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Metal Ammonium Phosphates and Their New Applications

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The review deals with the methods of preparation and applications of double salts comprising metal and ammonium phosphates. Particular attention has been given to the methods of preparation and properties of divalent metal compounds of composition $MNH_4PO_4.nH_2O$ which are interesting as complex, long-acting fertilizers.
The syntheses and investigations of those trivalent metal compounds which can be formed on interaction between water-soluble phosphorus fertilizers and soils are described extensively. The bibliography comprises 65 references.

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I. INTRODUCTION

Metal ammonium phosphates include a wide range of compounds which can be denoted by the common formula $a(NH_4)_2O.bMO.cP_2O_5.nH_2O$, where M is a divalent metal, and $a(NH_4)_2O.M_2O_3.cP_2O_5.nH_2O$, where M is a trivalent metal†.

Many of these compounds were already known in the 19th century. Compounds of the type $MNH_4PO_4.nH_2O$, which have found application in analytical chemistry, have been most thoroughly investigated. For example, the determination of phosphorus and magnesium is based on the isolation of $MgNH_4PO_4.6H_2O$, which is then converted to pyrophosphate by heat treatment, and the isolation of $ZnNH_4PO_4$, $MnNH_4PO_4.H_2O$, and $CdNH_4PO_4.H_2O$ constitutes the basis of the determination of the corresponding metals.

Recently the applications of these compounds have greatly increased. In particular investigators in the field of fertilizers have drawn attention to the fact that certain compounds of the type $MNH_4PO_4.nH_2O$ can be used as complex fertilizers containing three nutrient elements: nitrogen, phosphorus, and the corresponding metal (magnesium, manganese, zinc, copper, etc.). Copper, manganese, and zinc are required by plants in micro-amounts, while magnesium is required in comparatively large quantities.

Technological procedures for the preparation of magnesium, zinc, and iron ammonium phosphates have been developed at the Institute of Fertilizers, Insecticides, and Fungicides (NIUIF).[1] Magnesium ammonium phosphate monohydrate‡ was tested under field conditions on different crops and yielded positive results[2]. Manganese, copper, and zinc ammonium phosphates were subjected to vegetative tests and proved to be fairly effective under many conditions.

American workers showed[3] that the high assimilability of metal ammonium phosphates by plants can be explained by the rapid nitrification of their nitrogen content by soil bacteria, as a result of which the salt molecule breaks down and all the components become available to the plant.

At the beginning of the 1960's Grace and Co. in the USA[4,5] announced the manufacture and application as fertilizers of magnesium ammonium phosphate and certain other similar compounds. This communication was followed by a paper dealing with the study of the properties and tests of these fertilizers[3].

The bright colour of certain of the divalent metal compounds has led to their employment (mainly cobalt ammonium phosphate) as pigments in artists paints[6,7].

Iron ammonium phosphate and manganese ammonium phosphate have been suggested as components of priming paints in anti-corrosion coatings[6,8], since, apart from their other valuable properties, they behave as acceptors of acids and oxygen, whereby they prevent corrosion.

The method of extraction of doubly charged metal cations[9], in particular calcium and magnesium, from sea water to prevent the formation of scale is based on metal ammonium phosphates. In this procedure phosphoric acid and ammonia are added to sea water and the metal ammonium phosphates formed are used as fertilizers.

Salutsky and Dunseth[10] believe it to be more useful to extract cations such as Co^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Ba^{2+}, and Ca^{2+} from salt solutions of various types, including sea water, by passing them through a layer of $MgNH_4PO_4.H_2O$, where magnesium ions are replaced by the above cations.

† Compounds in which the ammonium ion is replaced by a monovalent metal (sodium, potassium, lithium) are also very widespread but these will be mentioned only incidentally.

‡ $MgNH_4PO_4.6H_2O$ is of no interest as a fertilizer, since it is unstable and contains a smaller percentage of nutrient substances than $MgNH_4PO_4.H_2O$.

Another valuable property of metal ammonium phosphates is the capacity to decompose in the temperature range 200–400°C (the region of cellulose inflammation) with evolution of ammonia and water and the formation of free phosphoric acid, which makes them suitable as fire-resistant agents.

Attempts have been made to impregnate wood with zinc and copper ammonium phosphates in aqueous ammonia in order to make it fire resistant[11]. Soviet workers suggested[1,12] that iron and aluminium ammonium phosphates be used as fire-resistant agents in the manufacture of non-combustible wood-fibre plates and certain other articles. Industrial methods have been devised for their preparation from readily available raw materials[12,13].

Aluminium and iron ammonium phosphates are formed in the reaction of the soluble fertilizer ammonium phosphates with a number of soils and are responsible for the conversion of water-soluble phosphates into an insoluble form. These studies will be described below. Compounds of aluminium and iron(III) of the type $MM'_3H_{14}(PO_4)_8.4H_2O$, where M = Na, K, or NH_4 and M′ = Fe or Al, have been used as baking powders[14].

Since the applications of metal ammonium phosphates are extremely varied, communications concerning them are published in journals dealing with diverse fields. This review presents a wide variety of information about this large class of compounds.

