (pH 7.8).

J. It is sometimes possible to obtain a pure component from a system which produces mixtures such as are encountered here by carrying out the reaction in more dilute solutions. Accordingly, ethylenediamine was added to a solution containing 15 millimoles each of zinc sulfate and pyrophosphoric acid in about 550 ml. of solution. Figure 25 records the variation in pH which accompanied this reaction. The solid product (Preparation J) was isolated at pH 6.6; its X-ray pattern is shown in Plate XI-D. The mixture is again obtained.

K. Impurities in the pyrophosphoric acid also had to be considered as responsible for the production of mixtures. Therefore pure pyrophosphoric acid was prepared by ion-exchange. Eight grams of "reagent grade" tetrasodium pyrophosphate, which had been recrystallized twice and dehydrated at 105°C, were equilibrated (to constant pH)

FIGURE 24

Change in pH as 0.56 M en is added to a solution which contains 23.5 ml. of 0.64 M $H_4P_2O_7$, 19 ml. of 0.78 M $ZnSO_4$, and 4 gm. of $(enH_2)Cl_2$. The initial molar ratios of $ZnSO_4:H_4P_2O_7:(enH_2)Cl_2$ are 1:1:2.

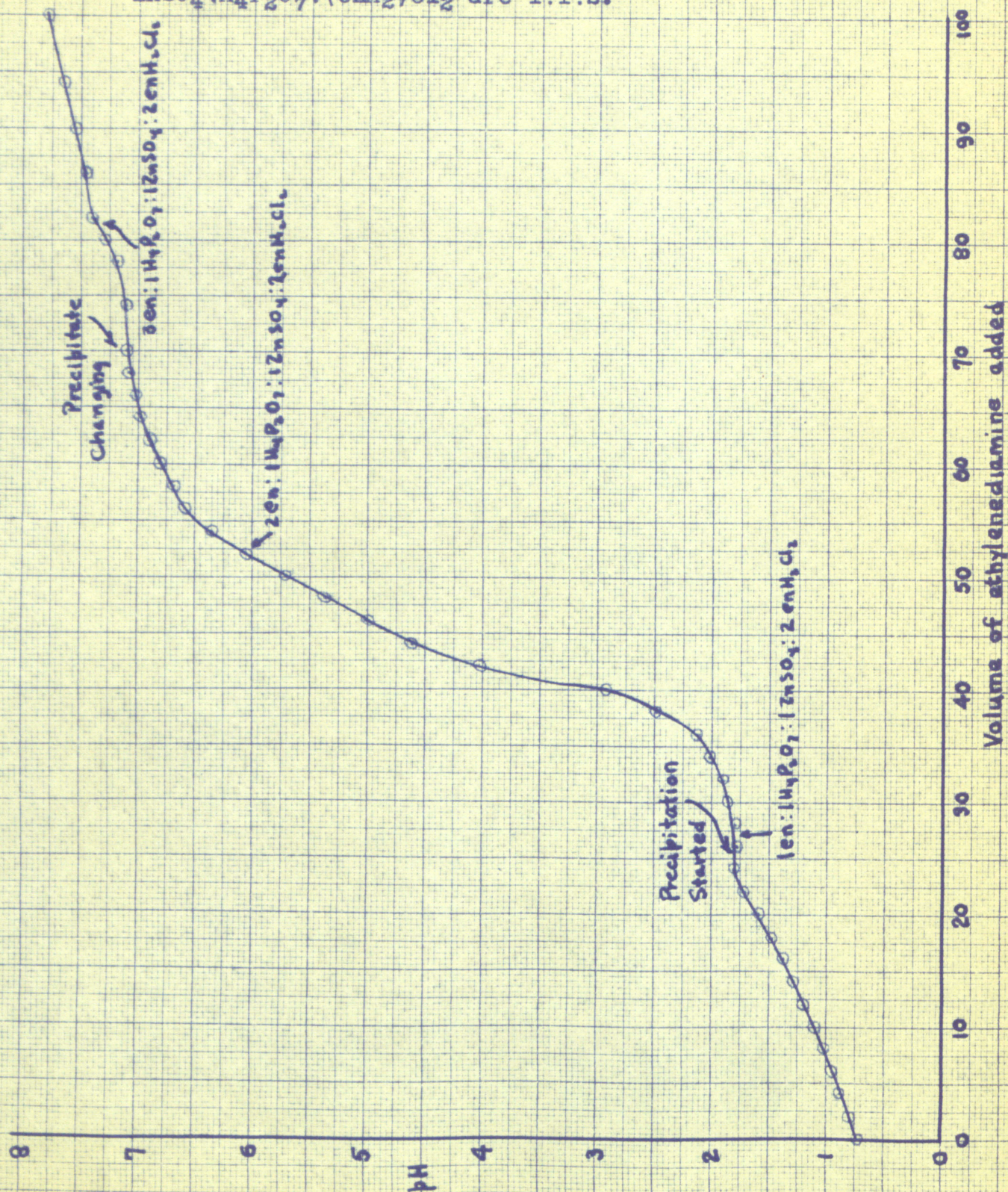
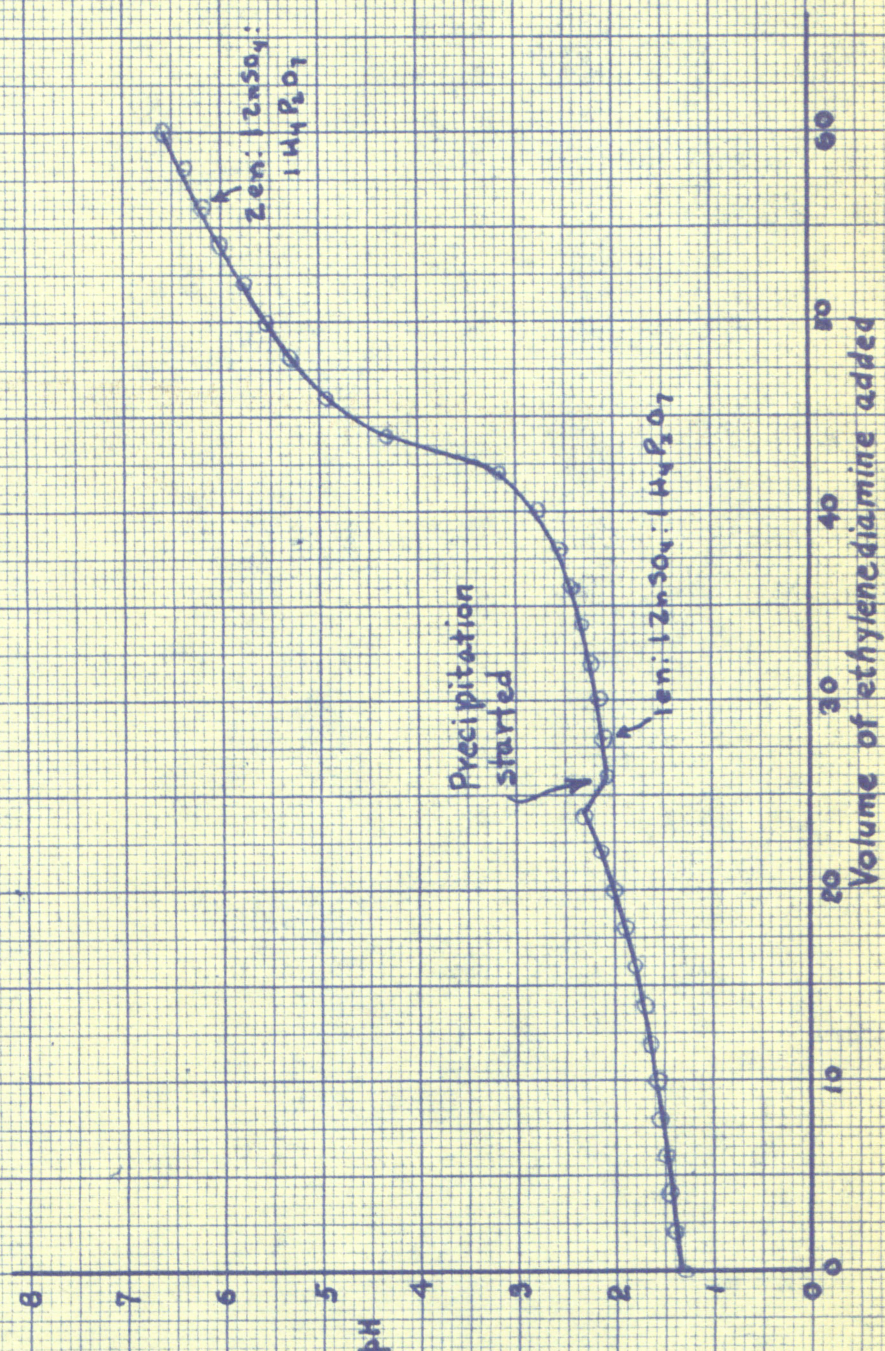


FIGURE 25

Change in pH as 0.54 M en is added to a solution which contains 22 ml. of 0.69 M $\text{H}_4\text{P}_2\text{O}_7$, 18 ml. of 0.82 M ZnSO_4 , and 500 ml. of H_2O . The initial molar ratio of $\text{ZnSO}_4:\text{H}_4\text{P}_2\text{O}_7$ is 1:1.



with three successive 200 ml. batches of Amberlite IR 120 cation exchanger. Fifteen millimoles of zinc sulfate solution was added to the acid, then the pH was raised by adding ethylenediamine. The reaction followed the same course as the one depicted in Figure 21; and the solid was separated at pH 6.5. Plate XII-A is the X-ray pattern of the product. The product had the same composition and X-ray pattern as other comparable preparations, and hence was the same mixture.

L. Such mixtures as are encountered here can sometimes be purified by dissolving the product in acid, and reprecipitating by addition of base. This procedure was carried out by dissolving 3.3 grams of the mixture in 100 ml. of water and 7 ml. of 1:1 hydrochloric acid. Dilute 2:3 ethylenediamine was added dropwise until the pH reached 6.3. At this point, the reaction was stopped, and the solid material isolated. It gives the X-ray pattern in Plate XII-B.

The same mixture again resulted.

The analyses on the foregoing preparations are summarized in the following table. There is satisfactory cation-anion balance on all preparations except the low pH products, and preparation F. The low pH products probably contain some acidic pyrophosphate as part of the anion content. The inflections in the reaction pH curves support this fact. Preparation F is largely amorphous and may

Results of Chemical Analysis of Zinc
Ethylenediammonium Pyrophosphate Preparations

Products from below pH 4

Preparation	P		Zn		N	
	Per Cent	Gram-Atoms	Per Cent	Gram-Atoms	Per Cent	Gram-Atoms
B	16.53	0.532	31.24	0.477	1.67	0.119
E	16.02	0.517	31.18	0.476	0.91	0.065
G	17.29	0.558	29.30	0.447	2.51	0.184

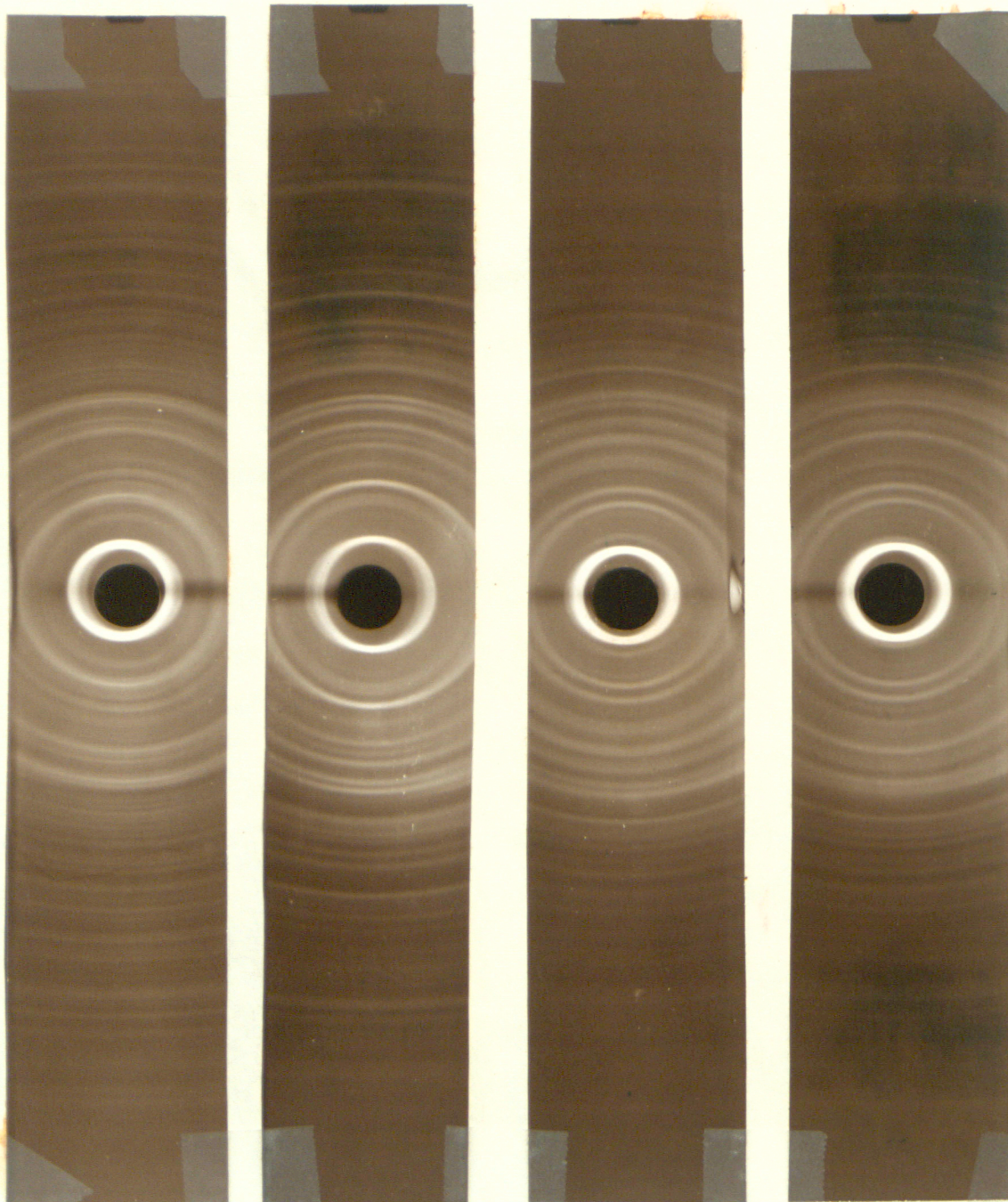
Remaining Products

A	16.36	0.527	27.78	0.425	3.37	0.241
C	17.63	0.568	22.37	0.343	7.13	0.510
D	18.54	0.597	20.75	0.316	7.99	0.572
F	14.75	0.475	29.55	0.453	6.12	0.437
H	20.43	0.657	20.61	0.314	9.45	0.675
I	19.02	0.617	18.85	0.288	9.31	0.665
J	18.82	0.607	22.61	0.346	7.10	0.507
K	18.61	0.602	20.77	0.318	7.72	0.552
L	18.84	0.608	22.34	0.341	7.27	0.519

Zn ₂ P ₂ O ₇ ·5H ₂ O	15.69		33.10			
Zn ₂ (NH ₂) ₂ (P ₂ O ₇)	19.45		20.50		8.79	
·H ₂ O						
(hypothetical)						

Ratios:	B	1.00	Zn:1.12 P; or	1.00	N:4.00	Zn:4.44 P
	E	1.00	Zn:1.08 P	(nitrogen not significant)		
	G	1.00	Zn:1.25 P; or	1.00	N:2.43	Zn:3.03 P
	A	1.00	N:1.76	Zn:2.19	P	
	C	1.49	N:1.00	Zn:1.65	P	
	D	1.81	N:1.00	Zn:1.89	P	
	F	1.00	N:1.04	Zn:1.09	P	
	H	2.15	N:1.00	Zn:2.09	P	
	I	2.31	N:1.00	Zn:2.14	P	
	J	1.46	N:1.00	Zn:1.75	P	
	K	1.73	N:1.00	Zn:1.90	P	
	L	1.52	N:1.00	Zn:1.78	P	

PLATE IX



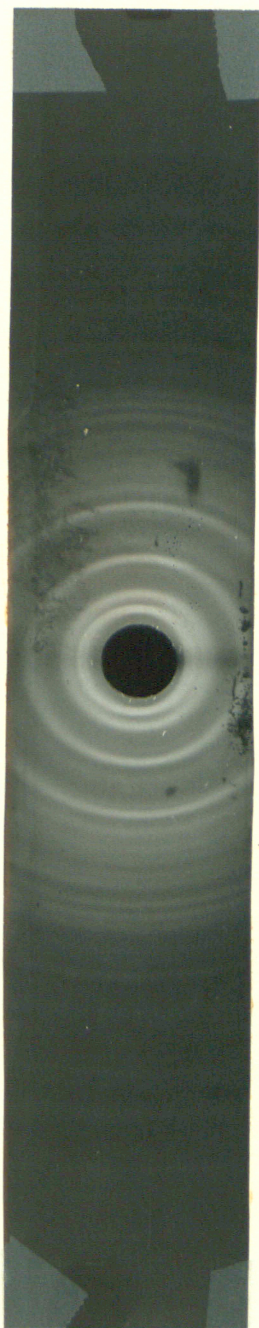
A

B

C

D

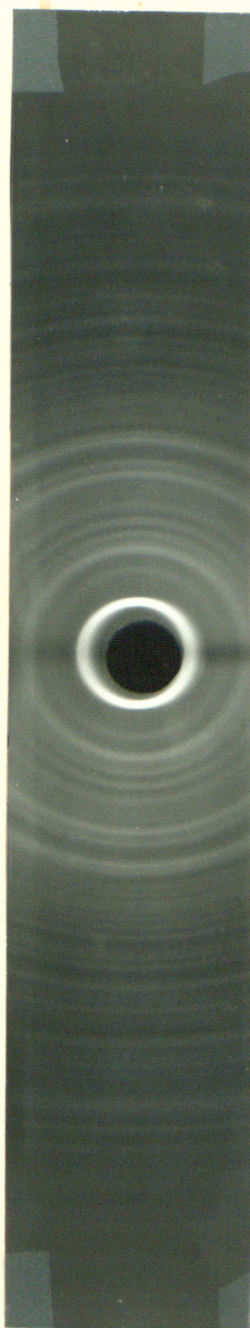
PLATE X



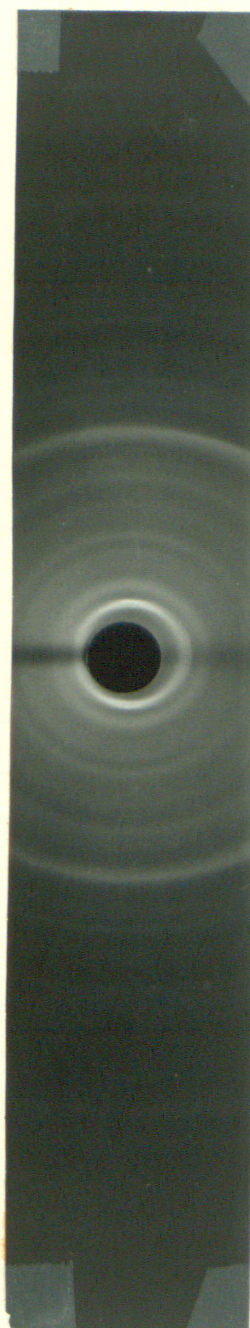
A



B

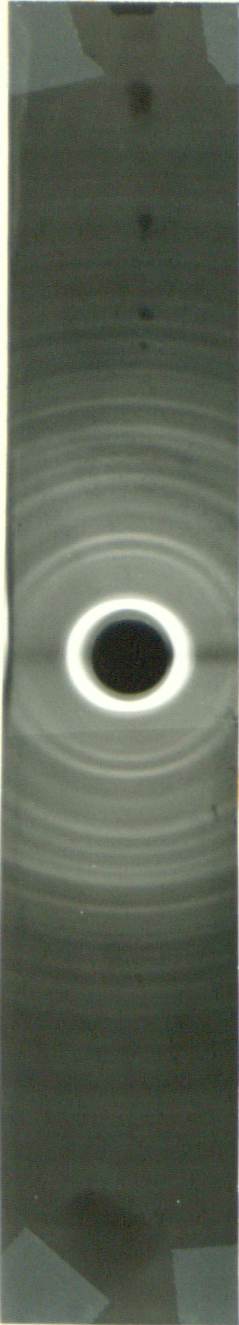


C

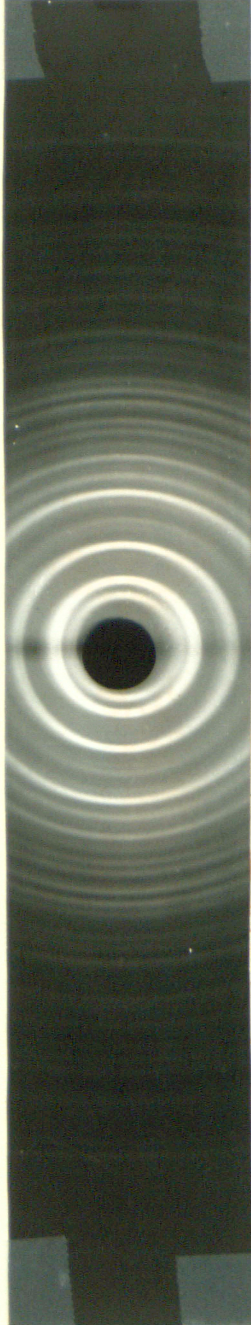


D

PLATE XI



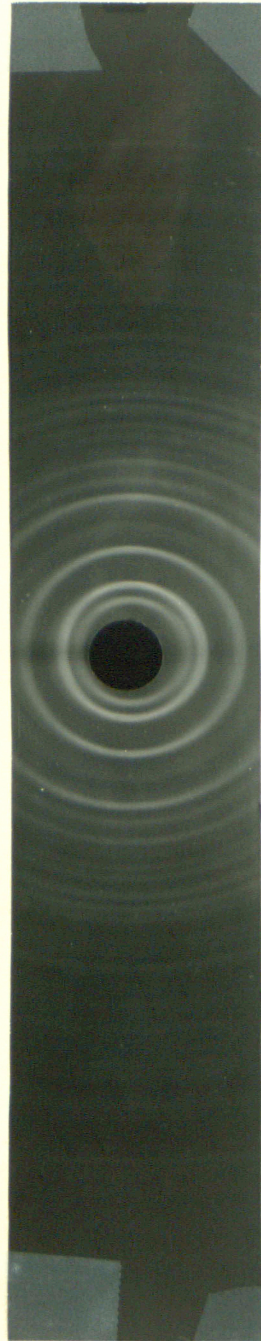
A



B

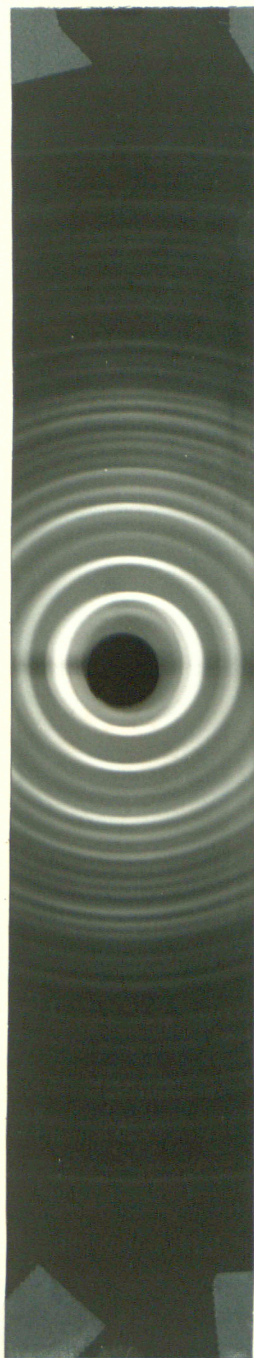


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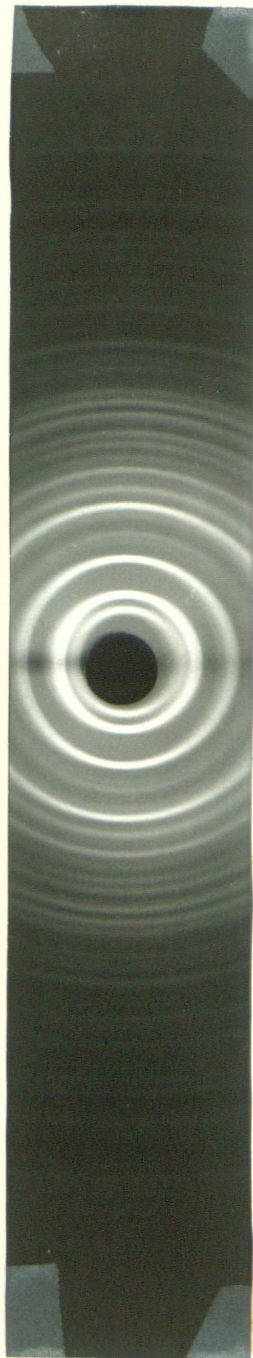


D

PLATE XII



A



B

contain zinc hydroxide.

None of the atomic ratios indicates a pure compound.

For purposes of comparison, the calculated percentages for $\text{Zn}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ and a hypothetical compound $\text{ZnenH}_2(\text{P}_2\text{O}_7) \cdot \text{H}_2\text{O}$ are included.

The X-ray patterns, show that some $\text{Zn}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ is present in all preparations except I.

The reference tri and pentahydrated zinc pyrophosphates were prepared as follows (35):

$\text{Zn}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$: One gram of purified anhydrous tetrasodium pyrophosphate was dissolved in 70 ml. of water, and the pH adjusted to 5.5. Then 25 ml. of a solution containing 12 grams of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was added very slowly (15 minutes) with vigorous stirring, and the pH readjusted to 5.5 by careful addition of 0.2 N sodium hydroxide. Stirring was continued for 30 minutes. The solid was then filtered off and air-dried. (Plate IX A).

$\text{Zn}_2\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$: This preparation followed exactly the same procedure that was used for the pentahydrate, except that the temperature of the reaction mixture was maintained at 70°C . The product was filtered hot, dried in an oven heated beforehand to 70°C . The capillary for the X-ray camera was loaded and sealed immediately. (Plate IX B).

The X-ray patterns from both preparations were

checked by comparison with patterns of the $\text{Zn}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ and $\text{Zn}_2\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ of known purity.

The foregoing discussion may be briefly summarized: All attempts to prepare a $\text{Zn}(\text{NH}_2)(\text{P}_2\text{O}_7)$ lead to spherulite mixtures (intergrown crystals). In all except one preparation (I), $\text{Zn}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ was identified by X-ray powder patterns as one constituent of the mixtures. The product from low pH regions is predominantly $\text{Zn}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$. As the pH is raised, strong lines of some other material appear in the X-ray patterns. In view of the appreciable nitrogen content of the preparations obtained above pH 4, the new material may be zinc ethylenediammonium pyrophosphate. In the preparation from a reaction mixture containing excess ethylenediammonium ions (I), no lines from zinc pyrophosphate appear on the X-ray pattern. However, the results of analysis still indicate a mixture. Perhaps if the latter reaction mixture were aged for a period of months, a pure zinc ethylenediammonium pyrophosphate could be obtained. The occurrence of such mixtures, intergrown crystals and slow solid phase changes are also described by Basset et al. (9) in their study of pyrophosphate double salts.

Exploratory Reactions

These reactions were carried out by adding 1:1 hydrochloric acid to a solution of 15 millimoles of the sodium

salt of the condensed phosphate in 50 ml. of water until the pH was lowered to at least one. Then 15 millimoles of zinc sulfate solution were introduced, and the pH raised by adding small amounts of ethylenediamine.

Sodium Triphosphate: Figure 26 shows the variation in pH as the reaction with this material is carried out. A flocculent precipitate forms at pH 3, and this immediately changes to a crystalline solid. Chemical analysis of the product from the foregoing reaction gave the data:

Constituent	PerCent Found	Gram-Atoms	Atomic Ratio	Calculated PerCent for $\text{NaZn}_2\text{P}_3\text{O}_{10} \cdot 9\text{H}_2\text{O}$
Zn	23.00	0.352	1.00	22.98
N	0	-----	-----	-----
P	16.67	0.538	1.52	16.38

The product was identified by calculating the spacings of the X-ray pattern of the present preparation and comparing them with the spacings for $\text{NaZn}_2\text{P}_3\text{O}_{10} \cdot 9\text{H}_2\text{O}$ (35).

Sodium Trimetaphosphate. When the reaction is carried out with this salt, precipitation begins at pH6 (For details of the procedure see Figure 27). The product is amorphous (Plate XIII-B), and has the composition: 33.01 per cent zinc, 3.52 per cent nitrogen, and 15.78 per cent phosphorus. The corresponding gram-atoms are 0.504 phosphorus, 0.253 nitrogen, and 0.503 zinc, in a ratio of 2 phosphorus : 1 nitrogen : 2 zinc. Since the nitrogens must occur in pairs

FIGURE 26

Variation in pH as 0.54 M en is added to a solution which contains 7.14 gm. of $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$, 18 ml. of 0.82 M ZnSO_4 , 75 ml. of H_2O , and enough 1:1 HCl to lower the initial pH to 1.0. The initial molar ratio of $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}:\text{ZnSO}_4$ is 1:1.

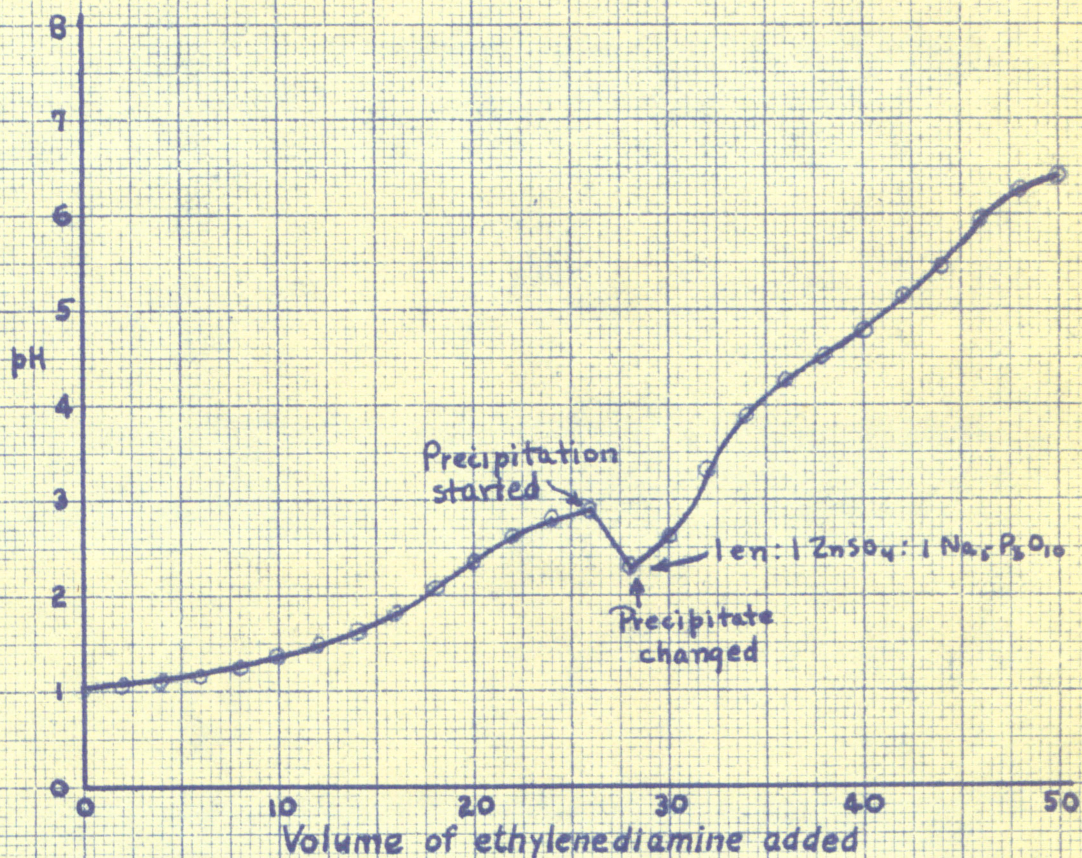
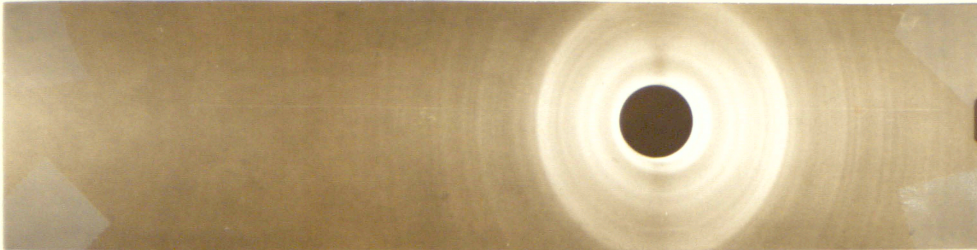
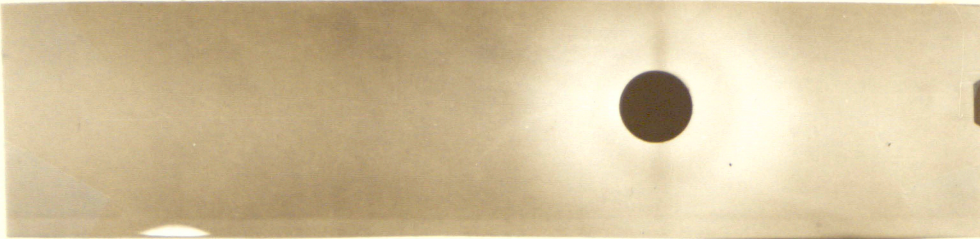


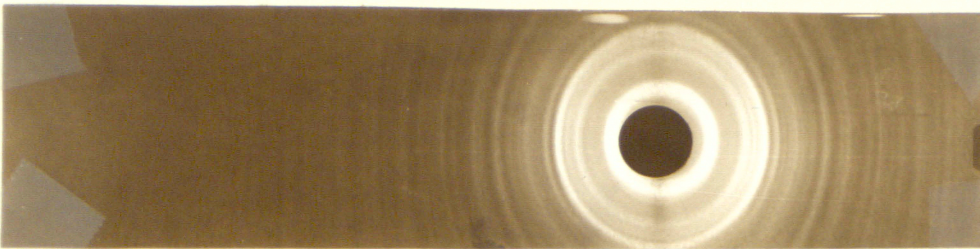
PLATE XIII



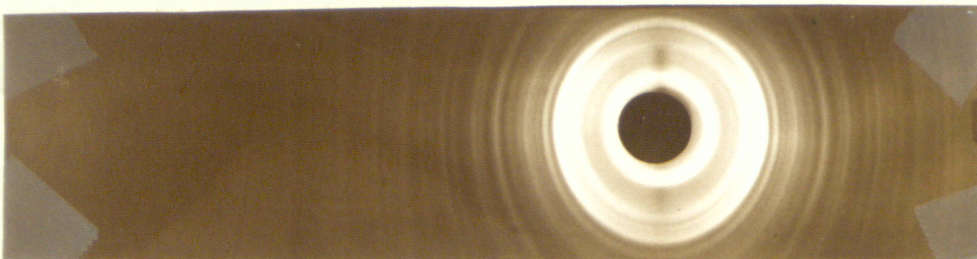
A



B



C



D

Comparison of X-Ray Pattern for $\text{NaZn}_2\text{P}_3\text{O}_{10} \cdot 9\text{H}_2\text{O}$
with that of Unknown Preparation

<u>d(observed)</u>	<u>d(reported)</u>	<u>I/I₀(observed)</u>	<u>I/I₀(reported)</u>
10.8	11	vs	vs
9.8	9.8	vs	vs
7.6	7.7	vs	vs
7.2	7.3	vs	vs
5.03	5.02	s	vs
4.78	4.80	s	vs
4.35	4.34	s	vs
4.17	4.19	s	vs
4.02	4.03	s	s
3.83	3.83	s	s
3.68	3.69	vs	vs
3.42	3.41	vs	vs
3.15	3.16	vs	vs
3.01	3.00	s	vs
2.84	2.84	s	vs
2.79	2.80	s	vs
2.60	2.61	m	s
2.40	2.41	m	s

vs = very strong
s = strong
m = medium

FIGURE 27

Change in pH as 0.54 M en is added to a solution which contains 4.60 gm. of $\text{Na}_3\text{P}_3\text{O}_9$, 18 ml. of 0.82 M ZnSO_4 , 50 ml. of H_2O , and enough 1:1 HCl to lower the pH to 0.7. The initial molar ratio of $\text{Na}_3\text{P}_3\text{O}_9$: ZnSO_4 is 1:1.

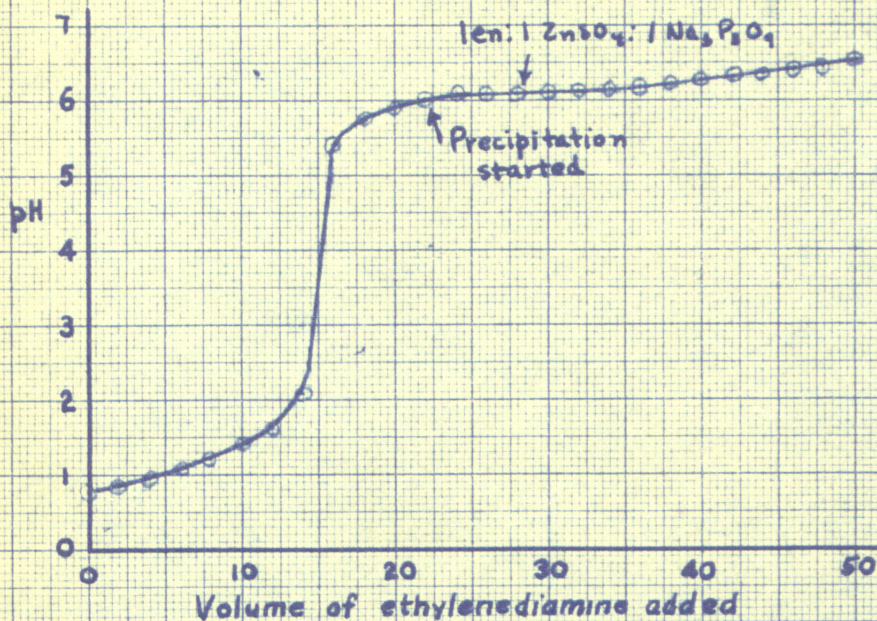
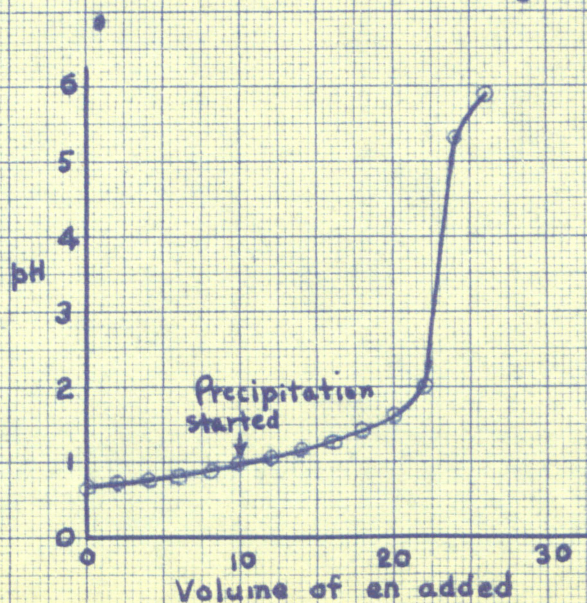


FIGURE 28

Change in pH as 0.54 M en is added to a solution which contains 7.20 gm. of $\text{Na}_4\text{P}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$, 18 ml. of 0.82 M ZnSO_4 , 50 ml. of H_2O , and enough 1:1 HCl to lower the pH to 0.7. The initial molar ratio of $\text{Na}_4\text{P}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$: ZnSO_4 is 1:1.



and since the phosphorus atoms come in "threes," the figures are difficult to reconcile into a plausible formula.

Sodium Tetrametaphosphate: Figure 28 shows the pH variation as this reaction proceeds. As in the magnesium tetrametaphosphate reaction (p. **68**), precipitation begins at pH 1.0. Plate XIII-C is the X-ray diffraction pattern yielded by the present product. It is the same as that for the previous tetrametaphosphate preparation; therefore the two products are identical.

CHAPTER VIII

MANGANOUS ETHYLENEDIAMMONIUM PHOSPHATES

All reactions with manganese, unless otherwise noted, were carried out at temperatures between 30 and 35°C. The products were washed with two 25 ml. portions of alcohol, followed by a like treatment with ether, then air-dried.

Manganese fluoresces with CuK_α radiation, and therefore the X-ray patterns were only of limited value.

Orthophosphate Studies

The direct combination of the three ions by bringing together solutions of manganous sulfate and ethylenediammonium phosphate does not produce a pure compound. The following such reactions were carried out:

A. When manganous sulfate solution is added to ethylenediammonium phosphate (Figure 29), the pH curve is not reproducible; equilibrium is reached very slowly. The first precipitate is a mixture of amorphous-appearing material and prisms. After a small amount of manganous sulfate has been introduced, all of the precipitate becomes

FIGURE 29

Changes in pH which may occur when 0.76 M MnSO_4 is added to 0.29 M $\text{enH}_2(\text{HPO}_4)$ solution. 50 ml. of the latter solution were used.

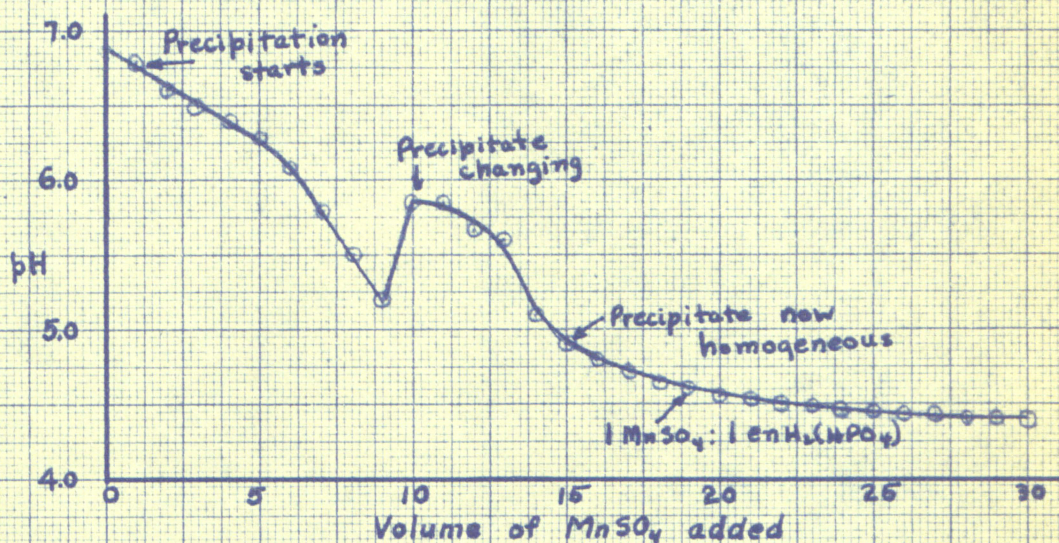
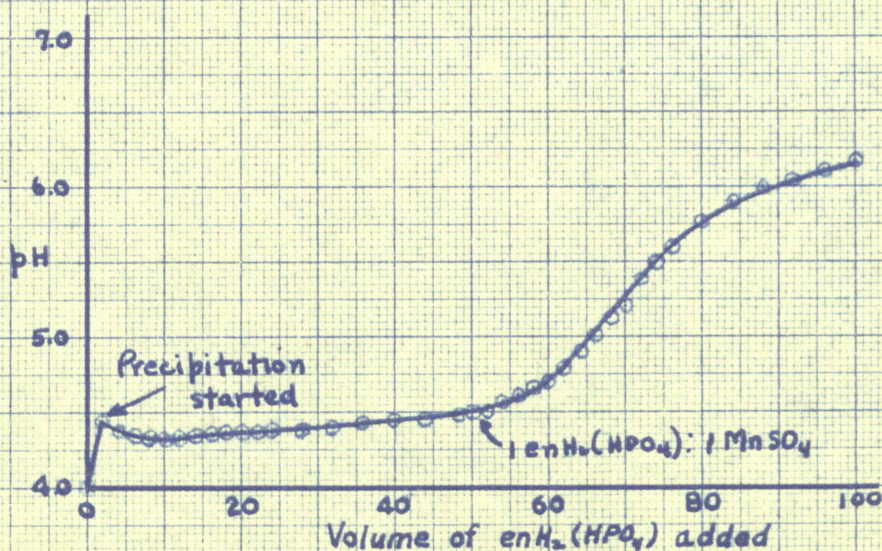


FIGURE 30

Variation in pH as 0.29 M $\text{enH}_2(\text{HPO}_4)$ is added to 25 ml. of 0.76 M. MnSO_4 .



amorphous in appearance. As the addition of manganous sulfate is continued, the product grows increasingly viscous until there was no point in continuing the reaction.

B. When the order of addition is reversed and the ethylenediammonium phosphate is added to the manganous phosphate, the amorphous solid (Figure 30) separates first, and remains unchanged throughout the reaction. The solution did not become viscous, and the product filtered well.

C. In the quantitative gravimetric precipitation of manganous ammonium phosphate, the manganous phosphate which first appears is converted into the desired product by heating the suspension. When reaction A is carried out at 70°C, the pH changes as shown in Figure 31. However, there is no improvement in the physical characteristics of the product. In fact, the suspension becomes viscous even sooner than does reaction A.

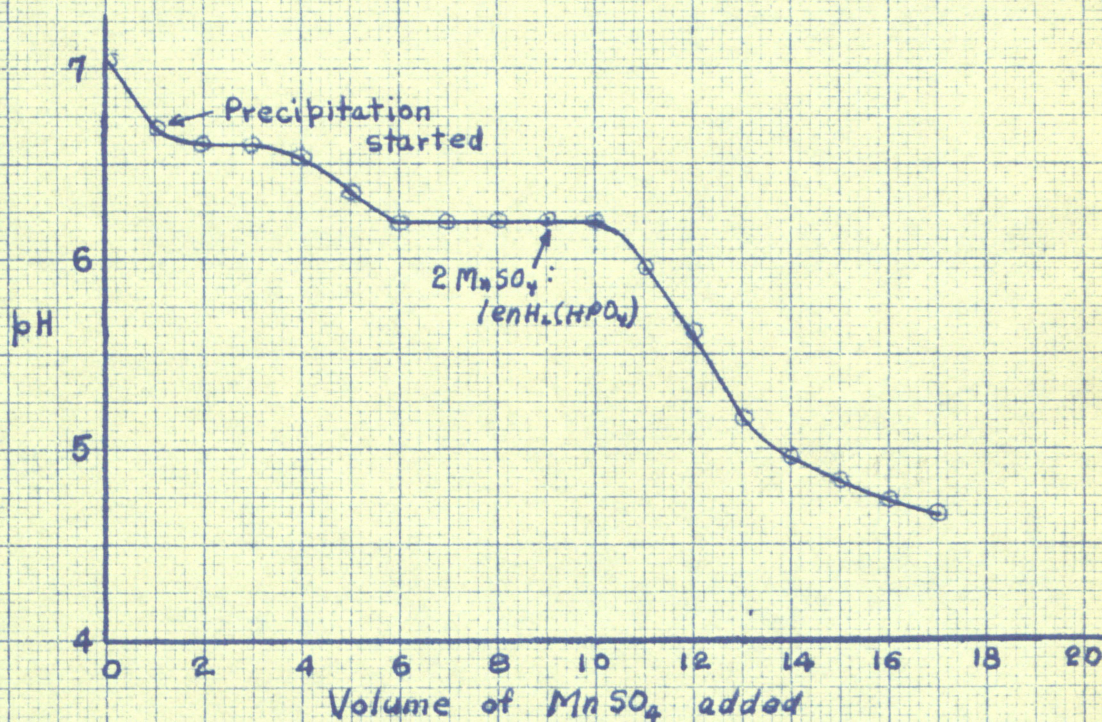
The analytical data on these preparations are as follows:

Preparation	P		N		Mn	
	Per Cent	Gram-Atoms	Per Cent	Gram-Atoms	Per Cent	Gram-Atoms
A	15.01	0.484	3.75	0.267	27.01	0.493
B	13.09	0.423	1.34	0.096	31.20	0.568
C	16.40	0.529	4.51	0.322	25.40	0.462

Atomic Ratio: A 1.00 nitrogen:1.29 phosphorus:1.31manganese
 B 1.00 phosphorus : 1.33 manganese
 C 1.00 nitrogen:1.64 phosphorus:1.43manganese

FIGURE 31

Changes in pH which may occur when 0.76 M MnSO_4 is added to 50 ml. of 0.29 M $\text{enH}_2(\text{HPO}_4)$. The temperature of the reaction is 70°C .