II. PREPARATION OF COMPOUNDS OF THE TYPE $MNH_4PO_4.nH_2O$

At the present time the following compounds of the above type have been isolated and described: $MgNH_4PO_4.nH_2O$ (n = 1 and 6); $ZnNH_4PO_4$; $FeNH_4PO_4.H_2O$; $MnNH_4PO_4.H_2O$; $CuNH_4PO_4.H_2O$; $CoNH_4PO_4.nH_2O$ (n = 1, 6, and 12); $NiNH_4PO_4.nH_2O$ (n = 1 and 6); $CdNH_4PO_4.H_2O$; $CaNH_4PO_4.nH_2O$ (n = 1 and 7); $BaNH_4PO_4.7H_2O$.

Under normal conditions monohydrates are usually precipitated. Exceptions are magnesium, cobalt, and nickel ammonium phosphates which are isolated as hexahydrates, and also zinc ammonium phosphate which is precipitated in the anhydrous state. Lasne[15] isolated calcium ammonium phosphate as the heptahydrate from a solution of calcium oxide in citric acid on introduction of ammonium phosphate into the latter. This salt is unstable, losing water and ammonia on standing in air.

Auger and Ivanoff[16] obtained $BaNH_4PO_4.7H_2O$ and $CaNH_4PO_4.7H_2O$ in the presence of a large amount of ammonium citrate at a low temperature (0–7°C).

Basset and Bedwell[17] described a general method for the preparation of metal ammonium phosphates. It consists in mixing solutions of the given metal chloride and diammonium hydrogen phosphate in a large excess, the mixture being stirred. The resulting mixture of precipitate and mother liquor is kept at room temperature or on a water bath until the precipitate becomes crystalline. It is then filtered off and washed with water, absolute alcohol, and absolute ether. The concentrations of the solutions for different compounds vary, but are in all cases comparatively low. In the individual methods recommended by Basset and Bedwell the amount of ammonium phosphate is reduced by the addition of a large quantity of ammonium chloride. The crystallisation of the hexahydrates required 12 h and that of monohydrates 1 h, except for copper ammonium phosphate which crystallised very slowly. With the ratio P : Cu ≃ 9, the crystallisation of $CuNH_4PO_4.H_2O$ required three months, while with P : Cu ≃ 40, 24 h was sufficient. Basset and Bedwell obtained by the above method all the compounds enumerated above, with the exception of iron, calcium, and barium ammonium phosphates. The hydrates which could not be isolated, for example the hexahydrates of manganese, copper, zinc, and cadmium ammonium phosphates, were obtained in the form of solid solutions in an excess of magnesium ammonium phosphate hexahydrate. The anhydrous compounds of cobalt and magnesium were obtained in the form of solid solutions in zinc ammonium phosphate. Using dipotassium hydrogen phosphate instead of diammonium hydrogen phosphate, the authors obtained a number of metal potassium phosphates by the method adopted for metal ammonium phosphates in particular $KMgPO_4.H_2O$, $KMnPO_4.H_2O$, $KCoPO_4.H_2O$, $KCuPO_4.H_2O$, $KCdPO_4.H_2O$, $KZnPO_4$, and $KMgPO_4.6H_2O$.

Grat-Cabanac[18] obtained the pure salt $CoNH_4PO_4.H_2O$ at 80°C from dilute $CoSO_4$ and $(NH_4)_2HPO_4$ solutions with a large excess of the latter.

Depending on the temperature (15–95°C), mixtures with different amounts of water of crystallisation were obtained. Frazier et al.[19] determined the amount of calcium ammonium phosphate monohydrate in the products of the ammonia treatment of superphosphate. Apart from $CaNH_4PO_4.H_2O$, two dimorphous salts with the composition $Ca(NH_4)_2.(HPO_4)_2.H_2O$ were found. The authors investigated the four-component system $CaO–P_2O_5–NH_3–H_2O$ at room temperature in the pH range 4–9 and established the regions of existence of these salts. The compounds were obtained in a pure form by adding calcium hydroxide or calcium carbonate to concentrated ammonium phosphate solutions with N : P molar ratios between 1 and 3.4 and at pH between 4.0 and 9.9. Their X-ray diffraction patterns and crystal-optical characteristics were determined.

The four-component system $MgO–P_2O_5–NH_3–H_2O$ was investigated by Abashkina[20] at 25°C in the concentration ranges 2.7–60.97% P_2O_5, 0.07–7.67% MgO, and 0.53–12.40% NH_3 and at 75°C in the concentration ranges 0.2–57.08% P_2O_5, 0.09–11.63% MgO, and 0.22–15.22% NH_3. It was established that the region of crystallisation of magnesium ammonium phosphate is located in the most alkaline part of the diagram both at 25° and at 75°C. At 75°C the stable phase is $MgNH_4PO_4.H_2O$, while at 25°C compounds with different degrees of hydration (between 6 and 1 moles of water per mole of salt) were found, depending on the concentration of phosphorus pentoxide in the liquid phase. This finding is inconsistent with the usual hypotheses, according to which the hexahydrate is precipitated at room temperature.

Much work has been done on the technological methods of preparation of metal ammonium phosphates, particularly magnesium ammonium phosphate, in view of their considerable value as fertilizers. Aseev[21] took out a patent for the simultaneous preparation of magnesium bicarbonate and magnesium ammonium phosphate hexahydrate from magnesium minerals, in particular dolomite. Vol'fkovich and Remen[22] developed a method for the preparation of magnesium ammonium phosphate monohydrate from hot concentrated solutions of magnesium chloride and diammonium hydrogen phosphate, which were neutralised with ammonia to pH 8–8.5 after mixing. The proportions of the reactants were close to the stoichiometric values, the time of reaction being 0.5 h. The precipitate was filtered off, washed with hot water, and dried at 106°C. Magnesium ammonium phosphate forms according to the reaction $MgCl_2 + (NH_4)_2HPO_4 + NH_4OH = MgNH_4PO_4.H_2O\downarrow + 2NH_4Cl$. The carbonate was also tested as the raw material; it was stirred in boiling water and allowed to react with the solu-

tion of monoammonium dihydrogen phosphate without additional neutralisation with ammonia. In both cases a product close to the theoretical composition was obtained.