There is no relationship between the constituents; the products must be mixtures.

In the following protracted reactions, the identification of mixtures was made by microscopic observations.

When ethylenediamine is added to a solution which contains manganous sulfate and orthophosphoric acid in an initial 1:1 molar ratio, precipitation begins at pH 3.5 (Fig. 32). The first solid to separate is a mixture of amorphous-appearing material and diamond-shaped tablets. The latter were obtained pure in a later preparation and were identified as $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$. At pH 4.4, the manganous phosphate changed to the form of needles; the amorphous material remained unaltered. The needles were also obtained pure later, and were then identified as $\text{Mn}_2\text{enH}_2(\text{HPO}_4)_3 \cdot \text{H}_2\text{O}$. When the pH reaches 6.6, the solid changes to a homogeneous precipitate, - very small, rectangular prisms (magnification X450). Plate XIV-A is the X-ray pattern given by the preparation.

The results of chemical analysis on the light pink product are as follows:

Constituent	PerCent Found	Gram-Atoms	Atomic Ratio	PerCent Calculated for $\text{Mn}_2\text{enH}_2(\text{PO}_4)_3 \cdot 5\text{H}_2\text{O}$
Mn	24.34	0.443	1.20	24.41
N	6.11	0.436	1.00	6.22
P	13.73	0.443	1.02	13.77
$\text{H}_2\text{O}(135^\circ)$	19.84	1.10	2.53	20.00

FIGURE 32

Change in pH as 0.54 M en is added to a solution prepared from 29.5 ml. of 0.51 M H_3PO_4 and 19.5 ml. of 0.76 M $MnSO_4$. The initial molar ratio of $H_3PO_4:MnSO_4$ is 1:1.

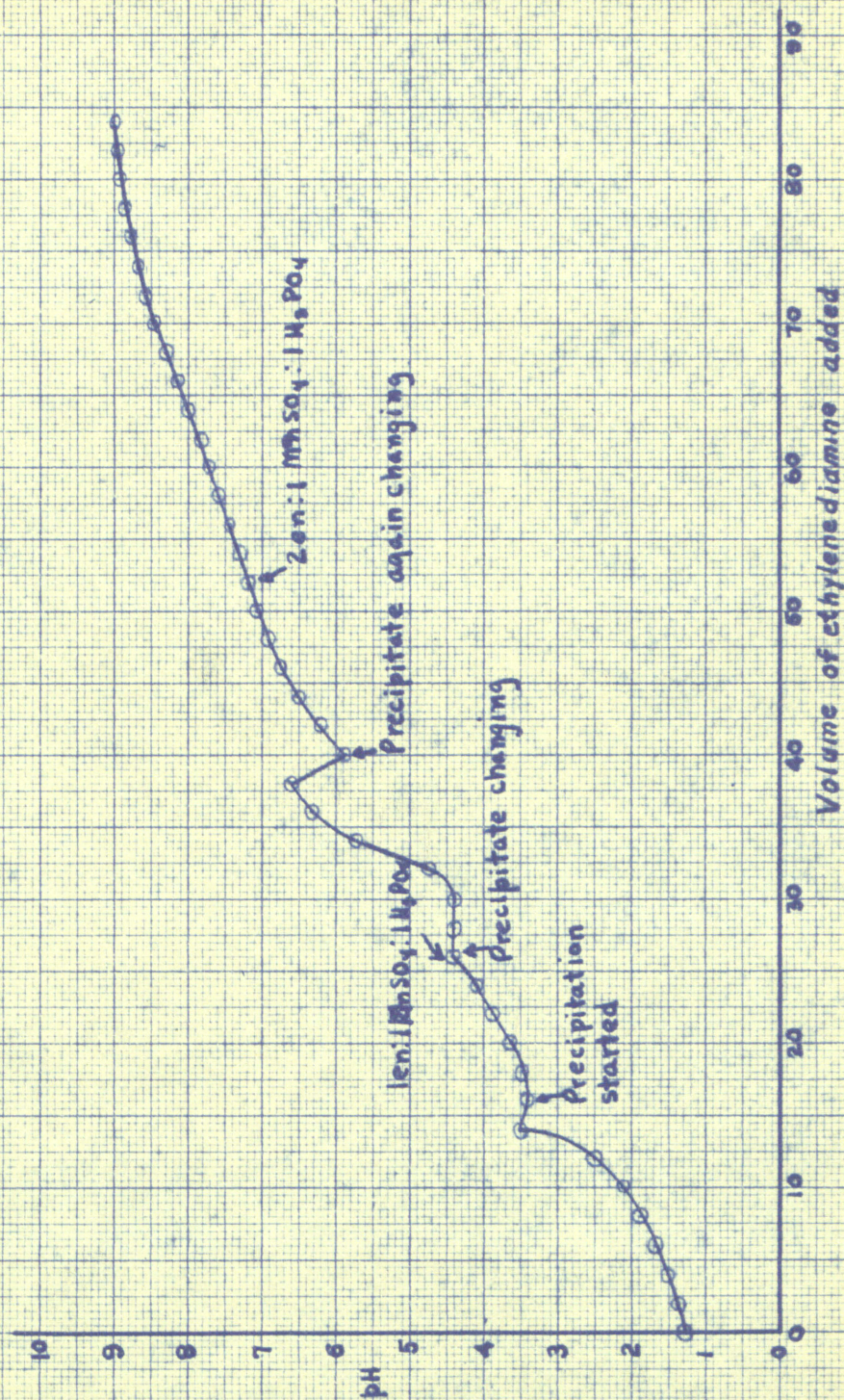
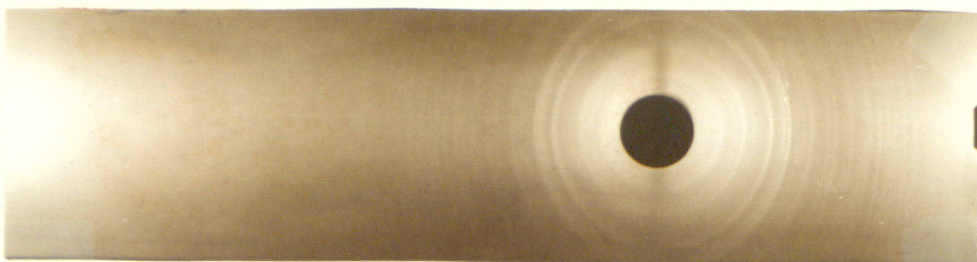
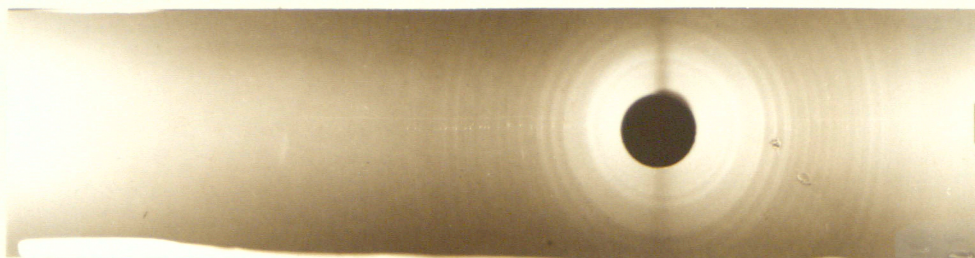


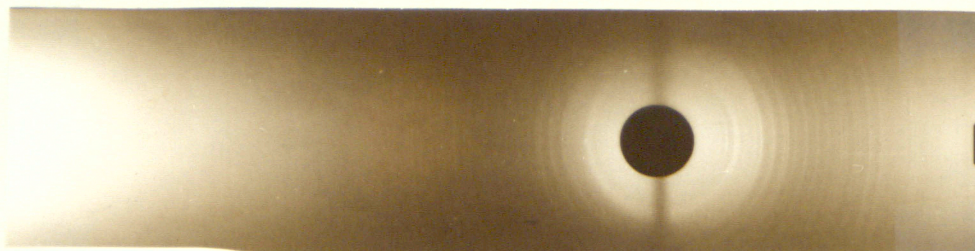
PLATE XIV



A



B



C



D



E

The equivalent weight of phosphorus in the compound is 15.4, thus confirming the tertiary ortho-phosphate formulation. The chemical evidence thus establishes the composition of the small prisms as $\text{Mn}_2\text{enH}_2(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$.

When the foregoing reaction was extended above pH 8, amorphous material again appears, and the color of the suspension gradually darkens, presumably due to the formation of manganous dhydroxide, which is quickly oxidized to hydrated manganese dioxide.

If the initial molar ratio of manganous sulfate to phosphoric acid is changed to 2:1, and ethylenediamine added, precipitation begins at pH 3.3. The crystals which separate are prisms with perfect pyramidal ends (magnification X100). At pH 4, this product changes into a mixture of amorphous-material and a few stray crystals of $\text{Mn}_2\text{enH}_2(\text{PO}_4) \cdot 5\text{H}_2\text{O}$. The mixture remains unchanged until pH 7.5, when the brown coloration develops rapidly (**Figure 33**).

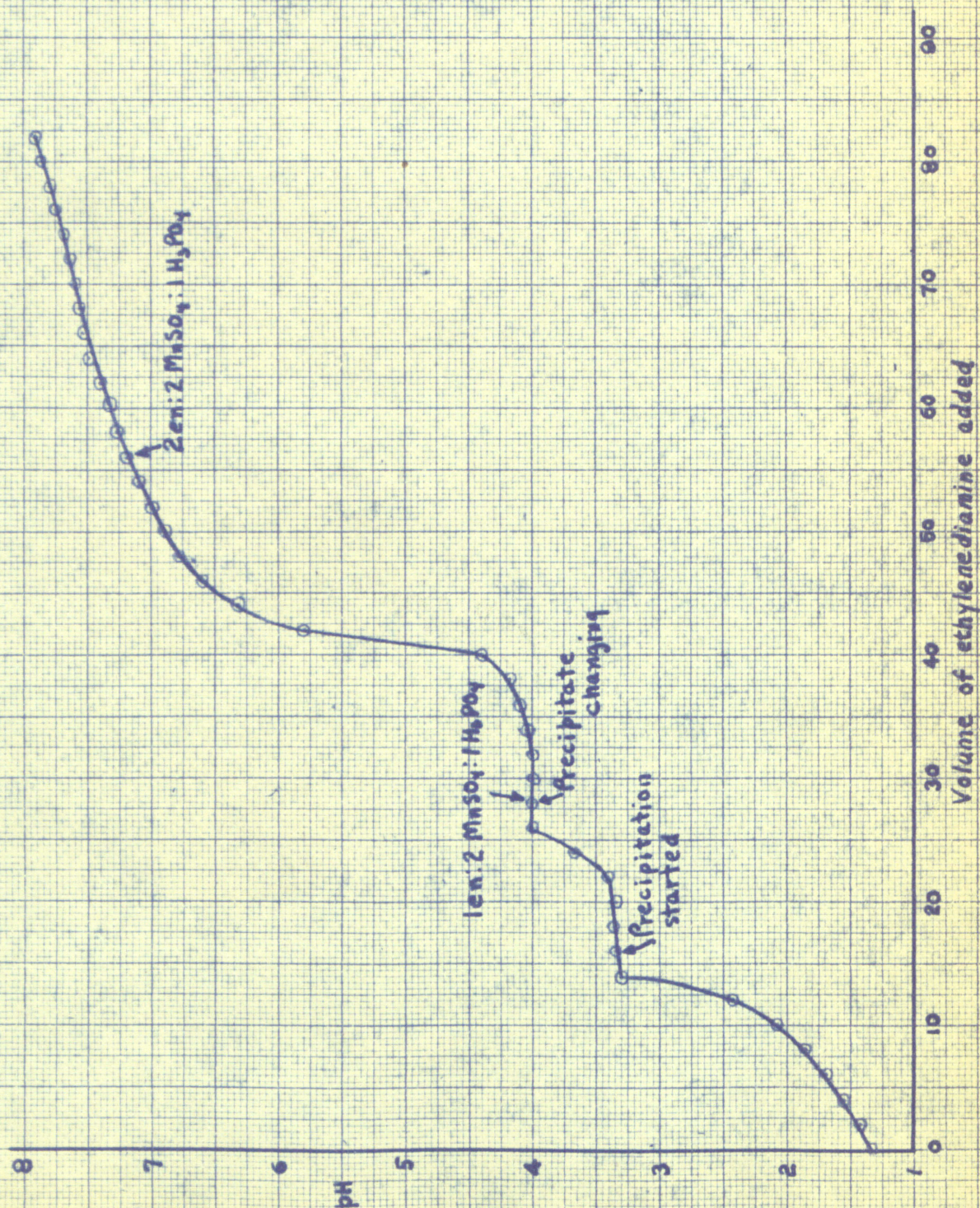
The pink prisms which separate in the low pH regions gave the X-ray pattern in Plate XIV-B, and the following chemical analysis:

Constituent	PerCent Found	Gram-Atoms	Atomic Ratio	PerCent Calculated For $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$
Mn	26.70	0.488	1.02	26.75
N	0	-----	-----	-----
P	14.85	0.480	1.00	15.08

The data presented indicate that the product is $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$.

FIGURE 33

Changes in pH as 0.54 M en is added to a solution prepared from 29.5 ml. of 0.51 M H_3PO_4 and 39 ml. of 0.76 M MnSO_4 . The initial molar ratio of $\text{MnSO}_4:\text{H}_3\text{PO}_4$ is 2:1.



The lines on the X-ray pattern were too poorly defined to calculate the spacings accurately.

The changes in pH which accompany the addition of ethylenediamine to a solution containing a 2:1 molar ratio of orthophosphoric acid to manganous sulfate are recorded in Figure 34. Three pure and distinctly different products appear as the pH rises.

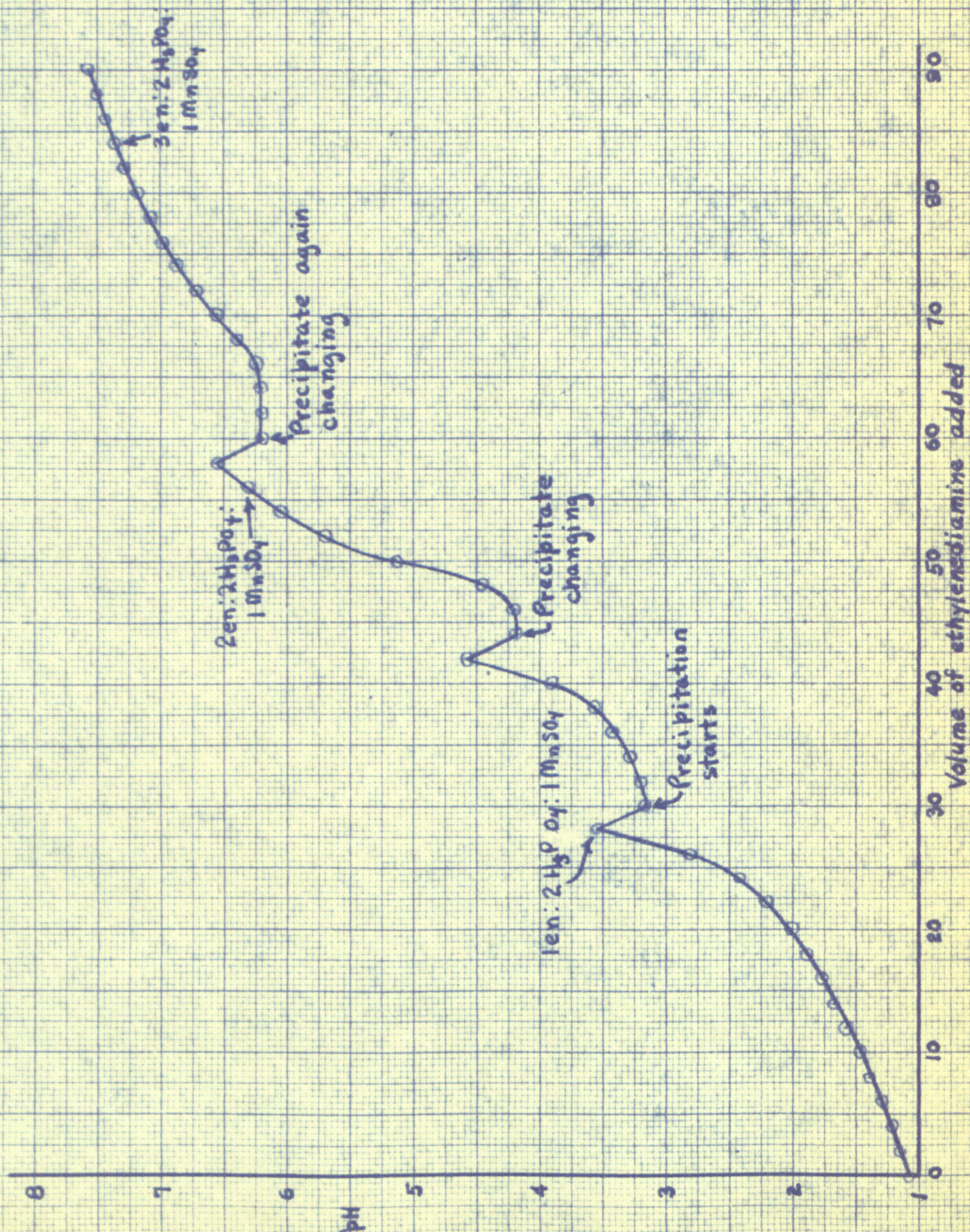
The first product separates at pH 3.5. Microscopic observation disclosed that it consisted of small diamond-shaped tablets. When the material was isolated and analyzed, it proved to be $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ again, even though its crystalline habit differed from that exhibited when the same compound was isolated in a previous reaction (p. 108). Plate XIV-C is the X-ray pattern produced by this preparation. The results of the chemical analysis were:

<u>Constituent</u>	<u>PerCent Found</u>	<u>PerCent Calculated for $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$</u>
Mn	26.79	26.75
P	14.90	15.08

When this reaction is carried to pH 4.6, the $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ changes to a new phase. This material, under microscopic observation, is acicular. When it was analyzed, the following results were obtained:

FIGURE 34

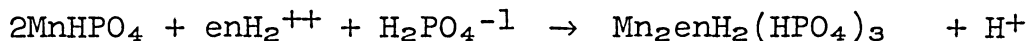
Changes in pH as 0.54 M en is added to a solution prepared from 59 ml. of 0.51 M H_3PO_4 and 19 ml. of 0.76 M MnSO_4 . The initial molar ratio of $\text{MnSO}_4:\text{H}_3\text{PO}_4$ is 1:2.



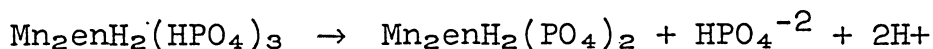
Constituent	PerCent Found	Gram-Atoms	Atomic Ratio	PerCent Calculated $\text{Mn}_2\text{enH}_2(\text{HPO}_4)_3 \cdot \text{H}_2\text{O}$
Mn	22.83	0.416	1.00	22.95
N	5.95	0.425	1.02	5.96
P	19.40	0.626	1.50	19.43
$\text{H}_2\text{O}(135^\circ)$	3.85	0.214	0.51	3.77

The equivalent weight of phosphorus was found to be 30.7 by an acidimetric titration, thus verifying the fact that the orthophosphate content is secondary. The X-ray pattern of the substance is shown in Plate XIV-D. The compound is therefore $\text{Mn}_2\text{enH}_2(\text{HPO}_4)_3 \cdot \text{H}_2\text{O}$.

The fall in pH when this material appears can be explained as follows: Since excess orthophosphoric acid was present at the start of the reaction, there is not enough manganese present to precipitate all of it as $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$. Consequently, additional phosphate is included in the product. When it forms, the phosphate contribution from $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ has no effect on the pH of the solution. However, the remaining HPO_4^{-2} ions must come from the solution in which $\text{H}_2\text{PO}_4^{-1}$ ions predominate. If this is to occur, hydrogen ions must be liberated. The foregoing may be summarized in the following equation:



The third and final phase change observed in the present reaction occurred at pH 6.5. Again hydrogen-ions are freed:



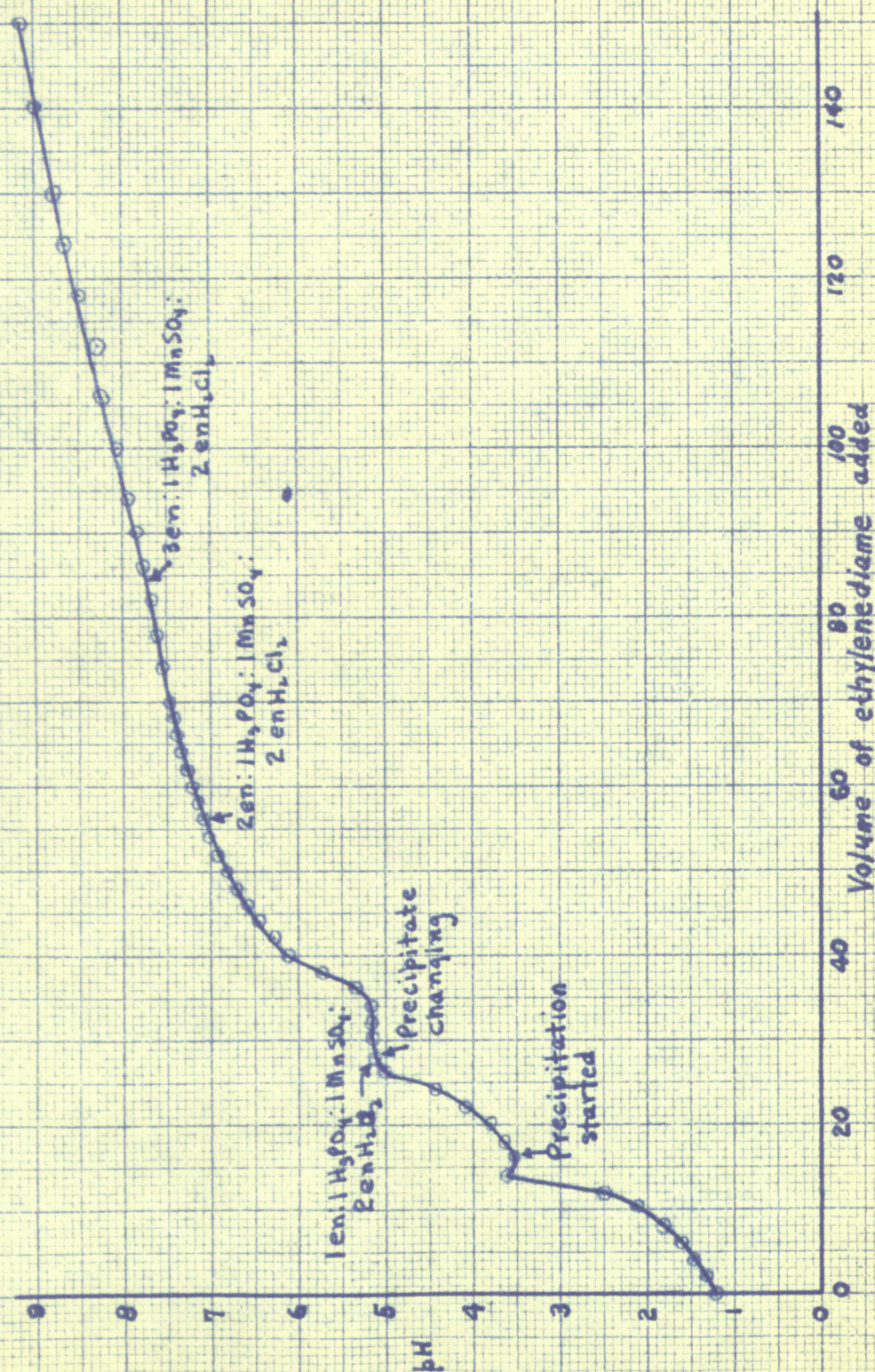
The product was the familiar minute rectangular prisms which had been previously identified (p. 106) as $\text{Mn}_2\text{enH}_2(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$. The X-ray pattern, Plate XIV-E, supports this identification.