Erskine et al.[8] synthesised $FeNH_4PO_4.H_2O$ for tests as a component of priming paints composed of a ferrous salt and diammonium hydrogen phosphate at pH 8.5. Vol'fkovich and Remen[1] obtained an experimental batch of this product under industrial conditions. The same workers developed a technological method for the synthesis of zinc ammonium phosphate from zinc or zinc oxide, phosphoric acid, and ammonia, on the basis of the reactions

$$ZnO + H_3PO_4 = ZnHPO_4 + H_2O,$$
$$ZnHPO_4 + NH_3 = ZnNH_4PO_4.$$

Salutsky et al.[23] (Grace and Co.) patented a method for the synthesis of metal ammonium phosphates consisting of the following operations: mixing of phosphoric acid with any compound of the corresponding metal soluble in phosphoric acid; (2) treatment of the mixture at 80–105°C for a period ranging from 10 min to 4 h, which results in the formation of a dimetal hydrogen phosphate salt; (3) introduction of ammonia until the attainment of pH 7–9; (4) treatment of the ammonia-pretreated mixture at 25–105°C for a period ranging from 1 h to several days; (5) washing of the precipitate with water; (6) drying at 65–105°C. They obtained by this method magnesium, iron, manganese, nickel, copper, zinc, and cobalt ammonium phosphates. Somewhat later the same firm[24] took out a patent for a continuous method of synthesis of magnesium, nickel, cobalt, and zinc ammonium phosphates, consisting in the continuous supply of a solution of the salt in phosphoric acid and of ammonia at 75–85°C with the pH in the reaction zone about 7.5; the average residence time was 6–9 min.

This method scarcely differs from the procedures developed earlier for the synthesis of magnesium, iron, and zinc ammonium phosphates. The preparation of the salt of the corresponding metal in phosphoric acid is not obligatory: all the compounds can be readily obtained by the simultaneous introduction of the metal salt, phosphoric acid (or ammonium phosphate), and ammonia. The manufacture of iron ammonium phosphate in the USSR is based on this procedure[12]. Apart from magnesium, zinc, and iron ammonium phosphates, manganese and nickel ammonium phosphates can be obtained by this method. Equilibrium in the system $CuO-P_2O_5-NH_3-H_2O$ is established very slowly and therefore a periodic process is more suitable for the synthesis of $CuNH_4PO_4.H_2O$.

In recent years, apart from American studies, communications from other countries have appeared, dealing with the preparation of metal ammonium phosphates, mainly magnesium ammonium phosphate, and their use as fertilizers. Japanese workers[25] have described a method for the synthesis of magnesium ammonium phosphate from magnesium hydroxide, phosphoric acid, and ammonia and investigated the effect of the atomic ratio N : P on the purity of the product.

Hungarian investigators[26] suggested that calcium hydrogen phosphate and ferrous sulphate be used as the starting materials. In this case gypsum is formed as a by-product. The process consists of three stages. The dihydrogen phosphate formed is neutralised with ammonia and the resulting ammonium dihydrogen phosphate is precipitated with the carbonate, oxide, or hydroxide of one of the divalent metals:

$$Ca(H_2PO_4)_2 + MSO_4 = \downarrow CaSO_4 + M(H_2PO_4)_2,$$
$$M(H_2PO_4)_2 + 2NH_3 + nH_2O = \downarrow MNH_4PO_4 \cdot nH_2O + NH_4H_2PO_4,$$
$$NH_4H_2PO_4 + M'CO_3 + nH_2O = H_2CO_3 + M'NH_4PO_4 \cdot nH_2O.$$

By this procedure, it is possible to obtain a mixed fertilizer containing several microelements by introducing into the first reaction the salt of one element and into the last reaction that of another. In the Research Laboratory of the Budapest Chemical Factory[27] a fertilizer containing microelements was obtained, with magnesium ammonium phosphate as the main substance.

There is a Japanese patent[28] for the synthesis of a complex fertilizer containing magnesium ammonium phosphate.

In the above method metal ammonium phosphates are produced in the form of powders. However, American workers believe[3] that, despite their low solubility, metal ammonium phosphates can be obtained in a granulated form, the rate of assimilation of the nutrient substances by the plants being regulated by the size of the granules. The firm Grace and Co. took out two patents for the synthesis of granulated magnesium ammonium phosphate[29,30].

In technological syntheses the formation of metal ammonium phosphates of definite composition is not achieved by means of a large excess of diammonium hydrogen phosphate but by establishing a strongly alkaline medium with the aid of ammonia. Possibly, under manufacturing conditions completely homogeneous products are not obtained, but their purity is quite satisfactory for technical purposes.

For other compounds of the type $a(NH_4)_2O.bMO.cP_2O_5.nH_2O$, there is early information about zinc ammonium phosphates of the composition $(NH_4)_2O.2ZnO.2P_2O_5.5H_2O$ and $4(NH_4)_2O.6ZnO.3P_2O_5$,[31] and also about the iron ammonium phosphate $(NH_4)_2O.FeO.P_2O_5.5H_2O$.[32]

In connection with the expansion of studies on fertilizers and the synthesis of new types of fertilizers, including those containing magnesium and microelements, the number of compounds of this type which have been isolated has greatly increased in recent years.

Lindsay et al.[33] established the presence of the compound $Ca_2(NH_4)_2(HPO_4)_3.2H_2O$ among the products of the interaction of diammonium hydrogen phosphate with soils.

Much work has been done by Frazier et al.[34] on the identification of the compounds formed when the phosphoric acid extract containing magnesium and microelements is treated with ammonia. In the presence of magnesium in the acid, the compounds $Mg_3(NH_4)_2H_4(PO_4)_4.8H_2O$ [empirical formula $(NH_4)_2O.3MgO.2P_2O_5.10H_2O$], corresponding to the mineral hannayite, and $Mg(NH_4)_2H_2(PO_4)_2.4H_2O$ [$(NH_4)_2O.MgO.P_2O_5.5H_2O$] were isolated in addition to $MgNH_4PO_4.6H_2O$ and the corresponding monohydrate. In the presence of aluminium the salt $MgAl(NH_4)_5H_2(PO_4)_4.6H_2O$ was found.

When phosphoric acid containing zinc was treated with ammonia, the salt $ZnNH_4H_3(PO_4)_2.H_2O$ [empirical formula $(NH_4)_2O.2ZnO.2P_2O_5.5H_2O$], mentioned earlier, was obtained in addition to $ZnNH_4PO_4$, and in the presence of potassium the salts $Zn_2KH(PO_4)_2.2H_2O$ and $ZnKPO_4$ were found.

III. PROPERTIES OF COMPOUNDS OF THE TYPE $MNH_4PO_4.nH_2O$.

1. Solubility

The compounds $MNH_4PO_4.nH_2O$ are crystalline salts sparingly soluble in water, which dissolve readily in mineral acids. The solubility of most of these compounds in water and dilute hydrochloric acid was determined by Bridger et al.[3], who estimated the solubility from the amount of phosphate ions passing into solution, assuming that the compounds dissolve congruently. However, Taylor and Frazier[35], who investigated the solubility of $MgNH_4PO_4.6H_2O$ under equilibrium conditions, established that this

compound dissolves incongruently with precipitation of $Mg_3(PO_4)_2$. From the compositions of the solutions in equilibrium with the solid phase at 25°C, they calculated the solubility product of $MgNH_4PO_4.6H_2O$ as 7.1×10^{-14}. The solubility of magnesium ammonium phosphate increases somewhat in the presence of other salts, especially ammonium salts[36] (with the exception of ammonium phosphate). A similar situation was found with $MnNH_4PO_4.H_2O$.[37] Investigations of this kind were not performed on other salts.

It has been established in a number of studies[2,3,5,38,39] that, despite their low solubility in water, many metal ammonium phosphates give rise to a satisfactory agrochemical effect. Lunt et al.[38] and Munk[39] studied the effect of soil conditions on the assimilability of magnesium ammonium phosphate.

2. Thermal Stability

A number of investigations have shown that the hexahydrates are very unstable—they begin to decompose even at room temperature. The monohydrates are much more stable.

Kiehl and Hardt[40] determined the vapour pressure over $MgNH_4PO_4.6H_2O$ and other compounds which might form in its decomposition. They established that below 60°C only water is lost, while above 60°C ammonia begins to appear in the gas phase with simultaneous evolution of the residual water. At 105°C the vapour pressure over $MgNH_4PO_4.6H_2O$ reaches 1 atm. According to the data of these workers, magnesium ammonium phosphate monohydrate begins to decompose at about 150°C, the vapour pressure reaching 1 atm at 250°C. It was established that, when $MgNH_4PO_4.H_2O$ is heated, ammonia is evolved together with water and that $Mg_2P_2O_7$ is formed at a very low temperature, of the order of 200°C, which can be accounted for by the high vapour pressure over $MgHPO_4$.

Auger and Ivanoff[16] found that, on drying $MgNH_4PO_4.6H_2O$ to constant weight at 55°, 70°, and 100°C, 28%, 42%, and 74% of ammonia relative to the initial amount is lost. Water is liberated together with ammonia; at 55°C the loss amounted to 20% and at 70°C to 82% of the total water content. These results show that magnesium ammonium phosphate monohydrate cannot be obtained from the hexahydrate by heating the latter.

Vol'fkovich et al.[41] investigated the stability of magnesium ammonium phosphate hexahydrate and monohydrate in order to determine how these products would behave on storage when used as fertilizers. They established, that when air is passed over a weighed sample of $MgNH_4PO_4.6H_2O$, a small ammonia loss is observed even at room temperature. The heating curves for $MgNH_4PO_4.6H_2O$ and $MgNH_4PO_4.H_2O$ were determined.

French workers made a systematic study of the thermal decomposition of many metal ammonium phosphates[42-44]. It involved the analysis of the intermediate products by X-rays spectroscopy and chromatography. The monohydrates of beryllium, manganese, magnesium, and cobalt ammonium phosphates were investigated. In addition, the thermal decomposition of $CoNH_4PO_4.6H_2O$ and $CoNH_4PO_4$, obtained by heating the monohydrates in a stream of ammonia at 260°C, was studied. $MgNH_4PO_4.H_2O$ was obtained from the hexahydrate by heating the latter in a stream of ammonia at 110°C. The weight loss was determined by means of a thermobalance, with simultaneous analysis of the gas phase for water and ammonia.