When ethylenediamine is added to a solution containing manganous sulfate, orthophosphoric acid and ethylenediammonium hydrochloride initially in a 1:1:2 molar ratio, the first solid to appear is again $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ (microscopic observation). A phase change occurs at pH 5.2, and a mixture of $\text{Mn}_2\text{enH}_2(\text{HPO}_4)_3 \cdot \text{H}_2\text{O}$ and $\text{Mn}_2\text{enH}_2(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ forms. This mixture remains unchanged up to the completion of the reaction at pH 9.1. When the preparation was allowed to stand overnight, a brown flocculent precipitate formed; it was probably manganese dioxide (*Figure 35*).

To learn if any of the new products from this system form under analytical conditions, 200 mg. of disodium orthophosphate ("reagent" grade, recrystallized and dehydrated at 105°C) was dissolved in 125 ml. of water. To this solution was added 5 ml. of 1:1 hydrochloric acid, 2.5 grams of manganous sulfate, and 6 grams of ethylenediammonium hydrochloride. The pH was then raised to 6.5 by dropwise addition of 2:3 ethylenediamine solution. The precipitate which formed was amorphous and gelatinous. Aging overnight had no effect on its physical properties. When an attempt

FIGURE 35

Changes in pH as 0.54 M en is added to a solution which contains 29.5 ml. of 0.51 M H_3PO_4 , 19 ml. of 0.76 M MnSO_4 , 4 gm. of enH_2Cl_2 , and 50 ml. of H_2O . The initial molar ratios of $\text{H}_3\text{PO}_4:\text{MnSO}_4:\text{enH}_2\text{Cl}_2$ are 1:1:2.



was made to filter the product, it clogged the filter.

In the formation of manganous ammonium orthophosphate under analytical conditions, the solution containing the unknown, ammonium, phosphate and ammonium chloride must be boiling in order to effect a conversion from manganous phosphate, $\text{Mn}_3(\text{PO}_4)_2$, to the desired manganous ammonium double salt, MnNH_4PO_4 * Therefore the above experiment was repeated, except that the solution was heated to boiling before adding the ethylenediamine. The product was not gelatinous, but it was still amorphous, and was in colloidal suspension and therefore could not be successfully filtered. This behavior indicates that a manganous phosphate formed, but not the desired manganous ethylenediammonium phosphate.

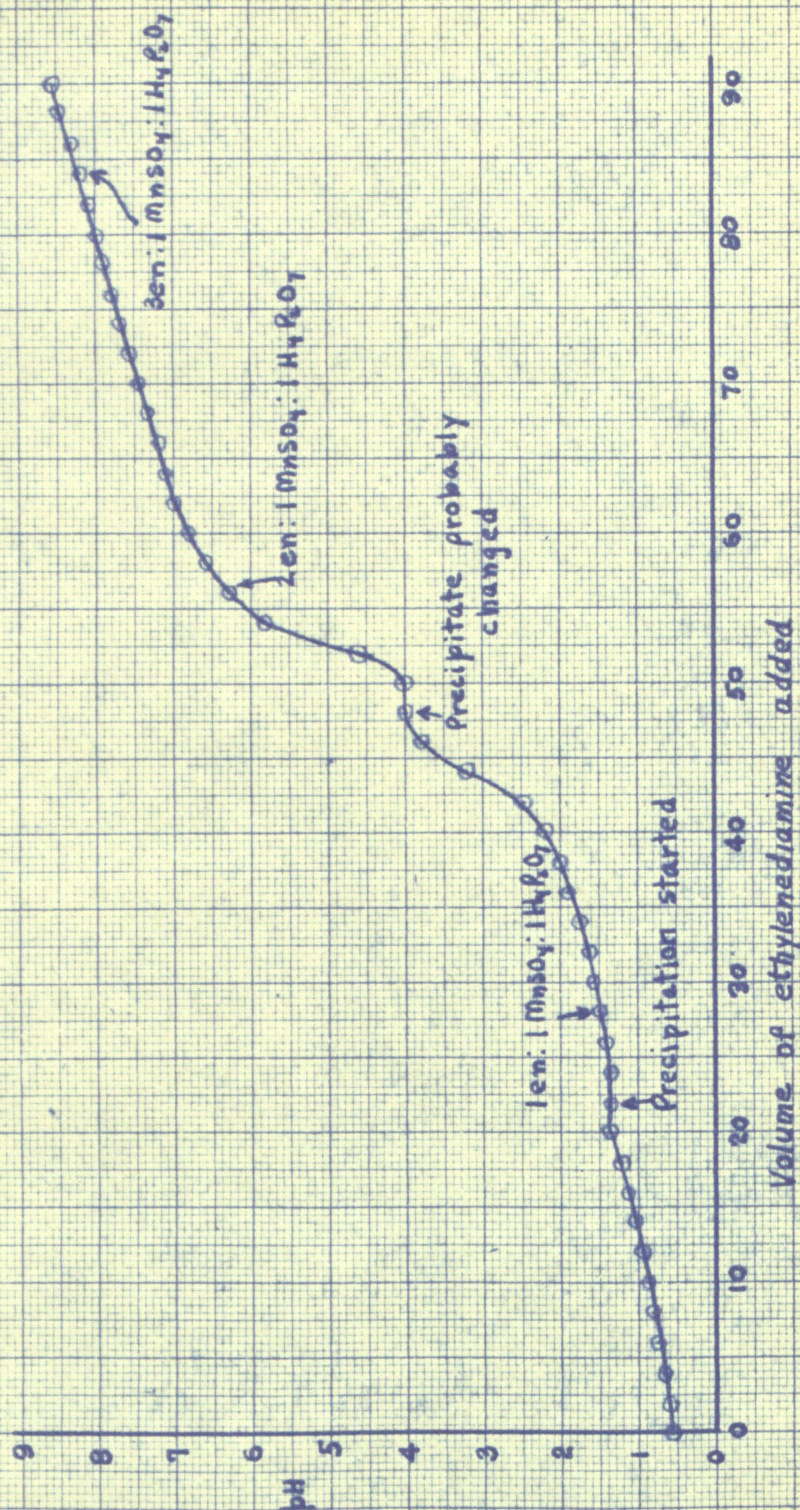
Pyrophosphate Studies

When ethylenediamine is added to a solution containing manganous sulfate and pyrophosphoric acid, in a 1:1 molar ratio, precipitation begins at pH 1.4. Figure 36 shows the changes in pH which accompany this addition. The external appearance of this first solid can only be described as non-

* Note that this procedure can be used to determine manganese only, not phosphorus, and that excess phosphate is present.

FIGURE 36

Variation in pH as 0.54 M en is added to a solution which contains 19 ml. of 0.76 M MnSO_4 , 18.5 ml. of 0.82 M $\text{H}_4\text{P}_2\text{O}_7$, and 25 ml. of H_2O . The initial molar ratio of $\text{MnSO}_4:\text{H}_4\text{P}_2\text{O}_7$ is 1:1.



descript fragments and clumps.

A sample of this material was isolated and analyzed. Plate XV-A was obtained for the X-ray pattern. The product had the composition: 25.78 per cent manganese, 37.3 per cent nitrogen, 17.70 per cent phosphorus. These percentages correspond to gram-atoms of 0.470 manganese, 0.195 nitrogen, and 0.573 phosphorus, or atomic ratios of 2.41 manganese : 1.00 nitrogen : 2.94 phosphorus. This product must therefore be a mixture.

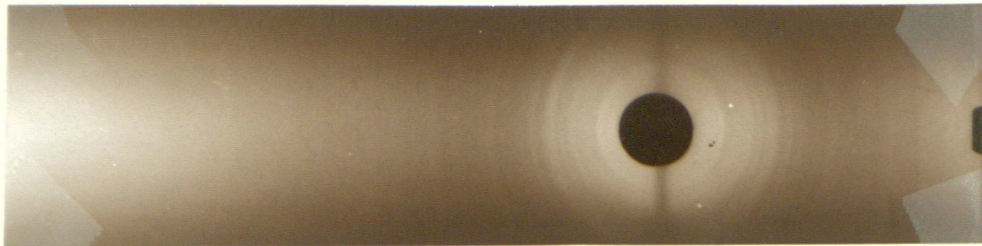
If the addition of ethylenediamine is continued a phase change occurs at pH 4.00. Extremely minute crystals form; they are so small that they appear to be circular when magnified 450 times. Their size was uniform. The material yields the X-ray pattern shown in Plate XV-B.

Chemical analysis of this light pink product yielded the following results:

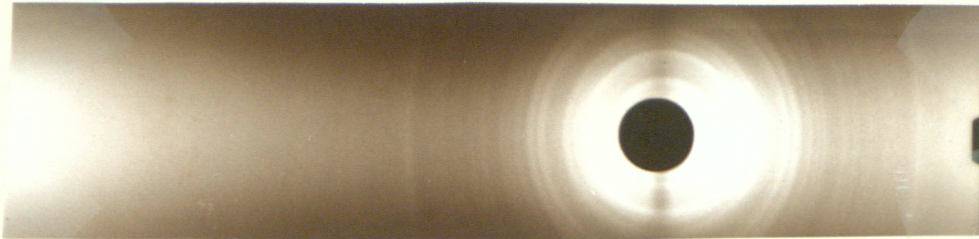
<u>Constituent</u>	<u>PerCent Found</u>	<u>Gram-Atoms</u>	<u>Atomic Ratio</u>	<u>Calculated PerCent for $\text{Mn}_2\text{H}_2(\text{P}_2\text{O}_7)\text{H}_2\text{O}$</u>
Mn	17.54	0.320	1.00	17.75
N	9.14	0.653	2.03	9.06
P	19.95	0.643	2.00	20.05
H ₂ O				5.83

The product could not be successfully dehydrated. It loses weight slowly, but fails to reach constant weight even as high as 155°C. At this temperature, it has lost only about 3.5 per cent of its original weight.

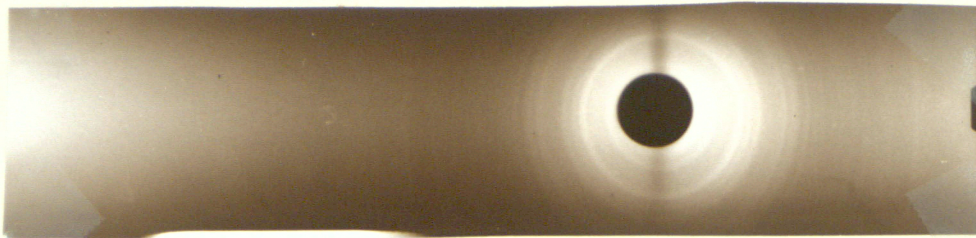
PLATE XV



A



B



C



D

This evidence confirms the product as $\text{Mn}(\text{H}_2\text{P}_2\text{O}_7) \cdot \text{H}_2\text{O}$.

When the reaction is continued into a higher pH range, no other changes occur before pH 8 is reached. There the color of the suspension gradually begins to assume a brownish cast, and it seems probable that hydrated manganese dioxide is forming.

If the starting solution contains excess manganous sulfate, and pyrophosphoric acid, the addition of ethylenediamine apparently produces no pure product (Figure 37). The first precipitate at pH 1.4 had the same nondescript appearance as did the first solid that formed in the preceding reaction. As the present reaction was continued, this material underwent no visible changes in form, but the reaction mixture became increasingly viscous and colloidal in nature. When the product was filtered, it turned from buff to brown during the lengthy filtering operation. No X-ray pattern could be obtained.

The pH changes which accompany the addition of ethylenediamine to a starting solution containing pyrophosphoric acid and manganous sulfate in an initial 2:1 molar ratio are shown in Figure 38. A nondescript precipitate, similar in appearance to that encountered in the preceding reactions, formed at pH 1.6. At pH 6.1, this material changes to very small spherulite crystals. The reaction was stopped at pH 6.5 in order to isolate this

FIGURE 37

Variation in pH as 0.54 M en is added to a solution which contains 38.5 ml. of MnSO_4 , 18.5 ml. of 0.82 M $\text{H}_4\text{P}_2\text{O}_7$, and 25 ml. of H_2O . The initial molar ratio of MnSO_4 : $\text{H}_4\text{P}_2\text{O}_7$ is 2:1.

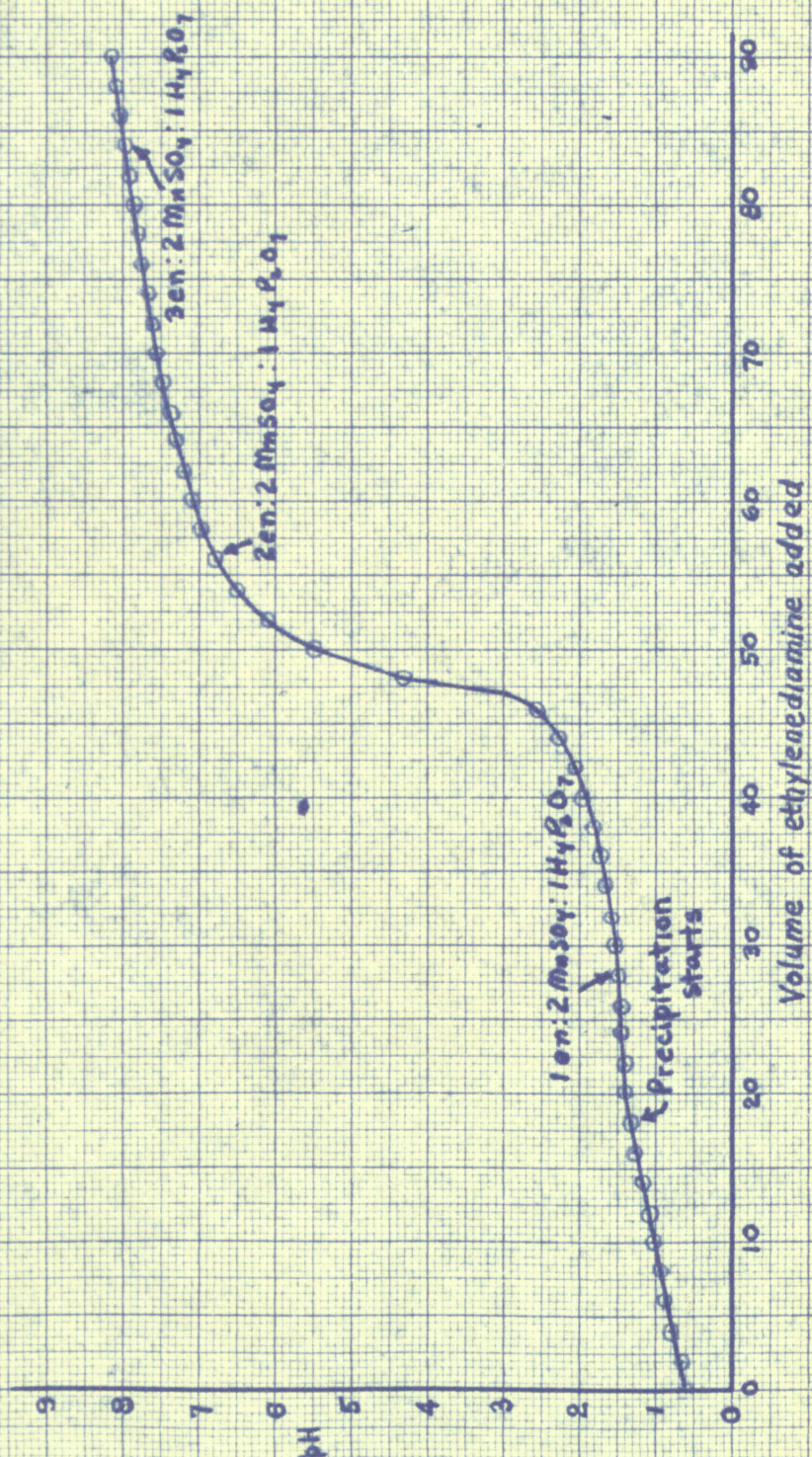
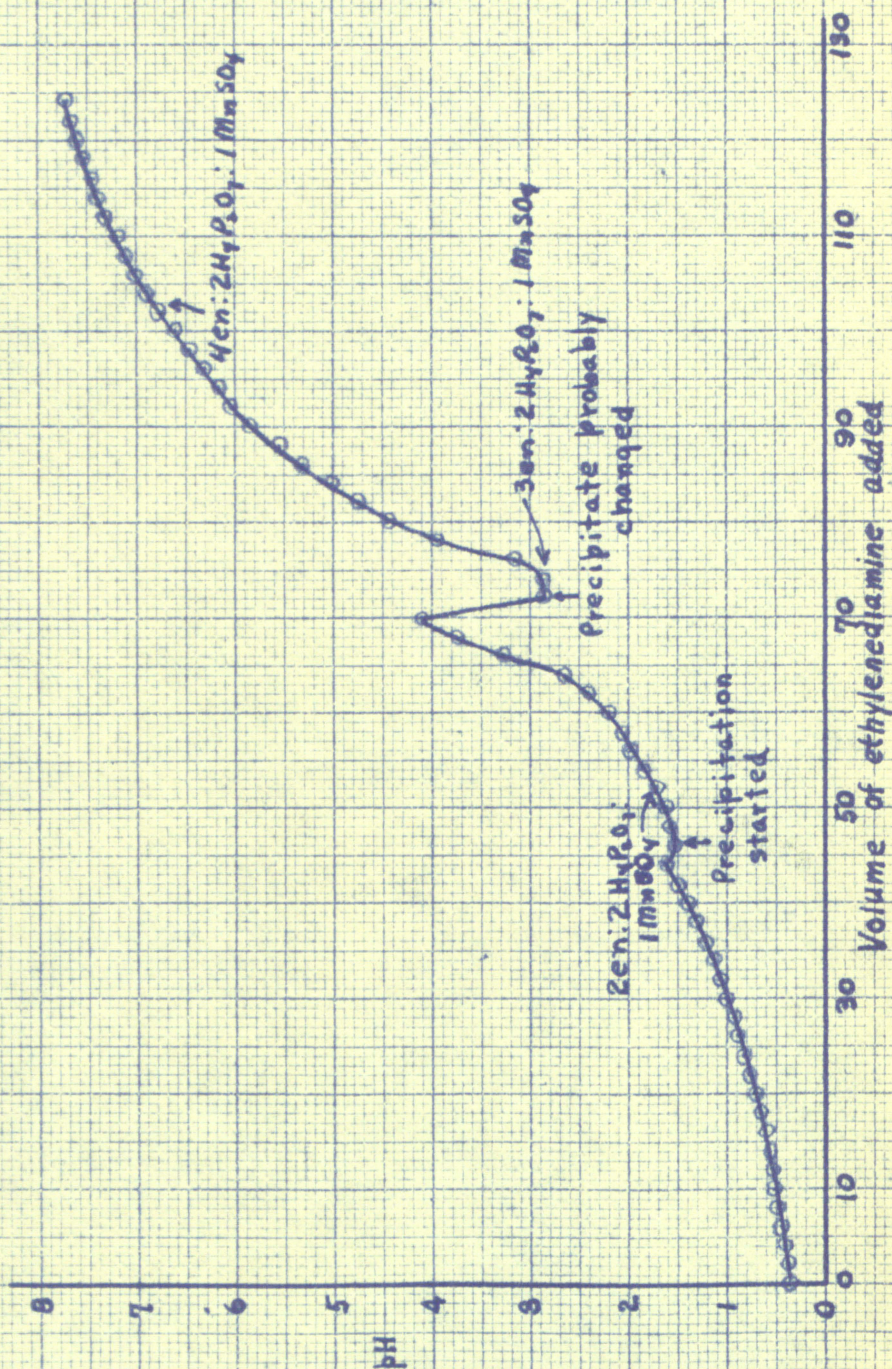


FIGURE 38

Changes in pH as 0.54 M en is added to a solution which contains 41 ml. of 0.74 M $H_4P_2O_7$, 19 ml. of 0.76 M $MnSO_4$, and 25 ml. of H_2O . The initial molar ratio of $MnSO_4:H_4P_2O_7$ is 1:2.



latter product before manganese dioxide formed. Plate X.V-C is the X-ray pattern of this material. This solid was analyzed, with the following results:

<u>Constituent</u>	<u>PerCent Found</u>	<u>Calculated PerCent for $\text{Mn}(\text{NH}_2)(\text{P}_2\text{O}_7)\cdot\text{H}_2\text{O}$</u>
Mn	17.59	17.75
N	9.20	9.06
P	19.95	20.05

The spherulites are therefore $\text{Mn}(\text{NH}_2)(\text{P}_2\text{O}_7)\cdot\text{H}_2\text{O}$.

The variation in pH accompanying the addition of ethylenediamine to a solution which contains manganous sulfate, pyrophosphoric acid, and ethylenediammonium hydrochloride in an initial 1:1:2 molar ratio is shown by Figure 39. The first precipitate, at pH 1.7 was again the nondescript product. At pH 5, this changed into small spherulites, which had the same appearance as those obtained in the previous reaction. The X-ray pattern of the final product (Plate X.V-D) also has the same general appearance as that given by the final product of the previous reaction. In view of these facts, the material is probably $\text{Mn}(\text{NH}_2)(\text{P}_2\text{O}_7)\cdot\text{H}_2\text{O}$.

The previous reactions in which a solution of metal ion is added to ethylenediammonium pyrophosphate yielded no pure products. The analogous reaction with manganous sulfate also fails to produce a single substance. The changes in pH which accompany the reaction are shown in

FIGURE 39

Variation of pH as 0.54 M en is added to a solution which contains 20.5 ml. of 0.74 M $\text{H}_4\text{P}_2\text{O}_7$, 19 ml. of 0.76 M MnSO_4 , 4 gm. of enH_2Cl_2 , and 50 ml. of H_2O . The initial molar ratios of $\text{MnSO}_4:\text{H}_4\text{P}_2\text{O}_7:\text{enH}_2\text{Cl}_2$ are 1:1:2.

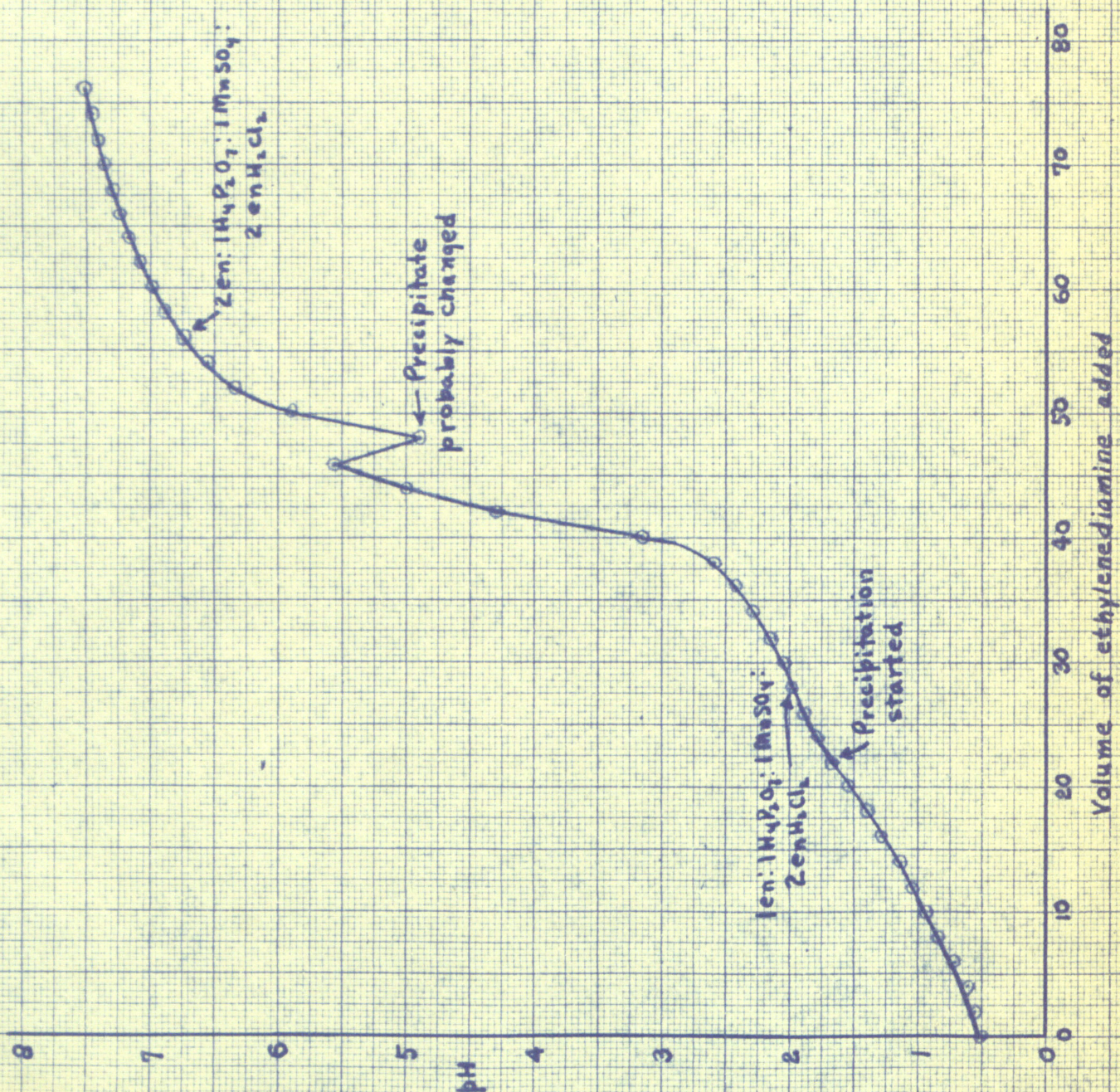


Figure 40. The material which precipitated was the non-descript appearing solid. This one proved to have the following composition: 25.40 per cent manganese, 4.51 per cent nitrogen, and 16.40 per cent phosphorus. The corresponding gram-atoms are 0.463 manganese, 0.322 nitrogen, and 0.529 phosphorus, or in ratios of 1.44 manganese : 1.00 nitrogen : 1.64 phosphorus. The figures indicate a mixture.

Figure 41 shows the changes which occur in conductance as this same reaction is carried out, i.e., adding manganous sulfate to ethylenediammonium pyrophosphate. The curve is again a straight line which gives little information about the reaction.

An experiment was carried out to determine if a suitable analytical precipitate is formed in this system. The reference material was again "reagent grade" tetrasodium pyrophosphate which had been recrystallized twice and dehydrated at 105°C. A 200 mg. sample of the pyrophosphate was dissolved in 125 ml. of water, and 5 ml. of 1:1 hydrochloric acid, 2.5 grams of manganous sulfate, and 6 grams of ethylenediammonium chloride added. The pH of the solution was then gradually raised to 6.5 by dropwise addition of 2:3 ethylenediamine. The precipitate was flocculent and gelatinous, remaining unchanged in appearance after being aged overnight. It first passed through, then clogged the

FIGURE 40

Variation of pH as 0.76 M MnSO_4 is added to 3 gm. of $\text{enH}_2(\text{P}_2\text{O}_7)$ dissolved in 75 ml. of water.

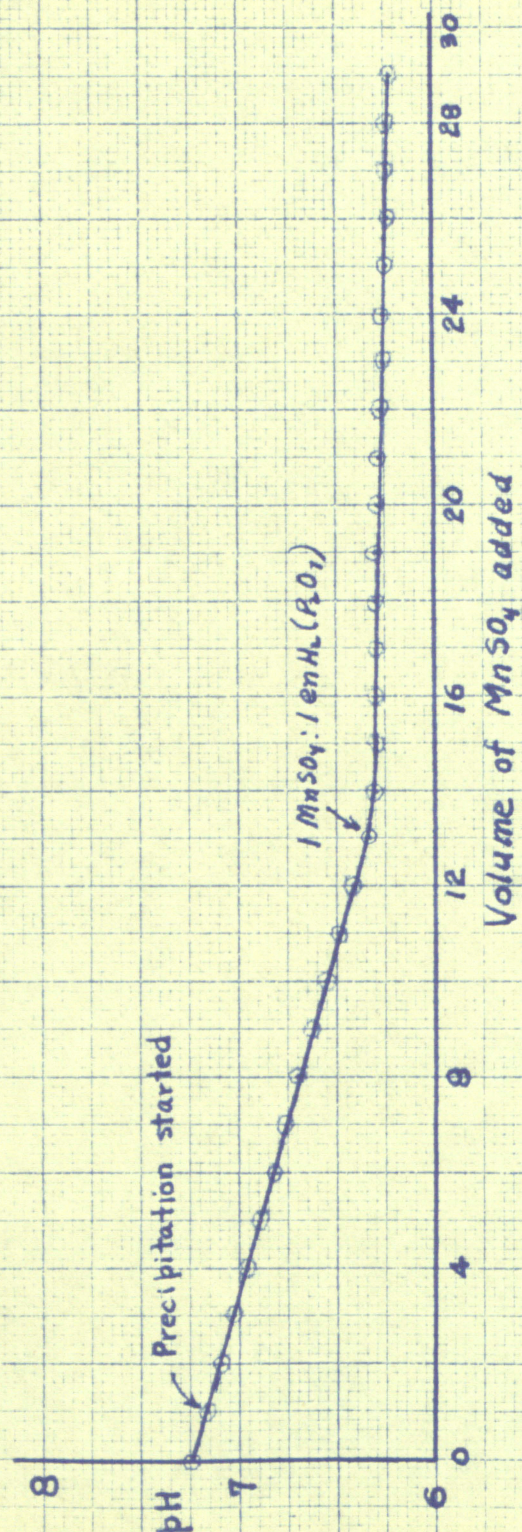
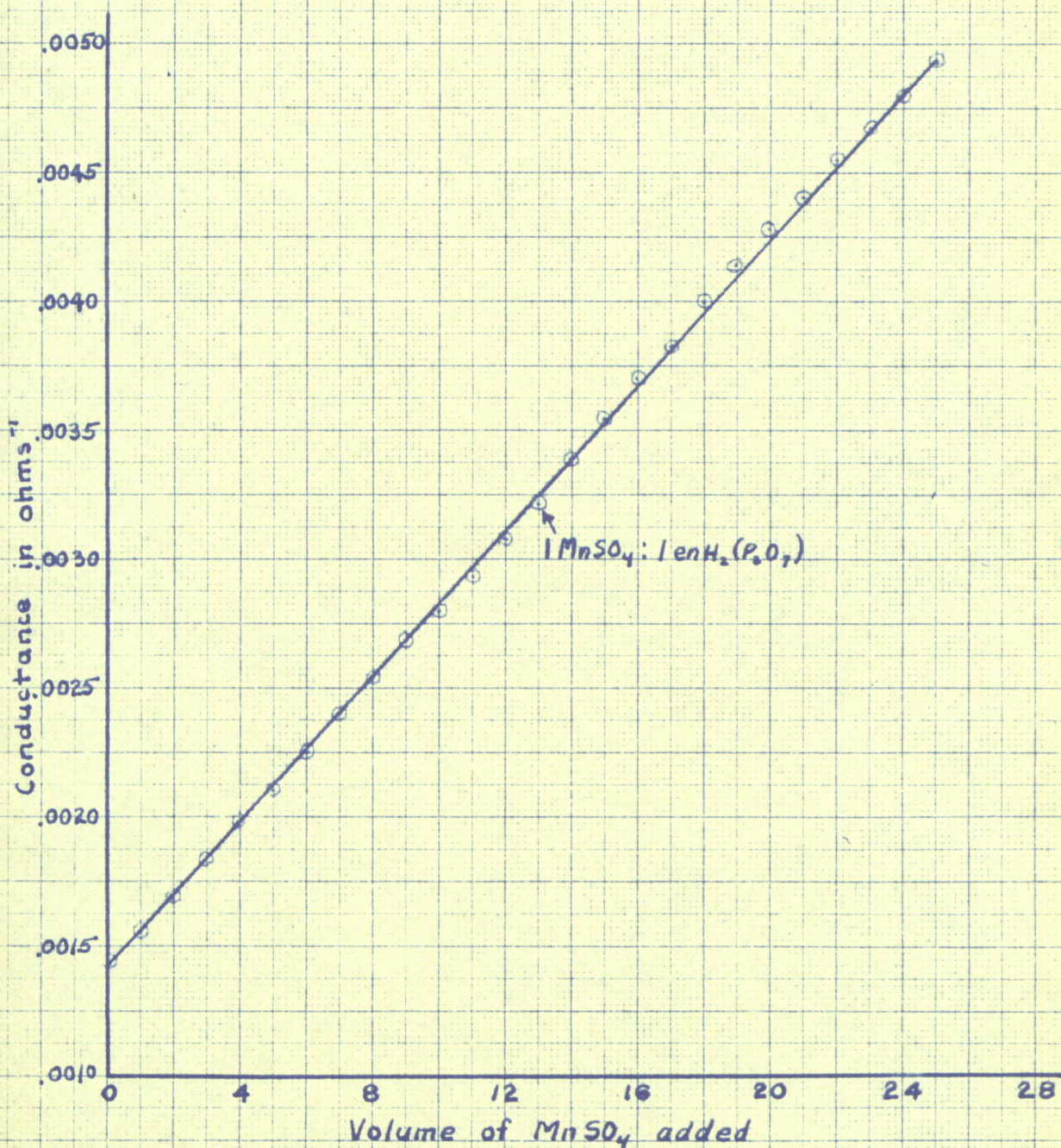


FIGURE 41

Changes in conductance as 0.76 M MnSO_4 is added to a solution of 3 gm. of $\text{enH}_2(\text{P}_2\text{O}_7)$ in 600 ml. of water.



pores of a "medium" sintered glass crucible. The product had all of the characteristics of a manganous pyrophosphate, and in no way resembled $\text{Mn}(\text{NH}_2)(\text{P}_2\text{O}_7) \cdot \text{H}_2\text{O}$.

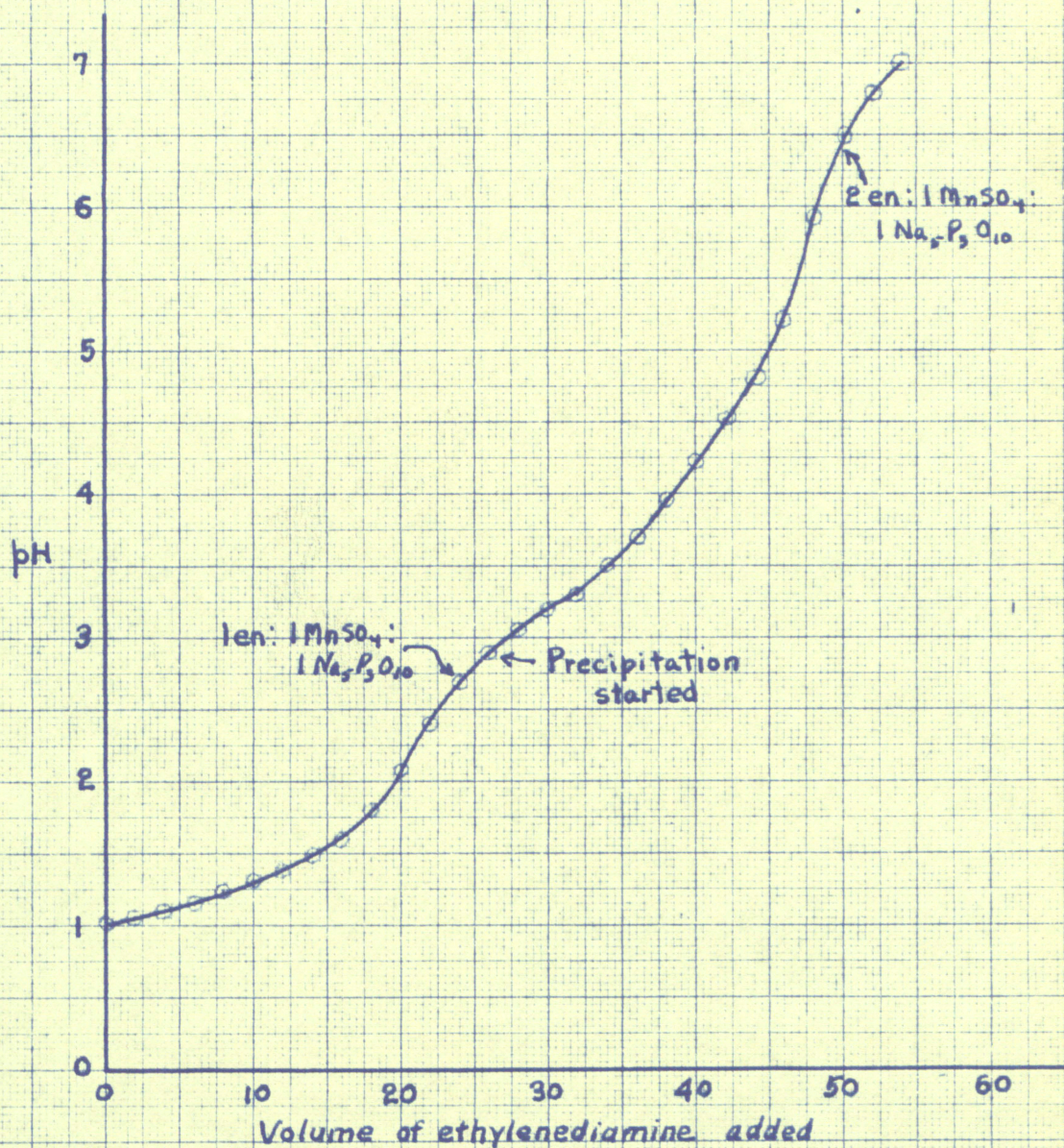
Exploratory Reactions

The procedure followed with manganese and the condensed phosphates was the same as that followed with the previous metal ions in the exploratory reactions. Fifteen millimoles of the sodium condensed phosphate were dissolved in 75 ml. of water. Dilute (1:1) hydrochloric acid was added until the pH had been lowered to about 10, then 15 millimoles of manganous sulfate solution were added. The resulting solution was then treated with ethylenediamine, added in 2 ml. portions.

Sodium Triphosphate: Figure 42 shows the variation in pH which accompanies the addition of ethylenediamine to the acidic sodium triphosphate-manganous ion solution. prepared as described above. Precipitation begins at pH 2.9. The product is amorphous in appearance, and apparently undergoes no changes during the reaction. It contains 13.10 per cent manganese, 8.18 per cent nitrogen, and 20.02 per cent phosphorus. These percentages correspond to gram-atoms of 0.239 manganese, 0.584 nitrogen, and 0.645 phosphorus or ratios of 1.00 manganese: 2.42 nitrogen: 2.70 phosphorus. These figures indicate a mixture; nevertheless, it is the

FIGURE 42

Changes in pH as 0.62 M en is added to a solution which contains 7.14 gm. of $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$, 20 ml. of 0.76 M MnSO_4 , and 75 ml. of water. The initial molar ratio of $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ to MnSO_4 is 1:1.



first triphosphate preparation obtained which contains ethylenediamine.

Sodium Trimetaphosphate: Ethylenediamine (0.58 M) was added to an acidic solution containing 4.85 grams $\text{Na}_3\text{P}_3\text{O}_9 \cdot \text{H}_2\text{O}$ and an equimolar quantity of manganous sulfate. No precipitation occurs below pH 7.

Sodium Tetrametaphosphate: When 0.58 M ethylenediamine was added to an acidic solution containing 7.20 grams of $\text{Na}_4\text{P}_4\text{O}_{12}$ and an equimolar quantity of manganous sulfate, precipitation begins at pH 1.1. The reaction is the same as the analogous tetrametaphosphate reaction with zinc and magnesium. The X-ray pattern of the product is back on Plate XIII-D (following p. 98), where it can be compared with the product from the zinc-tetrametaphosphate reaction. The two X-ray patterns are identical; therefore the products are the same, namely the solid which appears to be $\text{Na}_2(\text{enH}_2)(\text{P}_4\text{O}_{12}) \cdot 2\text{H}_2\text{O}$.

CHAPTER IX

STUDIES WITH NICKEL, CUPRIC, AND FERROUS IONS

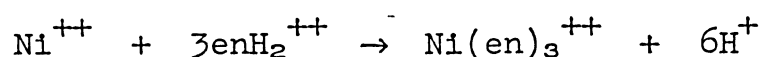
The ethylenediammonium ortho- and pyrophosphate systems of these divalent ions were investigated briefly to broaden the scope of this study. The reactions carried out with both ortho- and pyrophosphate were the addition of the metal sulfate to ethylenediammonium phosphate, and the more comprehensive reaction in which a solution containing metal sulfate and phosphoric acid in an initial 1:1 molar ratio is treated with ethylenediamine.

All reactions were carried out at 28-33°C, i.e., at the prevailing room temperature plus the heating effect from the magnetic stirrer. After being filtered the products were washed with two 25 ml. portions of alcohol, a like treatment with ether, then air dried.

Nickel Ethylenediammonium Phosphates

Orthophosphate: The changes in pH accompanying the addition of nickel sulfate to ethylenediammonium ortho-

phosphate are shown in Figure 43. The early additions of the Ni^{++} ion form a soluble complex, and a violet colored solution results. During this part of the reaction the fall in pH may be explained by the following type of reaction (assuming that Ni(en)_3^{++} is the soluble complex ion being formed):



When the pH reaches 6.1 precipitate forms, and the pH rises. This fact is explained by the soluble complex releasing ethylenediamine to form the double salt. During the formation of the precipitate (prisms), the color of the supernatant liquor passes from violet through blue to pale green. The solid which forms is also pale green. It gives the X-ray pattern of plate XVI-A and proved to have the following composition:

Constituent	PerCent Found	Gram-Atoms	Atomic Ratio	Calculated PerCent for $\text{Ni(enH}_2(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$
Ni	13.92	0.237	1.00	13.95
N	6.67	0.476	2.01	6.65
P	14.55	0.469	1.97	14.73
$\text{H}_2\text{O}(130^\circ\text{C})$	25.52	1.43	6.02	25.65

By acidimetric titration, the equivalent weight of phosphorus was 31.1, thus confirming the secondary orthophosphate formulation. The product is therefore $\text{Ni(enH}_2(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$.

FIGURE 43

Variation in pH as 0.73 M NiSO_4 is added to 50 ml. of 0.29 M $\text{enH}_2(\text{HPO}_4)$.

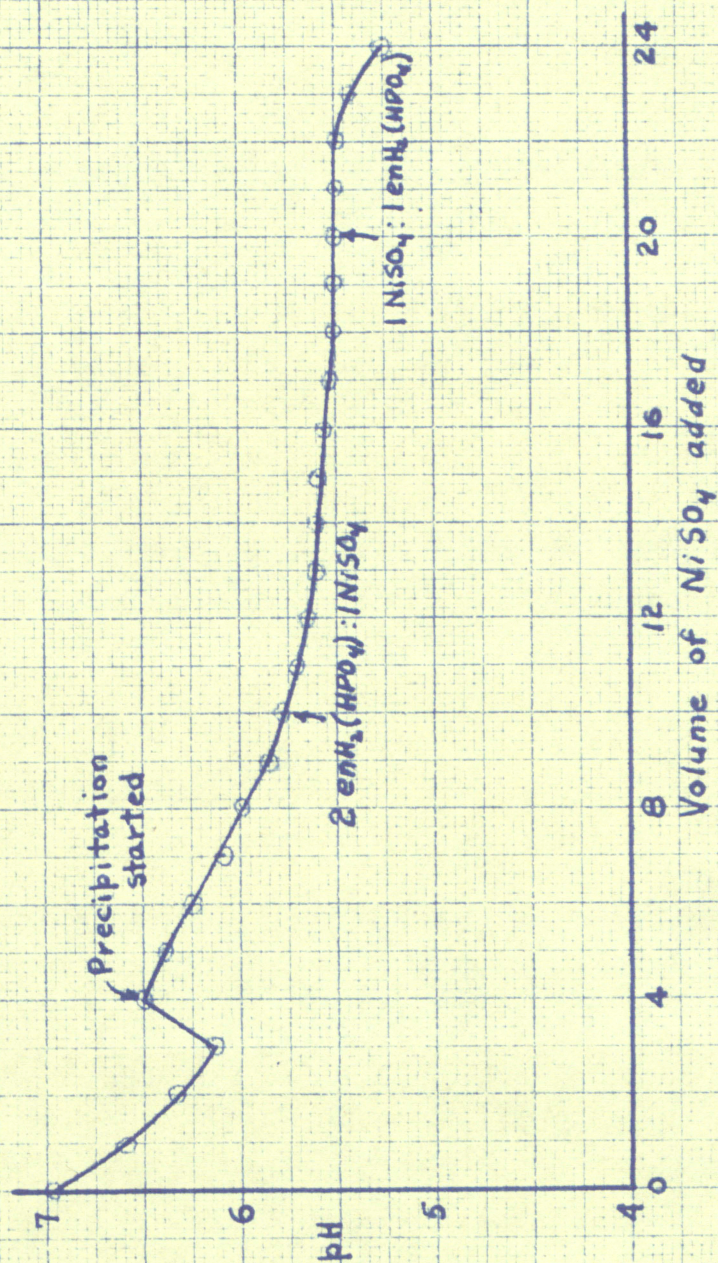
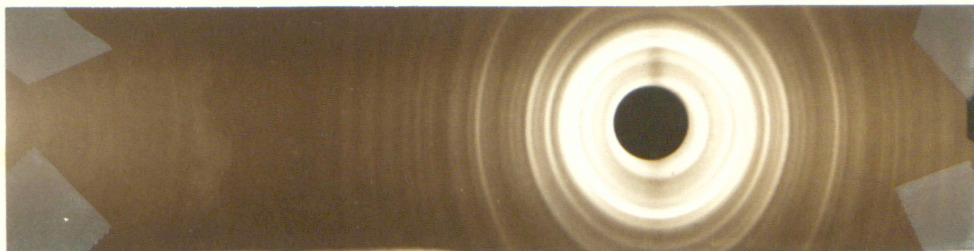


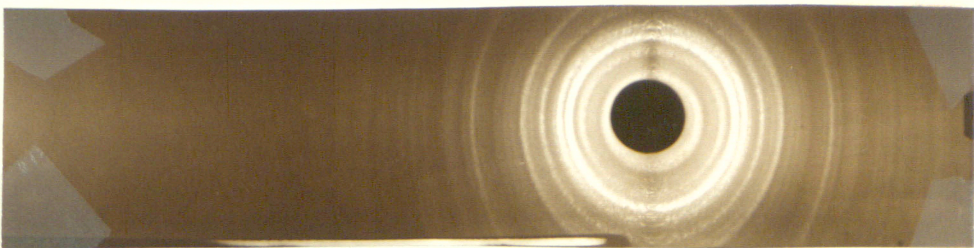
PLATE XVI



A



B



C



D

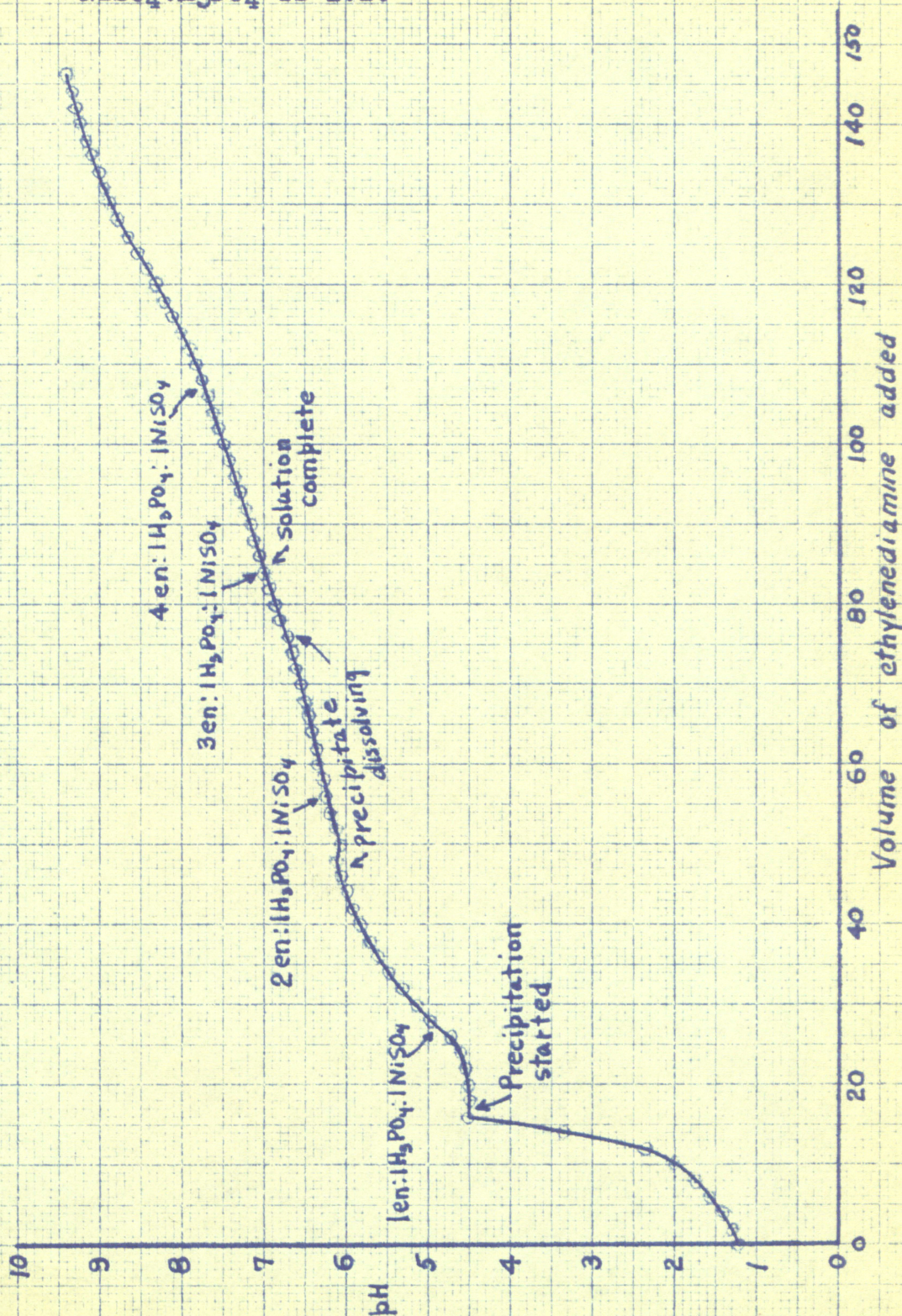
When a solution containing a 1:1 molar ratio of nickel sulfate to orthophosphoric acid is treated with ethylenediamine, the accompanying variation in pH is shown by Figure 44. Precipitation begins at pH 4.5, the solid appearing is amorphous as is demonstrated by its X-ray pattern (Plate XVI-B). At pH 4.7, some prisms begin to appear mixed with the amorphous material. This mixture persists until the precipitate begins to dissolve at pH 5.9, changing the color of the supernatant liquid from pale green to blue. As the ethylenediamine addition is continued, the color becomes purple. A slight drop in pH accompanies the solution process due to the liberation of hydrogen-ions since the ethylenediammonium ions incorporated in the precipitate become ethylenediamine when they are complexed.