The investigation showed that the decomposition of metal ammonium phosphates on heating proceeds via a series of intermediate compounds. In all cases the presence of an amorphous phase was established in the range 220–650°C. The range of existence of the phase is different for different compounds: for $CoNH_4PO_4.H_2O$, the amorphous phase is present between 390 and 415°C, while for $MgNH_4PO_4.H_2O$, the range of its existence is more extensive (225–650°C). Acid phosphates were not detected among the decomposition products, in agreement with the data of Kiehl and Hardt[40].

As a rule, the decomposition of the monohydrates begins at 150–200°C with evolution of water. Sometimes ammonia is liberated together with water. The evolution of water and ammonia takes place in several stages. The final products of the thermal decomposition are pyrophosphates. A simplified decomposition mechanism can be represented thus:

$$MNH_4PO_4 \cdot H_2O \xrightarrow{-NH_3,-H_2O} \text{amorph. phase} \xrightarrow{-NH_3,-H_2O} M_2P_2O_7 .$$

Ortho-, pyro-, and tri-phosphate ions were detected in the amorphous phase by chromatography. However, none of the intermediates was isolated in a pure form, since several processes superimposed upon one another take place in the decomposition. Traces of orthophosphate were detected even at 580°C, while the more dehydrated form (pyrophosphate) is sometimes observed at a temperature as low as 200°C.

The pyrolysis of $CoNH_4PO_4.6H_2O$ begins at 85°C. It resembles the decomposition of the monohydrates. The decomposition of anhydrous cobalt ammonium phosphate, which was first investigated by Etienne and Boulle[44], begins at 230°C and is also accompanied by the evolution of ammonia and water.

The above investigations show that the decomposition of metal ammonium phosphates is such that it is impossible to distinguish between the evolution of the water of crystallisation and the water of constitution. Hence one may conclude that these compounds have a more complex structure than might be expected from the formula $MNH_4PO_4.nH_2O$ attributed to them.

3. The Structure of Compounds of the Type $MNH_4PO_4.nH_2O$

Structural studies on compounds of the type $MNH_4PO_4.nH_2O$ are not recorded in the literature. Certain hypotheses have been put forward on the basis of their unusual behaviour on heating and the colour changes in the precipitation of coloured salts, mainly cobalt ammonium phosphate.

As early as the 19th century, it was noted that some of these compounds glow on heating. Basset and Bedwell[17] established that the intensity of the glow of the hexahydrates is greater than that of the monohydrates. On this basis, they concluded that the monohydrates are polymeric compounds, while the hexahydrates polymerise during heating and that this process is responsible for the luminescence.

Many investigators drew attention to the fact that the precipitation of $CoNH_4PO_4.H_2O$ is accompanied by a number of colour changes in the precipitate. Initially a pink flaky precipitate is deposited, which then assumes a bright blue colour, and is finally transformed into the violet-red monohydrate. Golynkin[6] and Grat-Cabanac[18] explained this by the initial formation of more hydrated forms, while Basset and Bedwell[17] concluded that the intermediate bright blue compound is anhydrous cobalt ammonium phosphate. Since the hexahydrates have a pure colour (pink for $CoNH_4PO_4.6H_2O$ and green for $NiNH_4PO_4.6H_2O$) corresponding to the colour of the hydrated cation, while the monohydrates assume also another tint, Basset and Bedwell concluded that

in the hexahydrates the metal is present in the cationic form and in the monohydrates partly in the cationic and partly in the anionic forms. Bearing this in mind and also the fact of a higher degree of polymerisation of the monohydrate which they established and the coordination numbers of the metals, they assigned to the hexahydrates the formula

$$NH_4^+ [M(H_2O)_6]^{2+} PO_4^{3-},$$

and to the monohydrates

$$(NH_4^+)_2 [M(H_2O)_4]^{2+} (PO_4MPO_4MPO_4MPO_4)^{6-}.$$

Evidently these formulae too fail to reflect the true structure of compounds of the type $MNH_4PO_4.nH_2O$. According to them, ammonia should be evolved first on heating. They do not explain why water and ammonia are evolved in several stages, suggesting that the bond between the metal and both water and ammonia is the same. More detailed studies in this field were not made and therefore the problem of the structure of these compounds still remains unresolved.

IV. PREPARATION OF COMPOUNDS OF THE TYPE $a(NH_4)_2O.bR_2O_3.cP_2O_5.nH_2O$

Compounds of this type, whose composition corresponds to the formula $(NH_4)_2O.(Al,Fe)_2O_3.2P_2O_5.2H_2O$, were obtained for the first time by Cohen[45] by mixing a concentrated solution of diammonium hydrogen phosphate and a solution of aluminium chloride (or ferric chloride) in hydrochloric acid in the presence of a large excess of phosphate ions ($PO_4 : Al = 23$, $PO_4 : Fe = 7$) and with prolonged heating. Somewhat later an iron salt of this composition was obtained by Weinland and Ensgraber[46] from freshly precipitated ferric hydroxide, phosphoric acid, and ammonia. It differed from Cohen's salt in its colour: Cohen's salt was white and Weinland's salt was pink.

The authors investigated it under the microscope and established that it consists of crystals comprising hexagonal rods narrowing at one end. Both Cohen and Weinland and Ensgraber suggested that this compound can be regarded as the ammonium salt of diphosphatoferric(III) acid, which they called "ammonium diphosphatoferrate", and assigned to it the formula $[Fe(PO_4)_2]H_2NH_4$. Apart from this salt, they obtained other compounds, to which they assigned the formulae $[Fe(PO_4)_2H_3]_3.NH_3.7H_2O$ [empirical formula $(NH_4)_2O.3Fe_2O_3.6P_2O_5.22H_2O$] and $2FePO_4.NH_3.4H_2O$ [empirical formula $(NH_4)_2O.2Fe_2O_3.2P_2O_5.7H_2O$], and also a salt with the ratios $Fe : PO_4 : N = 4 : 9 : 1.5$, which they regarded as the ammonium salt of di- and tri-phosphatoferric(III) acid $H_6Fe(PO_4)_3$. The salts obtained did not dissolve in water but dissolved readily in dilute hydrochloric acid and more slowly in nitric acid. They were decomposed by alkalis with formation of ferric hydroxide and ammonium phosphate. The solubility of $2FePO_4.NH_3.4H_2O$ is lower than that of the remaining salts.

Many investigators[47-49] failed to prepare ammonium aluminophosphate, described by Cohen, using his procedure. Yakimach[47] obtained a salt of this composition but by a procedure differing from that of Cohen: the precipitation was carried out at a higher concentration of phosphate ions and in the absence of hydrochloric acid. In contrast to Cohen's salt, that synthesised by Yakimach did not dissolve in acids. In the author's view this salt had nothing in common with Cohen's salt.

Angelescu and Balanescu[50] studied the composition of the precipitate deposited from solutions containing Fe^{3+} and PO_4^{3-} ions in the presence of different amounts of ammonia. They established that ferric phosphates of definite compositions can be obtained from acid solutions, but in alkaline solutions "adsorption complexes" are formed, whose composition varies with concentration, temperature, etc.

The composition of the insoluble products formed in the synthesis of ammonium phosphates from a phosphate starting material containing aluminium and iron was investigated at the Institute of Fertilizers, Insecticides, and Fungicides (NIUIF). At pH 4.5 and 3.5 for the aluminium salt and at pH 2.5 for the ferric salt in the presence of a large excess of phosphate ions ($PO_4 : Al = 13$; $PO_4 : Fe = 7.5$), Sannikova[51] obtained salts whose compositions were comparatively close to those of Cohen's salts. The salts were precipitated by mixing together at 45°C solutions of the hydroxide in phosphoric acid and of aqueous ammonia followed by prolonged exposure of the resulting precipitate to this temperature. The salts thus prepared were sparingly soluble in water, more so in 2% citric acid, and completely soluble in a solution of ammonium citrate neutralised with ammonia to pH 8 (Peterman's solution). Using a similar procedure, Kheifets[52] obtained at pH 4.8 a yellow-green salt, close in composition to the salt $2FePO_4.NH_3.4H_2O$ described by Weinland and Ensgraber[46], and at pH 1.7 she obtained a lilac-pink preparation similar to the salt $[Fe(PO_4)_2H_3]_3NH_3.7H_2O$. A product approaching the composition of $Fe(PO_4)_2H_2NH_4$, but nevertheless differing from the latter appreciably, was obtained at pH 3.8. The form of the crystals obtained by Kheifets differed as a rule from that of the salts described by Weinland and Ensgraber.

The results of different investigators show that the composition and properties of the precipitates deposited from solutions containing phosphate ions and the corresponding metal and ammonium ions depend to a high degree on the precipitation conditions. This has been confirmed by a study[53] where precipitates of different compositions were obtained by varying the concentration of the solutions, the pH of the medium, or the proportions of the reactants.

Haseman et al.[54] isolated a number of ammonium and potassium phosphato-ferrates(III) and -aluminates from dilute solutions under conditions imitating those obtaining in soils, namely by prolonged storage in a sealed vessel of precipitated aluminium and ferric phosphates with solutions containing potassium and ammonium cations. Solutions of various concentrations, ranging from 0.001 M to 3.5 M, and at various pH between 1.5 and 8 were prepared by adding potassium hydroxide or ammonium hydroxide to standard phosphoric acid solutions. The precipitates were treated at temperatures between 27° and 145°C. The filtered and washed precipitates were dried at room temperature over calcium chloride.

Each specimen obtained was studied under the petrographic microscope and the optical properties of the crystals were determined. Almost all the products were well crystallised. The aluminium phosphates contained as a rule only one mineralogical variety, while certain of the ferric phosphate specimens contained two or more mineral types; in this case a relatively pure specimen was obtained by screening or elutriation. Homogeneous specimens were analysed chemically and their powder diffraction patterns were obtained.

On the basis of the diffraction patterns, crystal-optical properties, and chemical composition, Haseman classified all the specimens into nine groups of minerals, which are listed in Table 1. Each group is characterised by definite chemical composition, diffraction patterns, and crystal-

optical properties. The authors identified compounds of group 1 with the natural mineral taranakite. They also obtained the analogous ammonium compound. Smith and Brown[55], who investigated this compound by X-ray diffraction, concluded that it is more correct to assign to it the formula $3(NH_4)_2O.5Al_2O_3.8P_2O_5.42H_2O$ or, in an expanded form, $H_6(NH_4)_3Al_5(PO_4)_8.18H_2O$.

Table 1. Empirical formulae and the classification of phosphatoferrate and phosphatoaluminate minerals (according to Haseman et al.[54]).