The amorphous phase was isolated and analyzed. Its composition was 25.51 per cent nickel, 2.57 per cent nitrogen, and 14.16 per cent phosphorus. In gram-atoms, these are 0.437 nickel, 0.183 nitrogen, and 0.455 phosphorus, or they correspond to ratios of 2.39 nickel: 1.00 nitrogen: 2.48 phosphorus. These figures indicate a mixture.

The X-ray pattern of the mixture of amorphous material and prisms shows only the lines of $\text{Ni}(\text{H}_2\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Plate XVI-C). Therefore, it is the crystalline component of the mixture which exists between pH 4.7 and

FIGURE 44

Changes in pH as 0.54 M en is added to a solution which contains 21 ml. of 0.73 M NiSO_4 and 27 ml. of 0.55 M H_3PO_4 . The initial molar ratio of $\text{NiSO}_4:\text{H}_3\text{PO}_4$ is 1:1.



5.9 where the precipitate begins to dissolve.

Pyrophosphates: When nickel sulfate is added to a solution of ethylenediammonium pyrophosphate, the violet soluble complex forms first. Then as more nickel sulfate is added, a sticky gum appears which adheres to the glass and only partially crystallizes. The product was not studied further.

The addition of ethylenediamine to a solution containing nickel sulfate and pyrophosphoric acid in an initial 1:1 molar ratio produces the changes in pH recorded in Figure 45. Precipitation begins at pH 3.2. The first solid (pale green) which separates is again amorphous, as proven by its X-ray pattern (Plate XVI-D). Its composition is 20.11 per cent nickel, 4.51 per cent nitrogen, and 17.54 per cent phosphorus, or in terms of gram-atoms: 0.343 nickel, 0.323 nitrogen and 0.565 phosphorus. The atomic ratios are 1.06 nickel : 1.00 nitrogen : 1.75 phosphorus. The ratios are obviously non-integral numbers, and indicate a probable mixture.

When pH 6.1 is reached, the amorphous material changes into a crystalline mixture, half of which are prisms and the remainder are tablets. The X-ray pattern of this product (Plate XVII-A) showed only the lines of $\text{Ni}(\text{NH}_2)(\text{P}_2\text{O}_7) \cdot 4\text{H}_2\text{O}$. Therefore, both types of crystals were the same material in different crystalline habits. At pH 6.4 the

FIGURE 45

Changes in pH as 0.54 M en is added to a solution which contains 19 ml. of 0.80 M $\text{H}_4\text{P}_2\text{O}_7$, 21 ml. of 0.73M NiSO_4 , and 25 ml. of water. The initial molar ratio of NiSO_4 to $\text{H}_4\text{P}_2\text{O}_7$ is 1:1.

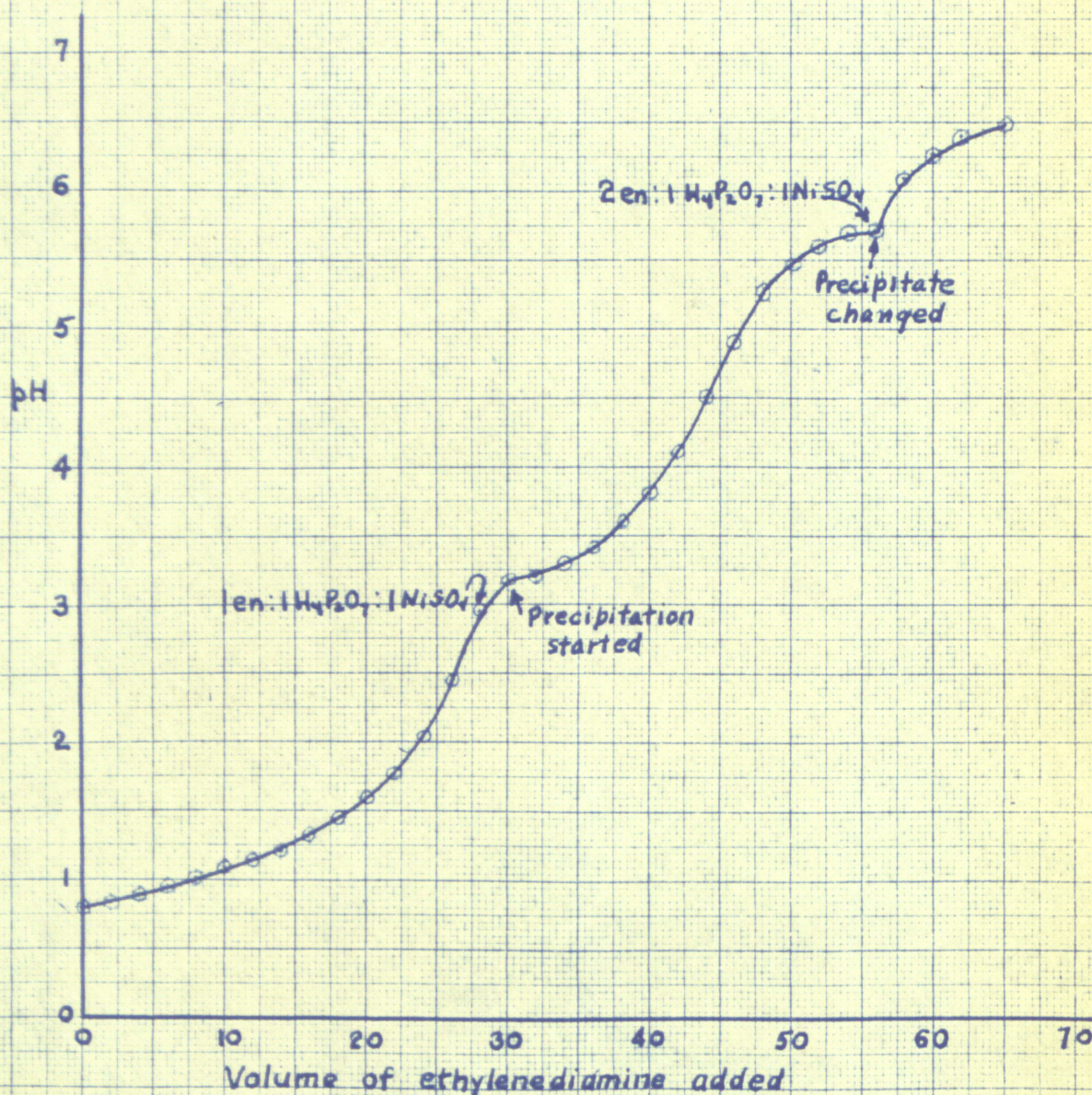
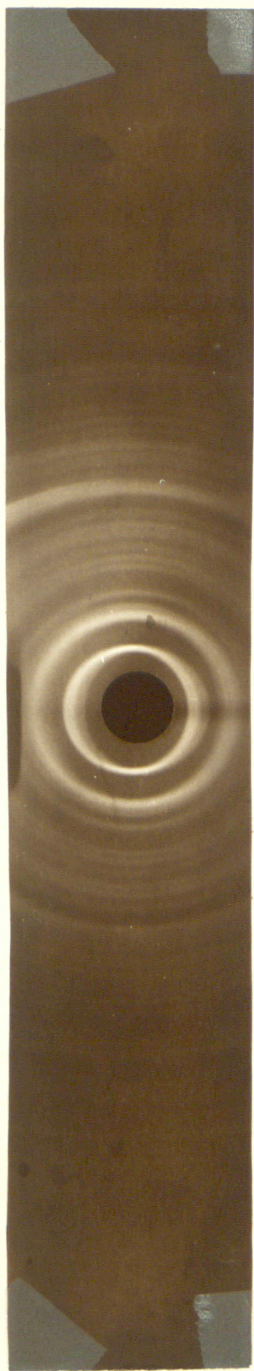
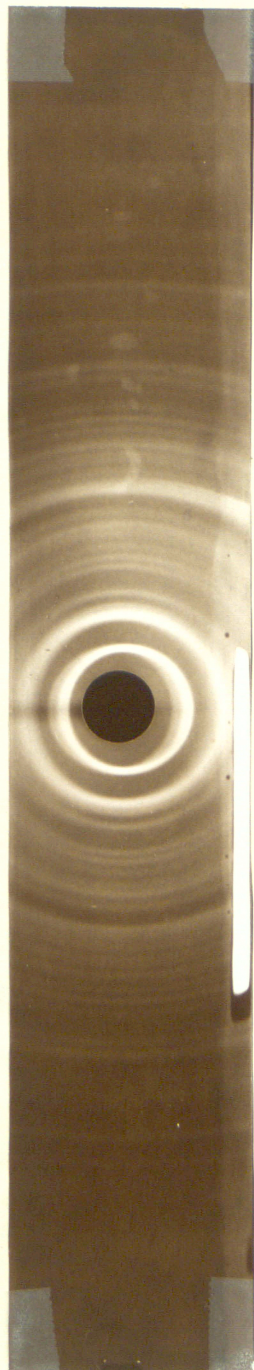


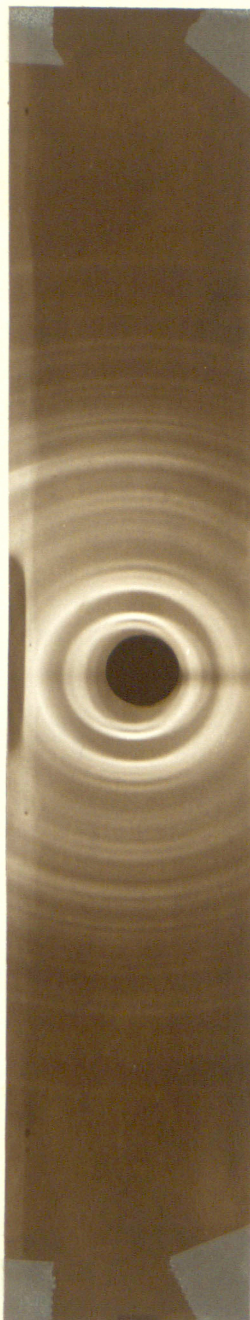
PLATE XVII



A



B



C

supernatant liquor has become blue, and the solid is slowly dissolving.

If the $\text{NienH}_2(\text{P}_2\text{O}_7) \cdot 4\text{H}_2\text{O}$ is completely dissolved by the addition of excess ethylenediamine, it can then be reprecipitated by adding dilute hydrochloric acid dropwise to the solution until all of the violet, then blue color is discharged. These apple-green crystals separate in the form of small prismatic spherulites. They give the X-ray pattern in Plate XVII-B, and the following analytical results:

Constituent	PerCent Found	Gram-Atoms	Atomic Ratio	Calculated PerCent for $\text{NienH}_2(\text{P}_2\text{O}_7) \cdot 4\text{H}_2\text{O}$
Ni	15.88	0.267	1.00	15.98
N	7.58	0.542	2.02	7.63
P	17.10	0.552	2.04	16.90
$\text{H}_2\text{O}(145^\circ\text{C})$	19.77	1.10	4.05	19.62

These data verify the formula $\text{NienH}_2(\text{P}_2\text{O}_7) \cdot 4\text{H}_2\text{O}$ for the product. Since the X-ray patterns of this preparation (XVII-B) and that for the original crystals at pH 6.1 are identical, the two solids are both $\text{NienH}_2(\text{P}_2\text{O}_7) \cdot 4\text{H}_2\text{O}$.

When the pH is raised above 6.4, i.e., to the point where the supernatant liquor is blue, but the solid has only partially dissolved, the product appears to be homogeneous when observed under the microscope. However, the crystals are no longer pure. The composition of a preparation obtained at pH 6.5 was:

Constituent	PerCent Found	Calculated PerCent For $\text{Ni enH}_2(\text{P}_2\text{O}_7) \cdot 4\text{H}_2\text{O}$
Ni	13.92	15.98
N	7.40	7.63
P	14.90	19.62

The X-ray pattern for this material (Plate XVII-C) shows both the lines of $\text{Ni enH}_2(\text{P}_2\text{O}_7) \cdot 4\text{H}_2\text{O}$ and also strong lines of some foreign substance. This fact supports the analytical data. The above percentages when translated to atomic ratios are 1.00 nickel : 2.25 nitrogen : 2.05 phosphorus. They are difficult to resolve into a satisfactory formula.

Copper Ethylenediammonium Phosphates

No pure compound was isolated from this system, in either the ortho- or pyrophosphate reactions.

Orthophosphate: The addition of 0.79 M copper sulfate to a 0.30 M solution of ethylenediammonium orthophosphate, $\text{enH}_2(\text{HPO}_4)$, causes changes in pH very much like those occurring in the analogous nickel reactions. The first few small additions of copper sulfate produce a rich violet solution, probably due to the formation of the Cu(en)_2^{++} ion. A drop in pH accompanies the development of this color. At pH 4.9, precipitation starts, and the pH goes up as the solid formed, and the deep color of the solution becomes light blue. Subsequent additions of copper sulfate then

gradually lower the pH. The turquoise blue solid was isolated at pH 4. It was nondescript in appearance. The results of chemical analysis are tabulated below under preparation A.

Analyses of Copper-Ethylenediamine-Orthophosphate Products

	Cu		N		P	
	Per Cent	Gram- Atoms	Per Cent	Gram- Atoms	Per Cent	Gram- Atoms
Preparation A	31.58	0.497	5.85	0.417	15.10	0.487
Preparation B	34.45	0.541	4.32	0.309	13.17	0.425

Ratios: A 1.19 Cu:1.00 N:1.16 P
 B 1.37 Cu:1.00 N:1.75 P

Preparation A yields the unusual X-ray pattern shown by Plate XVIII-A, characterized by the relatively few lines (10-12) as compared with previous patterns (30-40 lines). Figure 46 shows how the pH varies when a solution containing copper sulfate and orthophosphoric acid in an initial 1:1 molar ratio is reacted with ethylenediamine. A precipitate appears at pH 2.6. It is seemingly amorphous, and gradually changes into clumps of small anedral masses. Plate XVIII-B is the X-ray pattern given by this turquoise blue product, and the analytical findings are summarized as preparation B in the preceding table. Since the X-ray patterns of A and B are identical, and the chemical compositions differ, it seems likely that they are mixtures which contain some amorphous substance.

FIGURE 46

Changes in pH as 0.62 M en is added to a solution which contains 27 ml. of 0.55 M H_3PO_4 and 19 ml. of 0.79 M CuSO_4 . The initial molar ratio of CuSO_4 to H_3PO_4 is 1:1.

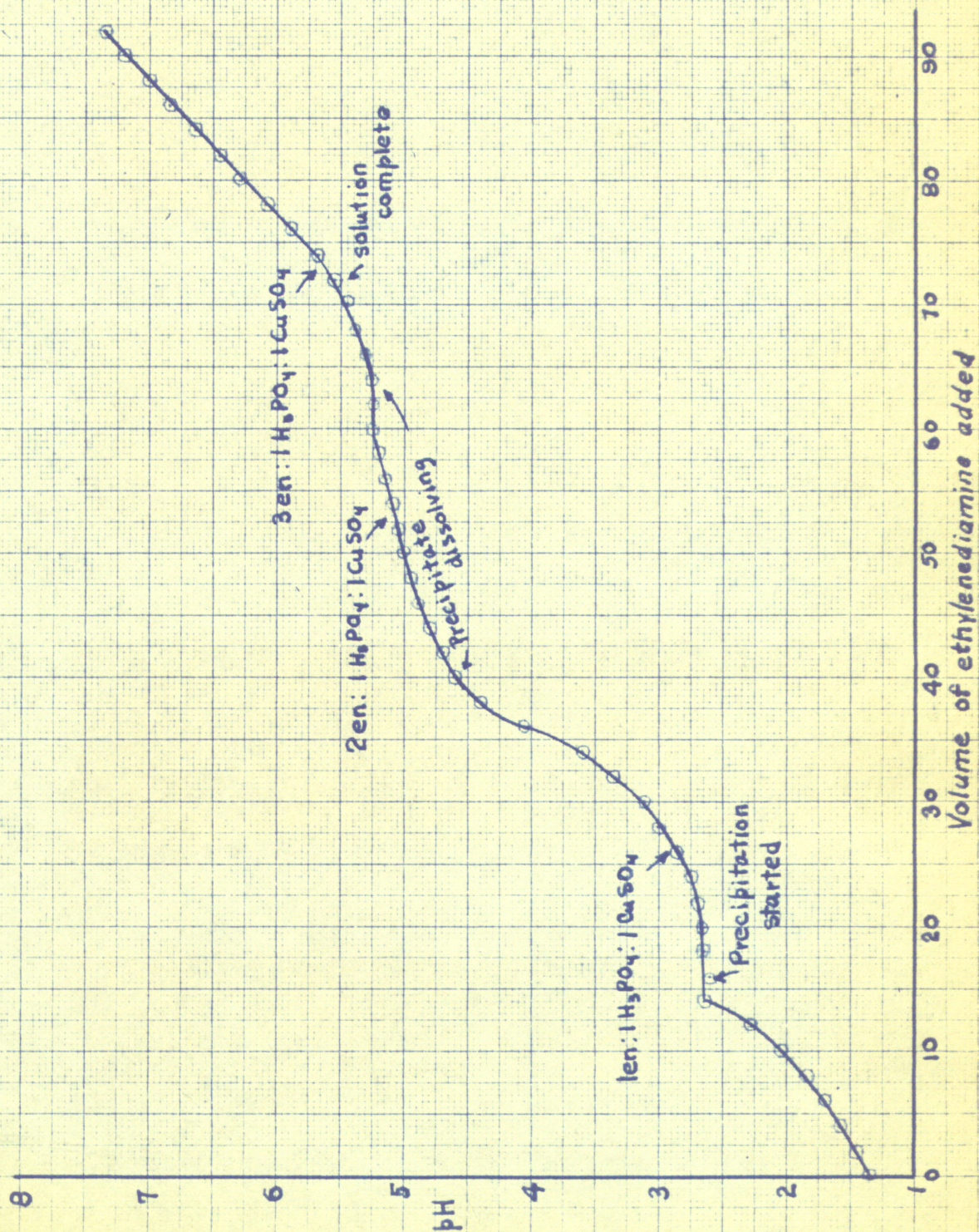
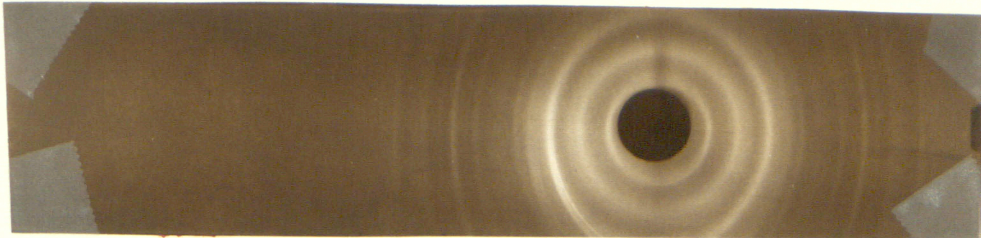
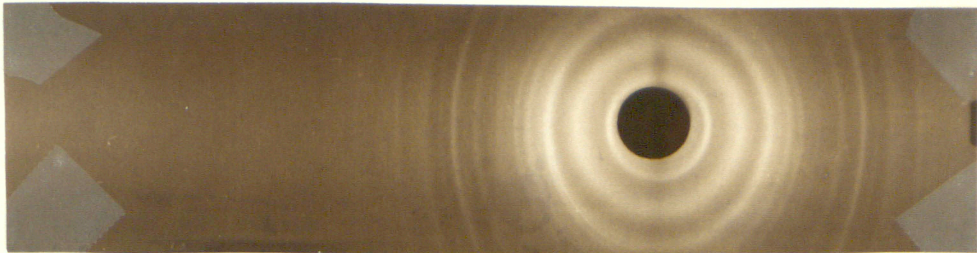


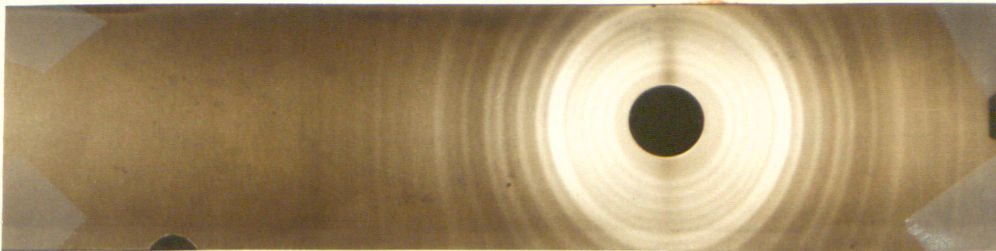
PLATE XVIII



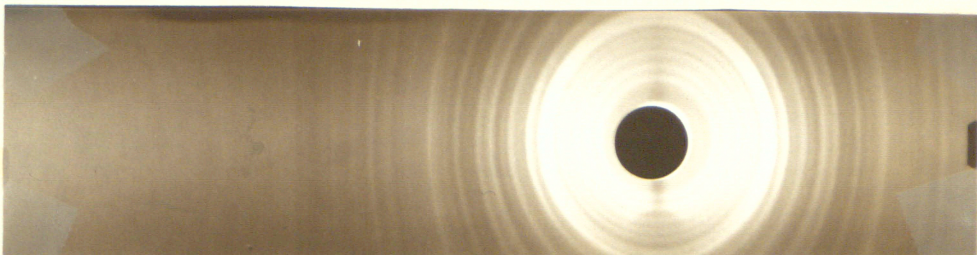
A



B



C



D

When the reaction is continued, the solid begins to dissolve at pH 4.7, with the formation of a violet solution.*

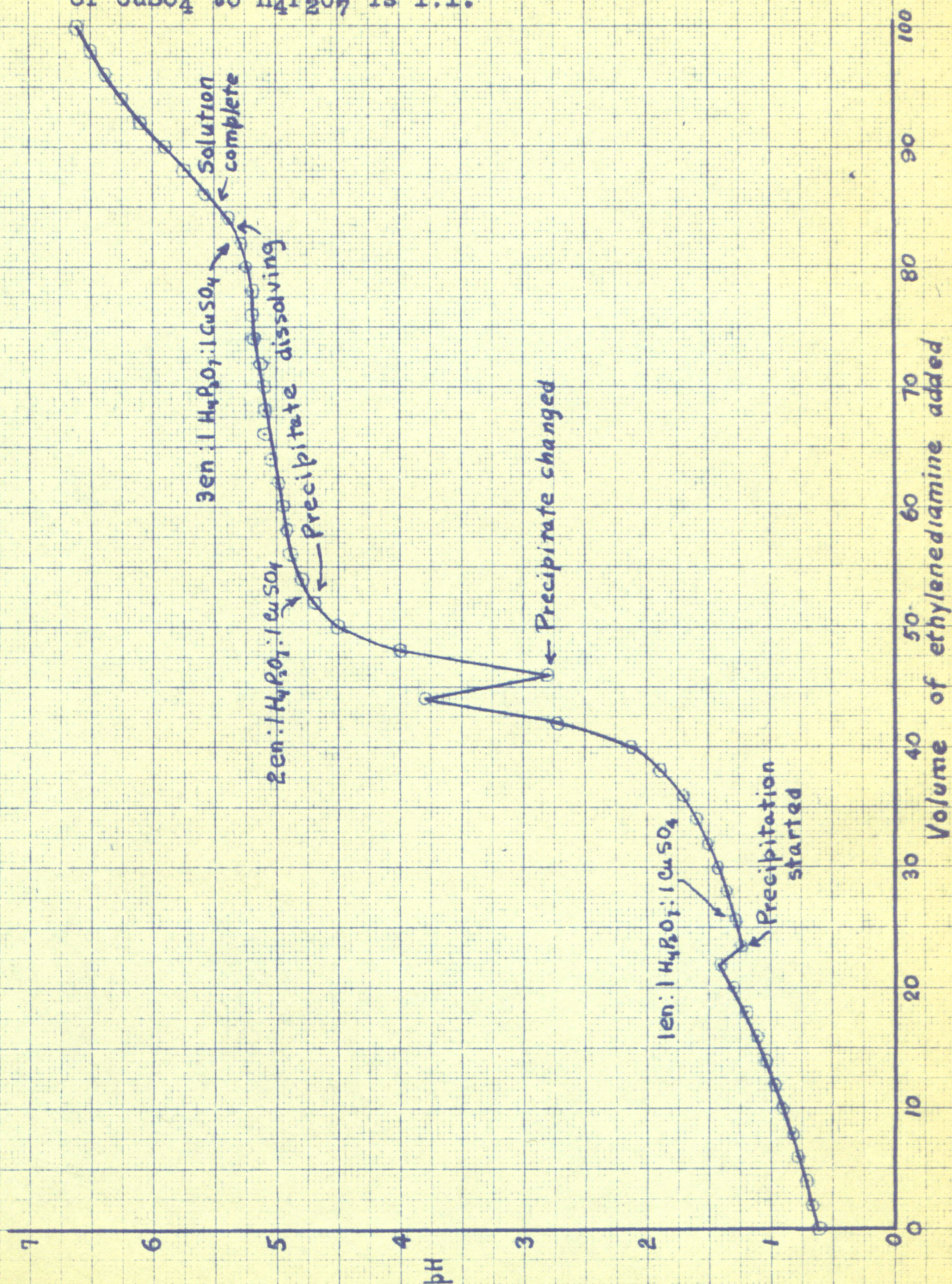
Pyrophosphates: The addition of copper sulfate to ethylenediammonium pyrophosphate led to the formation of a gum, which only partially crystallized. The phenomena observed in this reaction were the same as those which occurred when nickel sulfate was added to ethylenediammonium pyrophosphate (p. 134). This product was not studied further.