Product	Empirical formula	Classification group
A	$2K_2O\cdot3Al_2O_3\cdot5P_2O_5\cdot26H_2O$	1
B	$2K_2O\cdot3Al_2O_3\cdot5P_2O_5\cdot20H_2O$	1
C	$K_2O\cdot Al_2O_3\cdot2P_2O_5\cdot4H_2O$	2
D	$K_2O\cdot Fe_2O_3\cdot2P_2O_5\cdot4H_2O$	2
E	$K_2O\cdot Fe_2O_3\cdot2P_2O_5\cdot2H_2O$	3
F	$(NH_4)_2O\cdot Fe_2O_3\cdot2P_2O_5\cdot3H_2O$	3
G	$(NH_4)_2O\cdot Al_2O_3\cdot2P_2O_5\cdot3H_2O$	3
H	$K_2O\cdot2Al_2O_3\cdot2P_2O_5\cdot5H_2O$	4
HH	$K_2O\cdot2Al_2O_3\cdot2P_2O_5\cdot5H_2O$	4
I	$K_2O\cdot2Fe_2O_3\cdot2P_2O_5\cdot5H_2O$	4
J	$(NH_4)_2O\cdot2Al_2O_3\cdot2P_2O_5\cdot6H_2O$	4
K	$(NH_4)_2O\cdot3Fe_2O_3\cdot6P_2O_5\cdot20H_2O$	5
L	$K_2O\cdot3Fe_2O_3\cdot6P_2O_5\cdot20H_2O$	5
MM	$Al_2O_3\cdot P_2O_5\cdot4H_2O$	6
O	$0.9Fe_2O_3\cdot0.1Al_2O_3\cdot P_2O_5\cdot4H_2O$	6
P	$Fe_2O_3\cdot P_2O_5\cdot4H_2O$	6
Q	$Al_2O_3\cdot P_2O_5$	7
R	$K_2O\cdot Al_2O_3\cdot P_2O_5\cdot4H_2O$	8
S	$K_2O\cdot Al_2O_3\cdot P_2O_5\cdot2H_2O$	8
T	$K_2O\cdot2Al_2O_3\cdot2P_2O_5\cdot1.6HF\cdot6.2H_2O$	9

Lindsay et al.[33] identified 30 crystalline phosphates (apart from the amorphous precipitates) formed in the reaction between phosphate fertilizers and soils. They investigated the reaction of calcium hydrogen phosphate, ammonium dihydrogen phosphate, potassium dihydrogen phosphate, diammonium hydrogen phosphate, dipotassium hydrogen phosphate, and liquid ammonium-treated superphosphoric acid of type 11-33-0 with sandy and rich calcareous loams. Part of the compounds isolated, relevant to the present review, are listed in Table 2, which shows that the authors obtained ammonium and potassium taranakites and also compounds corresponding to products K, L, P and F in Haseman's classification, but the last product had a somewhat lower water content. The component ratio in the compound $NH_4Al_2(PO_4)_2OH.8H_2O$ corresponds to Haseman's product J but contains a much greater amount of water.

The salts obtained by Cohen and one of Weinland's salts correspond in their chemical composition to compounds or group 3§ (Table 2). However, the ammonium phosphatoferrate(III) described by Weinland consisted of pink crystals comprising hexagonal rods narrowing at one end, while Haseman's product consisted of colourless plates, i.e. the structures of the salts were different.

The present author obtained[53] from concentrated solutions of pH 5 a salt similar in composition to $(NH_4)_2O.Al_2O_3.2P_2O_5.3H_2O$ investigated by Haseman, but their powder diffraction patterns had nothing in common.

Unfortunately the system $(NH_4)_2O-Al_2O_3(Fe_2O_3)-P_2O_5-H_2O$ was not investigated in detail and therefore it is difficult to say whether the various properties of salts of the same composition are due to the fact that some investigators obtained metastable or contaminated compounds or whether it is due to the fact that there exists such a wide variety of compounds in this system at a small change in conditions leads to the formation of a new salt.

Tables 1 and 2 show that a considerable amount of ammonium phosphato-ferrates(III) and -aluminates was also isolated from dilute solutions. Some of these were obtained by many investigators and are well known. For example, there is no doubt that the reaction of ammonium phosphate with many soils results in the formation of a compound whose composition and properties correspond to the mineral taranakite. Such a compound was found by Lindsay[33] in the product of the reaction of calcium hydrogen and ammonium dihydrogen phosphates with sandy and rich calcareous loams. It was also obtained by Tamimi et al.[56] by the reaction of ammonium phosphate at pH 1.0–5.0 with gibbsite $[Al(OH)_3.3H_2O]$ and certain other soils. The same compound was prepared by Haseman in the reaction of aluminium phosphate with dilute solutions (between 0.001 and 1 M) of ammonium phosphate at pH between 1.7 and 5.5. Ammonium and potassium taranakites were also prepared by Taylor and coworkers[57–60], Egan et al.[61], Arlidge et al.[62], and, as already stated, Smith and Brown[55]. Lindsay and Taylor[58] investigated the assimilability of taranakite by plants.

Compounds of group 3 (according to Haseman's classification) were prepared by Lindsay[33] (iron derivatives) and Smith and Brown[55] (aluminium derivatives) and those of group 5 by the same authors and Arlidge et al.[62] However, the compound $NH_4Fe_3H_8(PO_4)_6.6H_2O$ differed in its X-ray diffraction characteristics from the compound described by Haseman.

§ Cohen's compounds contained a lower percentage of water, but this can be attributed to the inaccuracy of the determination, since it was found by difference.