The changes in pH which accompany the addition of ethylenediamine to a solution which initially contains copper sulfate and pyrophosphoric acid in a 1:1 molar ratio are shown in Figure 47. Solid separates at pH 1.3;

* Since mixtures have been common in the lower pH ranges in previous systems, the occurrence of one here is not surprising. Furthermore, at the pH where many previous mixtures have crystallized into a pure phase, the present one starts to dissolve. In view of these facts, the failure to obtain a homogeneous product may be at least, partially explained.

FIGURE 47

Changes in pH as 0.62 M en is added to a solution prepared from 17 ml. of 0.90 M $\text{H}_4\text{P}_2\text{O}_7$, 19 ml. of 0.79 M CuSO_4 , and 35 ml. of water. The initial molar ratio of CuSO_4 to $\text{H}_4\text{P}_2\text{O}_7$ is 1:1.



its appearance is that of nondescript crystalline clumps. This light blue product will be referred to below as preparation A. When pH 3.8 is reached, the precipitate appears to change into clumps of acicular crystals. The latter product, also light blue in color, will be referred to as preparation B. At pH 4.7, the solid begins to dissolve, forming the red violet solution.

Examination of the X-ray patterns for preparation A (Plate XVIII-C) and preparation B (Plate XVIII-D) discloses that they are identical. Furthermore, their composition is approximately the same (See the following table).

	Cu		N		P	
	<u>Per Cent</u>	<u>Gram-Atoms</u>	<u>Per Cent</u>	<u>Gram-Atoms</u>	<u>Per Cent</u>	<u>Gram-Atoms</u>
Preparation A	25.48	0.401	4.68	0.335	17.73	0.572
Preparation B	25.61	0.403	4.53	0.323	17.87	0.577

Atomic Ratios: A 2.40Cu : 1.00N : 3.43P
 B 2.50Cu : 1.00N : 3.57P

The analytical data indicate a mixture.

Ferrous Ethylenediammonium Phosphates

Because of the inherent instability of the ferrous solutions, the divalent iron was introduced into the reaction by the direct addition of purified solid ferrous sulfate (p. 23). No pure compounds were isolated from either the

orthophosphate or the pyrophosphate work.

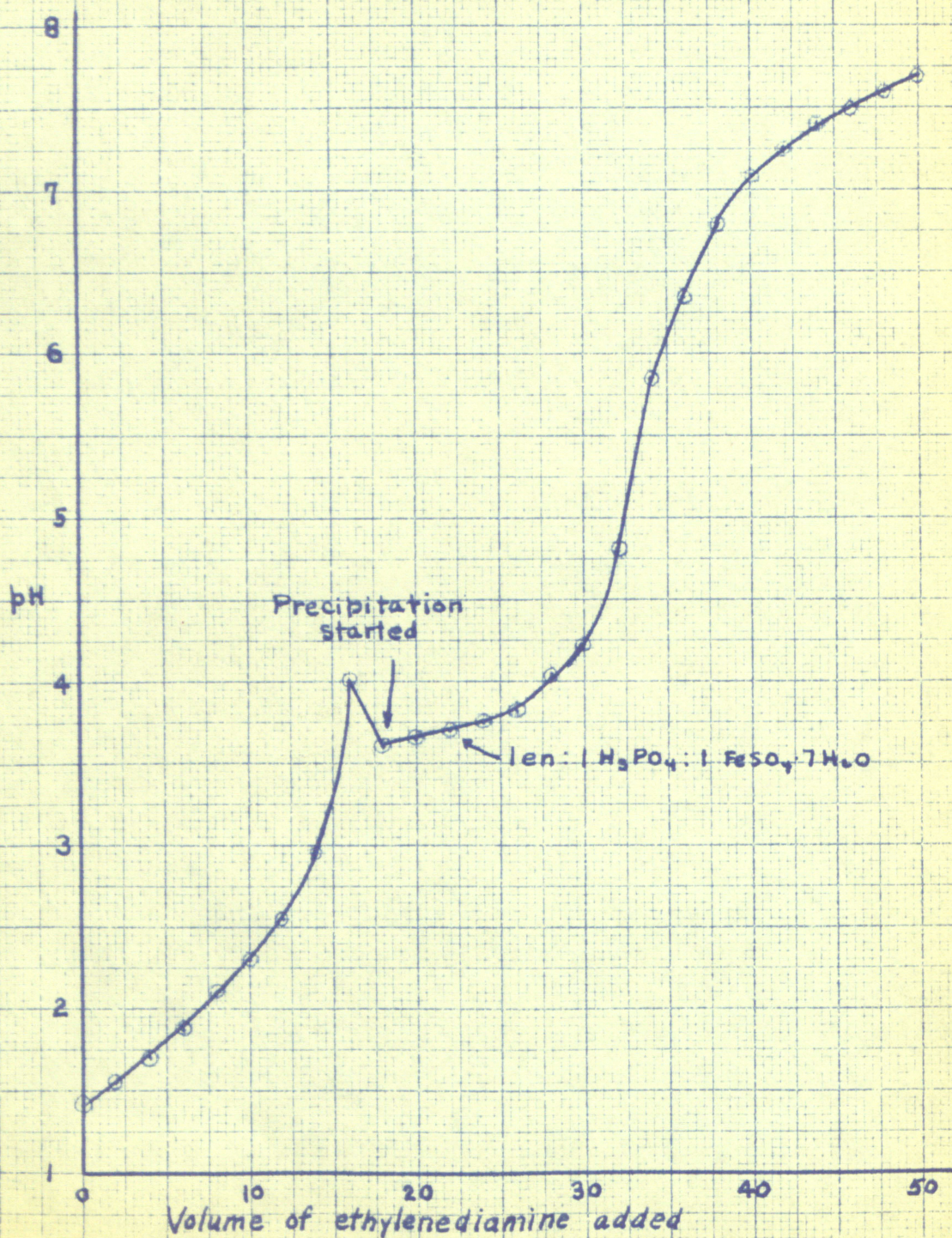
Orthophosphate: When 4.2 gram of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is added to a solution containing an equimolar quantity (2.4 gram) of ethylenediammonium orthophosphate, $\text{enH}_2(\text{HPO}_4)$, and the solution stirred vigorously, a light green (nearly white) amorphous precipitate forms. This initial solid gradually changes to acicular clumps. A color change to blue-green accompanies the solid transformation. Fifteen minutes was required for the precipitate to become homogeneous in appearance. The transformation was accompanied by a fall in pH from 6.95 to 3.85. A drop of this magnitude usually indicates the formation of a tertiary orthophosphate. The product was filtered as rapidly as possible, air-dried briefly, then stored over calcium chloride and sodium hydroxide. The preparation contained 20.42 per cent ferrous iron, 0.69 per cent nitrogen and 12.38 per cent phosphorus. The corresponding gram-atoms are 0.366 iron and 0.399 phosphorus, or a ratio of 1.00 iron to 1.09 phosphorus. This particular preparation is probably a mixture containing both ferrous and ferric iron. The first precipitate may be a ferrous tertiary orthophosphate, whose ferrous content is partially oxidized. The equivalent weight of phosphorus was found to be 15.3 indicating a tertiary orthophosphate. The cations and anions do not balance: Fe^{++} (0.366) divided by PO_4^{-3} (0.399) does not equal 1.5.

Figure 48 shows the changes in pH which accompany the addition of ethylenediamine to a solution containing ferrous sulfate and orthophosphoric acid initially in a 1:1 molar ratio. An amorphous tan solid forms at pH 3.00. Shortly thereafter, this material begins to change into small acicular spherulites. The crystals have the same appearance as the product of the previous reaction. The color of the solid gradually darkens to blue-green, and the spherulites increase in number as the reaction continues. However, the amorphous material does not disappear, and the final product is still a mixture when the reaction was stopped. The small amount of ethylenediamine required to reach pH 7.7 (50 ml. of 0.5 M solution), as compared with (100 ml.) in all the previous orthophosphate reactions, seems to indicate that the ethylenediamine took little part in the formation of the solid.

Pyrophosphates: Ethylenediamine was added to pyrophosphoric acid until the pH reached 8. Then 3 grams of ferrous sulfate was added slowly and with vigorous stirring. There was only a slight change in the pH (to 7.8) during a 15 minute period. At the end of this time, the product appeared to be homogeneous, - in the form of rhombohedra, occurring singly and in spherulite clusters. The product was filtered rapidly, washed with alcohol and ether, air-dried for 20 minutes, then stored over calcium chloride and

FIGURE 48

Variation in pH as 0.58 M en is added to a solution prepared from 27 ml. of 0.55 M H_3PO_4 , 4.20 gm. of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and 25 ml. of water. The initial molar ratio of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to H_3PO_4 is 1:1.



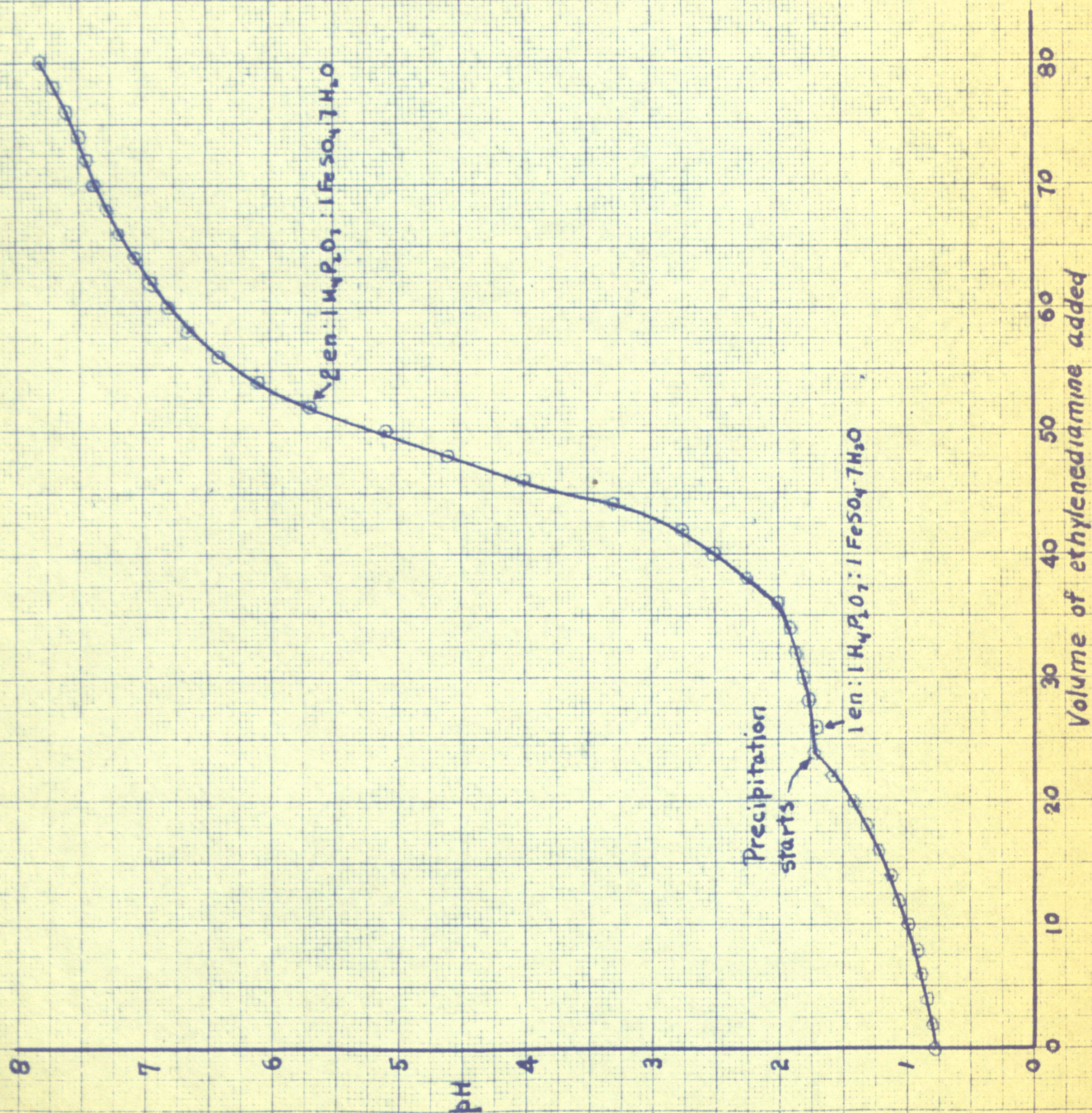
sodium hydroxide. The crystals were buff colored, and underwent no changes in color during the filtering operation. The material was found to contain 13.34 per cent ferrous iron, 8.60 per cent nitrogen, and 17.22 per cent phosphorus. In gram-atoms, the figures become 0.239 iron, 0.618 nitrogen, and 0.553 phosphorus, or atomic ratios of 1.00 iron : 2.57 nitrogen : 2.32 phosphorus. There is a satisfactory cation-anion balance: $\text{Fe}^{++} (0.239) + \text{enH}_2^{++} (0.309) = 0.548$; as compared with $0.553 \text{P}_2\text{O}_7^{-4}$, therefore very little oxidation from ferrous to ferric iron has occurred. However, the data lead to the conclusion that the preparation is a mixture. The mixture probably contains a ferrous ethylenediammonium pyrophosphate whose behavior toward air is similar to ferrous ethylenediammonium sulfate.

The pH changes which occur when ethylenediamine is added to a solution containing ferrous sulfate and pyrophosphoric acid in a 1:1 molar ratio, are shown in Figure 49. A gray precipitate is present over the pH range 2.5-4.0. It slowly becomes lighter until at about pH 5.5 it is faintly yellow. Both products were gelatinous and non-descript in appearance. Attempts were made to isolate each of the products. However, both of the finely divided materials clog the filter and undergo color changes to olive drab during the filtration.

The foregoing information, although sketchy,

FIGURE 49

Changes in pH as 0.58 M en is added to a solution which contains 19.7 ml. of 0.76M $\text{H}_4\text{P}_2\text{O}_7$, 4.20 gm. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and 35 ml. of water. The initial molar ratio of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to $\text{H}_4\text{P}_2\text{O}_7$ is 1:1.



indicates that a study of the ferrous ethylenediammonium phosphates is not a simple matter. It could well become the subject for an entire investigation. The reactions in such an investigation should probably be carried out under an inert atmosphere, and should also be accompanied by a study of the ferric ethylenediammonium phosphates in order to clarify the results.

CHAPTER X

X-RAY DIFFRACTION PATTERNS OF NEW MATERIALS

The spacings and relative intensities of the lines of the X-ray patterns given by the new materials isolated in the present investigation are tabulated on the following pages.

All measurements were made on films exposed in the large camera (114.6 mm. diameter). The accuracy of the calculations was checked against a pattern obtained for sodium chloride. This comparison is tabulated below.

<u>d</u> (observed)	<u>d</u> (literature)	<u>I/I₀</u> (observed)	<u>I/I₀</u> (literature)
3.23	3.25	W	W
2.80	2.81	VS	VS
2.00	1.99	S	S
1.70	1.70	W	W
1.62	1.63	M	M
1.40	1.41	M	M
1.29	1.29	VW	VW
1.26	1.26	M	M
1.15	1.15	M	M
1.08	1.08	VW	VW

d = spacing of lines

I/I₀ = relative intensity of lines

VVS = very very strong

VS = very strong

S = strong

M = medium

W = weak

VW = very weak

VVW = very very weak

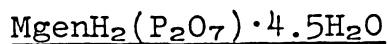
D = diffuse

MgenH₂(HPO₄)₂·6H₂O

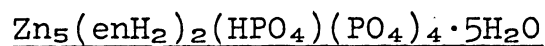
d	I/I ₀
7.31	S
6.97	M
6.26	S
5.81	S
5.44	S
4.95	S
4.66	S
4.09	VVS
3.83	W
3.69	VS
3.53	M
3.34	W
3.12	VS
3.00	W
2.86	M
2.82	W
2.72	W
2.65	VS
2.50	VW
2.46	W
2.37	W
2.28	W
2.22	W
2.16	VW
2.08	W
2.01	W
1.95	S
1.87	D
1.81	VVW
1.78	VVW
1.74	M
1.71	M
1.67	VW
1.57	VW
1.54	D
1.49	W
1.47	VVW
1.42	D
1.38	VVW
1.36	VVW
1.35	W
1.32	W
1.30	VVW
1.28	W
1.26	W
1.24	W
1.19	VW
1.17	D

The Product from High
pH Region of Magnesium-
Ethylenediammonium-
Orthophosphate System

d	I/I ₀
9.77	VVS
5.33	M
4.80	W
4.31	VS
3.58	M
3.39	W
3.21	S
3.09	W
2.81	M
2.67	M
2.39	S
2.22	W
2.14	W
1.92	VW
1.81	D
1.72	D
1.64	VW
1.60	VW
1.53	D
1.43	VW
1.40	W
1.33	D



d	I/I ₀
11.5	VVS
7.14	M
6.26	M
5.42	M
5.02	S
4.65	W
4.33	W
3.92	S
3.69	S
3.53	W
3.41	W
3.28	W
3.12	M
3.01	M
2.92	M
2.81	M
2.72	M
2.63	M
2.55	VVW
2.49	M
2.38	M
2.32	VVW
2.26	VVW
2.25	VVW
2.11	W
2.03	W
1.98	VW
1.93	W
1.80	D
1.71	W
1.64	M
1.60	VW
1.56	VW
1.52	VW
1.47	VW
1.38	VW
1.35	D
1.31	D
1.27	VVW



d	I/I ₀
10.3	W
8.59	S
7.31	S
6.28	VW
5.68	M
5.14	VW
4.86	VW
4.44	M
4.06	M
3.87	M
3.77	M
3.35	VS
3.27	VS
3.13	W
3.06	M
2.97	W
2.85	VW
2.73	M
2.67	M
2.62	M
2.57	M
2.41	VVW
2.30	M
2.19	W
2.10	VVW
2.03	D
1.97	VVW
1.93	NNW
1.88	M
1.83	M
1.77	VVW
1.73	VVW
1.67	D
1.61	W
1.57	VVW
1.52	W
1.48	VVW
1.45	VVW
1.44	W
1.42	VVW
1.40	VVW
1.37	W
1.32	W
1.29	VW

Zn₂enH₂(PO₄)₂

d	I/I ₀
7.14	VS
6.71	VS
5.62	M
5.10	VVW
4.46	M
4.08	S
3.77	S
3.40	VS
3.27	VS
3.09	M
2.72	S
2.67	W
2.62	W
2.56	W
2.49	W
2.30	M
2.19	M
2.13	VVW
2.05	VVW
1.98	VVW
1.95	VVW
1.87	M
1.83	M
1.65	M
1.65	W
1.61	W
1.58	VVW
1.52	W
1.47	VVW
1.43	W
1.40	VW
1.36	W
1.31	VW
1.29	VVW
1.26	VVW
1.24	VVW
1.23	VVW
1.21	W

Zn(enH₂)₂(PO₄)₂

d	I/I ₀
8.63	S
7.56	VVS
5.64	VW
4.95	S
4.74	W
4.27	M
3.92	M
3.77	M
3.53	VS
3.37	VW
3.20	VS
3.04	VS
2.88	W
2.72	M
2.58	M
2.39	W
2.28	W
2.19	VW
2.08	D
1.99	W
1.91	W
1.85	W
1.76	VW
1.70	M
1.64	VVW
1.60	W
1.53	VW
1.48	VW
1.43	W
1.41	VVW
1.39	VW
1.36	VVW
1.34	W
1.31	VW
1.29	VW
1.27	VW
1.25	VW

Ni₁₀H₂(HPO₄)₂·6H₂O

d	I/I ₀
8.27	W
7.31	M
5.81	W
5.47	W
4.98	S
4.67	M
4.42	VW
4.13	VVS
3.90	VW
3.71	S
3.53	M
3.40	VW
3.11	S
2.99	W
2.85	W
2.67	S
2.48	M
2.36	M
2.28	VW
2.21	W
2.09	VW
2.02	VW
1.94	M
1.85	W
1.79	VW
1.74	W
1.70	W
1.67	VW
1.60	VW
1.57	W
1.54	VW
1.49	W
1.42	D
1.34	VW
1.33	VW
1.27	VW
1.26	VW
1.24	VW

Ni₁₀H₂(P₂O₇)·4H₂O

d	I/I ₀
10.9	VS
7.16	S
6.39	M
5.72	M
4.72	M
4.42	M
4.13	W
3.83	M
3.65	M
3.41	W
3.08	D
2.85	VW
2.74	VW
2.67	VW
2.59	W
2.44	VW
2.35	W
2.25	VW
2.08	W
2.01	W
1.87	VW
1.79	VW
1.65	VW
1.62	VW
1.56	VW

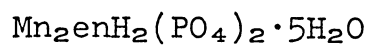
$\text{Na}_2\text{H}_2(\text{P}_4\text{O}_{12}) \cdot 2\text{H}_2\text{O}$
(Tentative Identification)

d	I/I ₀
7.44	S
6.42	VS
5.98	VW
4.81	VVW
4.19	S
3.93	S
3.72	S
3.52	S
3.34	VS
3.21	W
2.97	M
2.81	W
2.68	W
2.56	M
2.45	VW
2.38	VW
2.32	VW
2.28	VW
2.25	VW
2.12	M
2.08	W
1.94	W
1.87	D
1.70	VW
1.62	W
1.59	VVW
1.55	VVW
1.48	VW
1.42	VVW
1.39	VW
1.32	VVW
1.28	VW
1.26	VW
1.24	VW

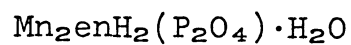
The X-ray facilities on the campus are not adequate for obtaining the patterns of the manganese-containing preparations from which spacings can be accurately calculated. However, Dr. A. Mabis of the Procter and Gamble Company generously provided the patterns. Chromium K_{α} radiation was the X-ray source used.



d	I/I ₀
12.39	VW
10.77	VVS
8.60	M
5.21	M
3.82	S
3.66	S
3.44	W
3.32	VW
3.16	M
3.08	M
2.87	VS
2.76	W
2.69	W
2.54	M
2.46	VVW
2.35	VVW
2.29	VVW
2.21	VVW
2.15	W
1.93	D
1.67	VW
1.62	VW



d	I/I ₀
12.2	VVS
9.57	VW
6.01	VW
5.53	VW
4.65	VW
4.20	M
3.73	VVW
3.51	VVW
3.18	S
3.02	VVW
2.85	S
2.74	S
2.58	VW
2.47	W
2.34	W
2.29	W
2.11	W
2.02	D
1.88	VVW
1.85	W
1.77	VVW
1.71	VVW
1.65	VW'
1.63	VW
1.59	VVW
1.58	VVW



d	I/I ₀
18.1	VW
9.77	VS
7.12	VW
6.50	S
5.23	VVW
4.77	VVW
4.35	S
3.88	D
3.54	M
3.36	VVW
3.12	VVW
2.95	VVW
2.83	M
2.66	VW
2.61	VW
2.54	VW
2.38	W
2.26	D
2.18	W
1.83	VW
1.72	VW

CHAPTER XI

SUGGESTIONS FOR FUTURE RESEARCH

The present investigation could be extended in many directions. Perhaps the most obvious is a study of ethylenediammonium phosphate double salts of other divalent ions such as cobalt, cadmium, and the alkaline earth metals. Another possibility is to change to metallic ions of different valence, such as the univalent ions lithium or silver, or trivalent ions such as the chromic or ferric ions.

Other diamines might be studied relative to the possible production of double salts such as those described here. An investigation of metal propane- or butanediammonium phosphates would be a logical extension. The valence of the amine could also be changed; furthermore, both monoamines and triamines might form interesting double salts.

Such studies could also be carried out with the higher condensed phosphates, the triphosphates, the tri- or tetrametaphosphates.

It therefore appears that the present investigation has merely initiated a much broader field of study.

CHAPTER XII

SUMMARY

1. The object of this investigation was to study the chemistry of a series of metal-ethylenediammonium-ortho- and pyro-phosphate systems.

2. The reactions were carried out titration style with standard solutions, and were followed with continuous pH measurements.

3. The composition of the products was established by chemical analysis, and the preparations were characterized by their X-ray diffraction patterns.

4. Magnesium-ethylenediammonium-orthophosphate system: The compound $\text{Mg}_n\text{H}_2(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ was found to precipitate over the pH range 4.5-8. In the presence of excess magnesium ion and above pH 8.2, it changed to $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. The product obtained from excess phosphate, and/or excess ethylenediamine had a constant composition, but a non-integral ratio of the atoms.

5. In the magnesium-ethylenediammonium-pyro-phosphate system, $\text{Mg}_n\text{H}_2(\text{P}_2\text{O}_7) \cdot 4.5\text{H}_2\text{O}$ was found to precipitate

over a wide range of conditions above 3.5.

6. Two products were established, and indications for the existence of a third were found in the zinc-ethylenediammonium-orthophosphate system. $\text{Zn}_2\text{enH}_2(\text{PO}_4)_2$ appears over a wide range of conditions. In the absence of excess zinc ions, a solid forms at pH 2.8. It appears to have the composition $\text{Zn}_5(\text{enH}_2)_2(\text{HPO}_4)(\text{PO}_4)_4 \cdot x\text{H}_2\text{O}$, where x may be 4 or 5. When excess zinc ion is present, the first product (pH 2.8) is $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. If $\text{Zn}_2\text{enH}_2(\text{PO}_4)_2$ is stirred with a 3M solution of ethylenediamine for about 20 minutes $\text{Zn}(\text{enH}_2)_2(\text{PO}_4)_2$ forms.

7. No pure product was isolated from the zinc-ethylenediammonium-pyrophosphate system. All preparations seemed to be mixtures of $\text{Zn}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ and some other material, possibly $\text{ZnenH}_2(\text{P}_2\text{O}_7) \cdot x\text{H}_2\text{O}$.

8. The manganous-ethylenediammonium-orthophosphate system is not so well defined. $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ appears in the pH range 3-5 in the presence of either excess manganous or excess orthophosphate ions. In the presence of excess orthophosphate, $\text{Mn}_2\text{enH}_2(\text{HPO}_4)_3 \cdot \text{H}_2\text{O}$ exists between pH 4.5 and 6.5. $\text{Mn}_2\text{enH}_2(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ appears under a wide variety of conditions over a pH range 4-7 or 8. Hydrated manganese dioxide appears in all cases above pH 8.

9. The product established in the manganous-ethylenediammonium-pyrophosphate system was $\text{MnenH}_2(\text{P}_2\text{O}_7) \cdot \text{H}_2\text{O}$.

It exists under varied conditions between pH 5 and 8. Mixtures were found below this pH range; at higher pH values, manganese dioxide appears.

10. A brief investigation of the nickel ethylenediammonium ortho- and pyrophosphate systems established the formation of $\text{Ni}(\text{H}_2\text{NCH}_2\text{CH}_2\text{N}(\text{H}_2\text{CH}_2)_2)_2(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{H}_2\text{NCH}_2\text{CH}_2\text{N}(\text{H}_2\text{CH}_2)_2)_2(\text{P}_2\text{O}_7) \cdot 4\text{H}_2\text{O}$. In similar brief investigations with cupric and ferrous metal ions, no pure compounds were isolated.

11. Exploratory reactions with some of the condensed phosphates are described.

12. All attempts to produce any of the foregoing compounds under analytical conditions as a quantitative precipitate for phosphorus failed. The presence of an appreciable concentration of phosphate ion appears to be necessary for the formation of the double salts.

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APPENDIX

Phosphates of Hydrazine

Introduction and History

Hydrazine, H_2NNH_2 , is structurally intermediate between ammonia and the diamines. It shows a chemical resemblance to both in that the aqueous solutions are basic in nature. Its ionization constants are: $K_1 = 8.5 \times 10^{-7}$, $K_2 = 8.9 \times 10^{-16}$. On the other hand, its behavior differs from that of the diamines in that hydrazine usually reacts as a monoprotic base. Salts in which hydrazine shows its dibasic property can be obtained only from strongly acidic solutions, whereas the only type of salts isolated with the diamines contained the dibasic diamine ion. Even aliphatic alkylenediammonium salts which were isolated from strong alkaline solutions contained two equivalents of acid.

Only two of the possible phosphates of hydrazine are described in the literature. Both are primary orthophosphates, namely $\text{N}_2\text{H}_6(\text{H}_2\text{PO}_4)_2$ or $\text{N}_2\text{H}_4 \cdot 2\text{H}_3\text{PO}_4$ and $\text{N}_2\text{H}_5(\text{H}_2\text{PO}_4)$ or $\text{N}_2\text{H}_4 \cdot \text{H}_3\text{PO}_4$. Sabanejeff, in 1898 (1), prepared these salts during a study of isomerism among the various phosphates of ammonia and hydrazine.

The compound $\text{N}_2\text{H}_5(\text{H}_2\text{PO}_4)$ is obtained by adding hydrazine to orthophosphoric acid until the methyl orange end point is reached. The solution is evaporated to a syrupy consistency. Crystallization is then induced by vigorous stirring and scratching the walls of the container.

The solid product is soft and very hygroscopic.

The other secondary orthophosphate, $\text{N}_2\text{H}_8(\text{H}_2\text{PO}_4)_2$ is prepared by adding hydrazine to orthophosphoric acid until the methyl orange end point is reached, and then adding orthophosphoric acid equivalent to the amount originally present. This compound crystallizes much more readily than the salt just described. The crystals are acicular and have respectable physical properties.

These two salts do not exhaust the possibilities of the orthophosphates of hydrazine. Furthermore, no hydrazine pyrophosphates have been reported.

This brief study was undertaken to learn if other phosphates of hydrazine can be conveniently prepared. A further objective was to gain an insight into how a base of this amine type behaves when it demonstrably reacts in a stepwise fashion. The investigation was carried out prior to the study which comprises the main body of this thesis.

Materials

The hydrazine used in this investigation was the commercial grade obtained from Eastman Kodak Company. It was used without further purification. Before being used in a reaction, the hydrazine was diluted to approximately 3 M. No solution was used in which any decomposition

occurred, as evidenced by the appearance of bubbles of nitrogen in the solution. Trace amounts of heavy metals which sometimes occur in distilled water will catalyze such a decomposition. All reactions were carried out in a well ventilated hood due to the toxicity of hydrazine.

Merck "reagent grade" orthophosphoric acid was used. It was diluted to approximately 6 N for the reactions.

Commercial grade pyrophosphoric acid, provided by the Monsanto Chemical Company, was used as received. It was diluted to about 6 N for the reactions.

General Procedure

The hydrazine and the phosphoric acid were brought together until the pH was reached where a particular compound was to be expected. Then the following crystallization techniques were applied:

1. Alcohol was added to the solution until cloudiness developed. An oily layer always formed on standing. This layer did not crystallize even with vigorous stirring and when the container was scratched.

2. The mixture, prepared as described, was repeatedly frozen and thawed in an acetone-dry ice bath. The oils merely solidified to a clear glass which promptly reverted to the oil when returned to room temperature.

3. When the hydrazine-acid reaction mixture was

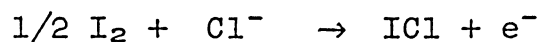
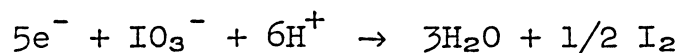
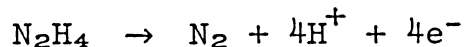
added to cold alcohol, the same type of viscous oil was obtained.

4. A successful procedure for crystallizing the products was to store the original container, with no added solvent, in a desiccator over calcium chloride until the water was largely removed. Such preparations went through a "viscous oil" stage, and with a combination of occasional stirring and long periods of standing in the desiccator, a reaction mixture would sometimes solidify.

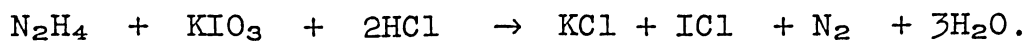
When a solid product was obtained, it was identified by chemical analysis.

Analytical Methods

Hydrazine: This constituent was determined by the volumetric direct iodate method. The titration is based on the following partial reactions (2):



or summarizing the partial reactions



The details of the analytical procedure were (3):

A sample containing about 40 mg. of hydrazine was transferred to a 500 ml. glass stoppered Erlenmeyer flask, and dissolved in 50 ml. of water. Then 60 ml. of 12 N hydrochloric acid and 5 ml. of chloroform were introduced. The addition of the acid causes a decided heating effect. Accurate results are not obtained unless the solution is cooled to room temperature before the titration is started. The standard iodate solution was then added from a burette until the aqueous layer started to turn from brown to light yellow. From this point on, the iodate was added dropwise and the solution shaken vigorously after the addition of each drop. When the violet iodine color was completely discharged from the chloroform layer, the burette was read. The final acid normality is critical; it should be between 3 and 5 N for accurate results.

Phosphorus: This constituent was determined by the gravimetric magnesium ammonium phosphate method, and followed the procedure described on page 27 .

Orthophosphate Studies

The changes in pH which accompany the addition of hydrazine to a solution of orthophosphoric acid are shown in Figure 1. It should be noted that the molar ratio of hydrazine to orthophosphoric acid at the inflection point at pH 4.1 is 1:1. At the corresponding point in the pH curve

for ethylenediamine and orthophosphoric acid, the molar ratio of ethylenediamine to orthophosphoric acid is 1:2.

The preparation of the two previously reported hydrazine orthophosphates was repeated (p. 165) and their composition verified by a determination of their hydrazine content. The results were:

	Hydrazine PerCent <u>Found</u>	PerCent <u>Calculated</u>
$\text{N}_2\text{H}_8(\text{H}_2\text{PO}_4)_2$	14.11	14.03
$\text{N}_2\text{H}_5(\text{H}_2\text{PO}_4)$	24.66	24.61

Equimolar solutions (6 N) of hydrazine and orthophosphoric acid were prepared. Enough of the phosphoric acid solution was added to the hydrazine to make the molar ratio of acid to hydrazine 1:4 (pH 8.7). This solution was concentrated over calcium chloride and sodium hydroxide. The resulting soft crystals were very hygroscopic. They dissolve in the atmospheric water vapor on a hot humid summer day.

The samples had to weighed by difference.

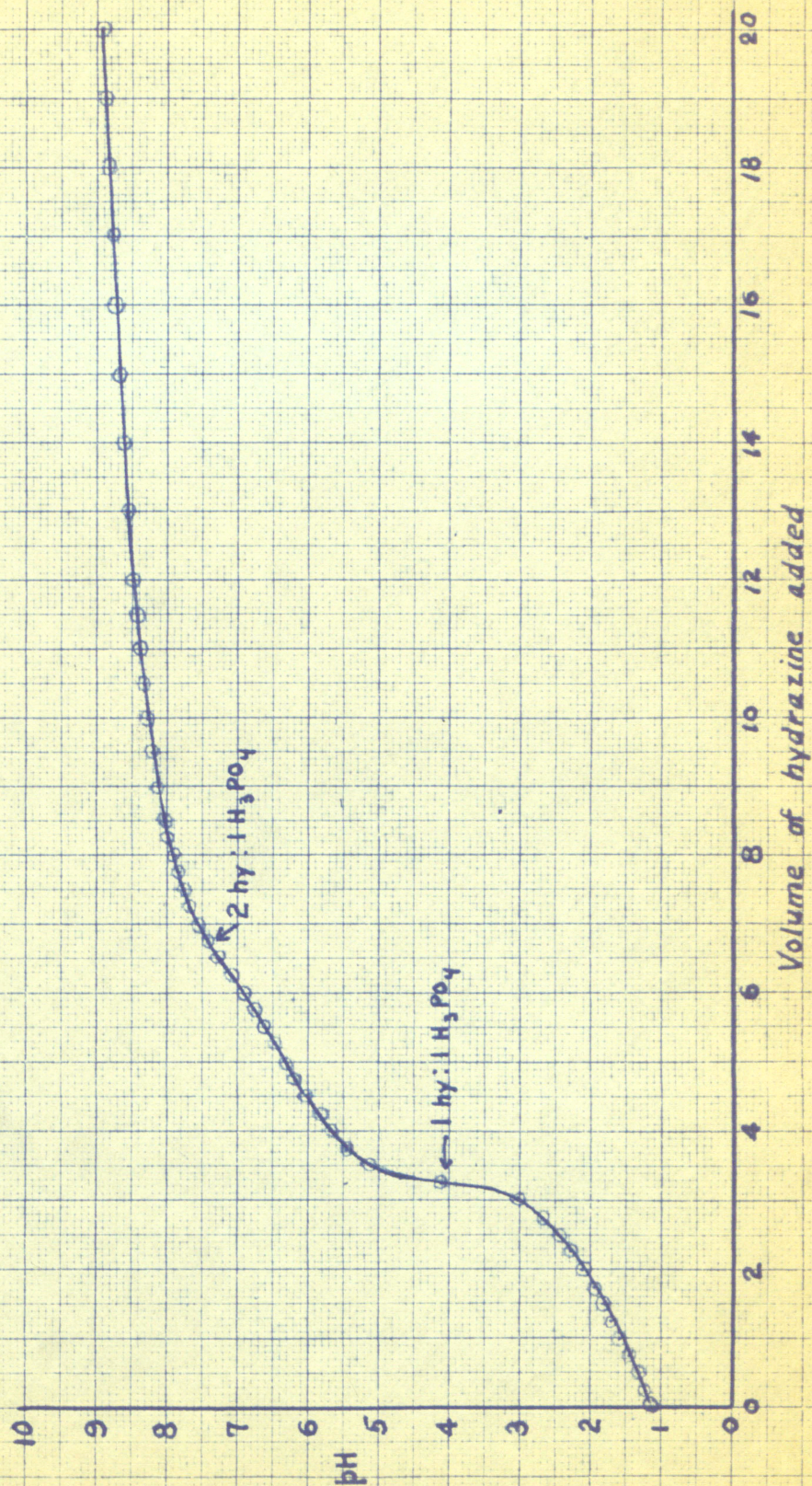
The product has the composition:

<u>Constituent</u>	<u>PerCent Found</u>	<u>PerCent Calculated for $(\text{N}_2\text{H}_5)_2\text{HPO}_4$</u>
Hydrazine	39.35	39.26
Phosphorus	18.97	19.02

The analytical results verify the compound as $(\text{N}_2\text{H}_5)_2\text{HPO}_4 =$

FIGURE 1

Changes which occur in pH as 3.87 M hydrazine is added to 25 ml. of 0.51 M H_3PO_4 .



$2\text{N}_2\text{H}_4 \cdot \text{H}_3\text{PO}_4$. A melting point could not be obtained because of the hygroscopicity of the product.

Pyrophosphate Studies

The pH curve which was obtained by adding hydrazine to pyrophosphoric acid is shown in Figure 2. The molar ratio of hydrazine to pyrophosphoric acid at the inflection point (pH 3.9) is 2:1. By way of comparison, the molar ratio of ethylenediamine to pyrophosphoric acid is 1:1 at the corresponding pH.

If hydrazine is added to pyrophosphoric acid until a 1:1 molar ratio exists (about pH 1.5), the resulting solution solidifies after a week or 10 days over calcium chloride and sodium hydroxide. The crystalline material is very hygroscopic. Analysis of the product gave:

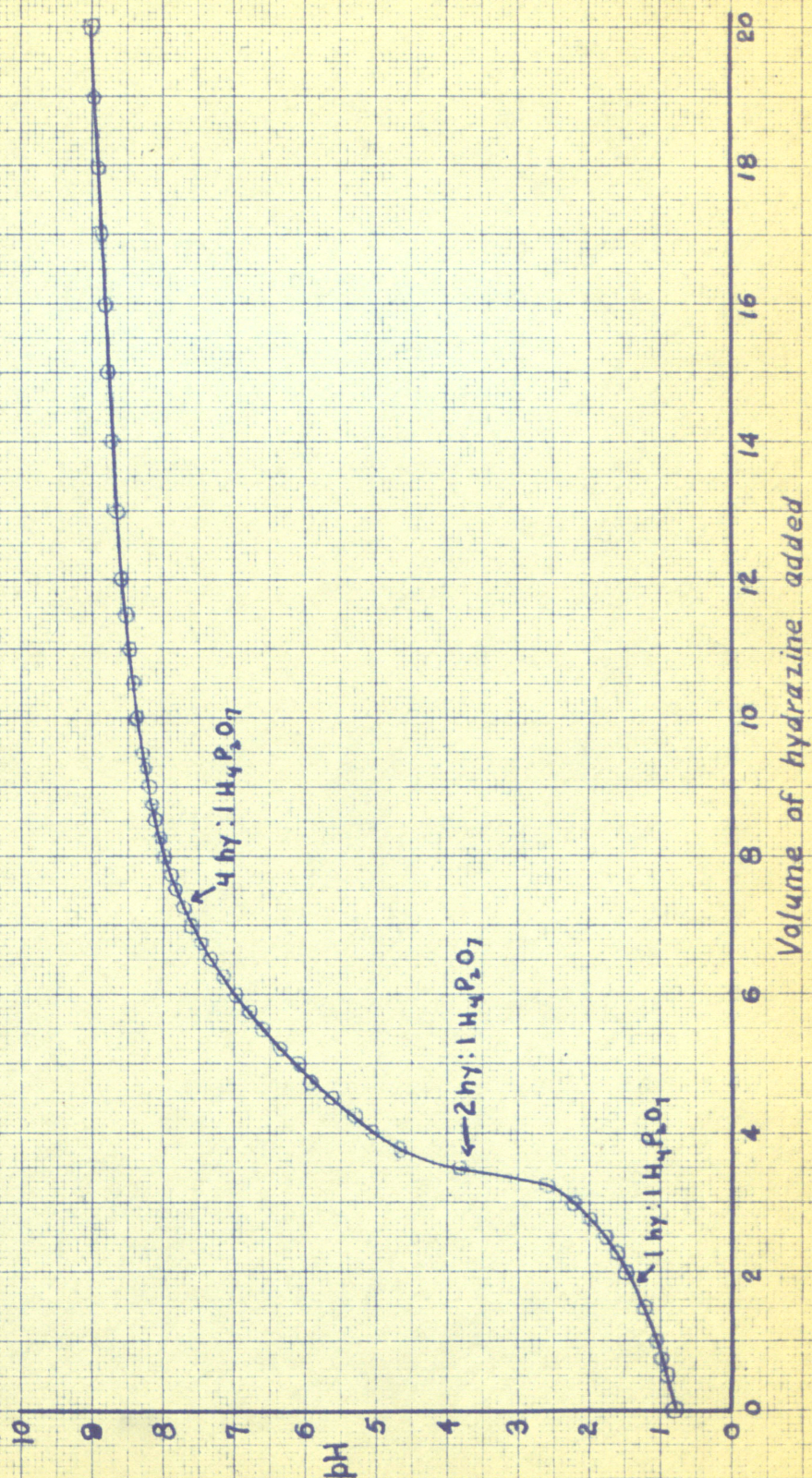
<u>Constituent</u>	<u>PerCent Found</u>	<u>PerCent Calculated for $\text{N}_2\text{H}_8(\text{H}_2\text{P}_2\text{O}_7) \cdot \text{H}_2\text{O}$</u>
Hydrazine	13.98	14.04
Phosphorus	27.41	27.19

The substance cannot be dehydrated by heating. It decomposes between 60° and 70°C , as evidenced by a strong odor of hydrazine.

Attempts to prepare compounds of the composition $(\text{N}_2\text{H}_5)_2\text{H}_2\text{P}_2\text{O}_7$ and $(\text{N}_2\text{H}_5)_3\text{HP}_2\text{O}_7$ did not produce solid products. In the first case, 6 N hydrazine was added to 3 solutions

FIGURE 2

Changes which occur in pH as 3.87 M hydrazine is added to 25 ml. of 0.28 M $\text{H}_4\text{P}_2\text{O}_7$.



of 6 N pyrophosphoric acid until the pH values were 3.5, 4, and 4.5 respectively. All preparations were concentrated in a desiccator, and without exception, the final product was a clear, sticky gum which persisted in this state for as long as 2 or 3 months. When the preparation of $(\text{N}_2\text{H}_5)_3\text{HP}_2\text{O}_7$ was tried, the same procedure was followed, except that the original pH of the solutions subjected to concentration were 6.5, 7, and 7.5. This was the pH range in which $(\text{enH}_2)_3(\text{HP}_2\text{O}_7)_2$ was obtained (4). Again final products were clear sticky gums which remained unchanged after long periods of desiccation.

When pyrophosphoric acid is added to hydrazine (pH 11-12) until the pH falls to 10 or 9.5, the resulting solution solidifies readily after reaching the "oil" stage in the desiccator evaporation. The time required was about a week or 10 days. If the adhering excess hydrazine is washed off with alcohol, the product has the composition $(\text{N}_2\text{H}_5)_4\text{P}_2\text{O}_7$ or $\text{N}_2\text{H}_4 \cdot \text{H}_4\text{P}_2\text{O}_7$.

Constituent	PerCent Found	PerCent Calculated for $(\text{N}_2\text{H}_5)_4(\text{P}_2\text{O}_7)$
Hydrazine	42.80	43.14
Phosphorus	20.19	20.26

Summary

1. This brief investigation has produced one new hydrazine

orthophosphate; namely $(\text{N}_2\text{H}_5)_2\text{HPO}_4$.

2. Two previously unreported pyrophosphates of hydrazine were isolated, namely $(\text{N}_2\text{H}_6)\text{H}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ and $(\text{N}_2\text{H}_5)_4\text{P}_2\text{O}_7$.

Attempts to prepare $(\text{N}_2\text{H}_5)_2(\text{H}_2\text{P}_2\text{O}_7)$ and $(\text{N}_2\text{H}_5)_3\text{HP}_2\text{O}_7$ lead to the formation of clear gums.

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