Table 2. Phosphatoaluminates and phosphatoferrates(III) identified in the products of the reaction of phosphate fertilizers with soil[33].

No.	Chemical formula	Empirical formula	Mineral	Form of phosphate fertilizer
1	(K, H) (Fe, Al)$_3$H$_8$(PO$_4$)$_6$·6H$_2$O	$K_2O(H_2O)3Fe_2O_3(Al_2O_3)\cdot6P_2O_5\cdot20H_2O$		$Ca(H_2PO_4)_2$
2	(NH$_4$, H) (Fe, Al)$_3$H$_8$(PO$_4$)$_6$6H$_2$O	$(NH_4)_2O(H_2O)\cdot3Fe_2O_3(Al_2O_3)\cdot6P_2O_5\cdot20H_2O$		ditto
3	Colloidal (Fe, Al)PO$_4$·n H$_2$O			$Ca(H_2PO_4)_2$; $NH_4H_2PO_4$, $(NH_4)_2HPO_4$
4	FePO$_4$·2H$_2$O	$Fe_2O_3P_2O_5\cdot4H_2O$	strengite	Ca $(H_2PO_4)_2$
5	FePO$_4$·2H$_2$O	ditto	metastrengite	ditto
6	K$_3$Al$_5$H$_6$(PO$_4$)$_8$·18H$_2$O	$3K_2O\cdot5Al_2O_3\cdot8P_2O_5\cdot42H_2O$	K-taranakite	$Ca(H_2PO_4)_2$; KH_2PO_4
7	(NH$_4$)$_3$Al$_5$H$_6$(PO$_4$)$_8$·18H$_2$O	$3(NH_4)_2O\cdot5Al_2O_3\cdot8P_2O_5\cdot42H_2O$	NH_4-taranakite	$Ca(H_2PO_4)_2$; $NH_4H_2PO_4$
8	NH$_4$Fe(HPO$_4$)$_2$	$(NH_4)_2O\cdot Fe_2O_3\cdot2P_2O_5\cdot2H_2O$		$NH_4H_2PO_4$
9	NH$_4$Al$_2$(PO$_4$)$_2$OH·8H$_2$O	$(NH_4)_2O\cdot2Al_2O_3\cdot2P_2O_5\cdot17H_2O$		$(NH_4)_2HPO_4$

Tables 1 and 2 do not exhaust the wide variety of compounds which can be prepared from dilute solutions. In the study of the reaction of ammonium phosphate with gibbsite at a pH in excess of 5.4, Taylor et al.[57] found the following compounds which had not been described earlier: $(NH_4)_2AlH(PO_4)_2.4H_2O$ [empirical formula $2(NH_4)_2O.Al_2O_3.2P_2O_5.9H_2O$] and $NH_4AlPO_4(OH).2H_2O$ [or $(NH_4)_2O.Al_2O_3.P_2O_5.5H_2O$]. Somewhat later the presence of the same compound was established in the precipitate deposited in the reaction of wet-process phosphoric acid with ammonia[34]. The above salts were also prepared artificially by Frazier and Taylor[60]. The composition of the salts is close to that of potassium phosphatoaluminate (product of R of group 8), differing from the latter only in a higher water content, which can be attributed either to an error in its determination or to the capacity of these compounds to form numerous hydrates.

Arlidge et al.[62] obtained the ammonium derivatives $NH_4Fe_2(PO_4)_2.(OH).2H_2O$ corresponding to the mineral leucophosphite (product I, group 4).

In future the above list will probably be extended.

V. PROPERTIES OF COMPOUNDS OF THE TYPE $a(NH_4)_2O.bR_2O_3.cP_2O_5.nH_2O$

As already mentioned, Haseman et al.[54] investigated in fair detail the compounds synthesised, including certain metal ammonium phosphates.

In recent years much attention has been devoted to the study of the physicochemical properties of taranakite and certain other products of the reaction of soluble phosphates with soils. Taylor and Gurney[59] determined the solubility of the synthetic taranakites $H_6K_3Al_5(PO_4)_8.18H_2O$ and $H_6(NH_4)_3Al_5(PO_4)_8.18H_2O$. Their solubility products were calculated from the compositions of the solutions in equilibrium with the solid phase. The negative logarithm of the solubility product of ammonium taranakite was found to be 175.5. This value is regarded as approximate, since account was not taken of the possibility of the formation of complex ions in the liquid phase.

It has been established that, in solutions where the activity product $a_{Al}a_{PO_4}$ exceeds 1×10^{-20}, taranakite dissolves incongruently with formation of amorphous aluminium phosphate.

Egan et al.[61] gave the heat capacities, entropies, and enthalpies of taranakite over a wide range of temperatures, between 10° and 310°K. The entropy at 298.16°K, the enthalpy, and the heat of formation from the elements of $H_6(NH_4)_3Al_5(PO_4)_8.18H_2O$ are respectively 339.9 ± 0.6 e.u., 57 170 cal $mole^{-1}$, and −4432 kcal $mole^{-1}$.

Smith and Brown[55] determined by X-ray diffraction analysis the lattice constants and densities of the compounds $(NH_4)_2O.Al_2O_3.2P_2O_5.3H_2O$ (item D, group 3), $(NH_4)_2O.3Fe_2O_3.6P_2O_5.20H_2O$ (product K, group 5), $(NH_4)_2O.3Al_2O_3.6P_2O_5.20H_2O$, and a series of potassium compounds.

Arlidge et al.[62] recorded the powder diffraction patterns and infrared spectra of a large number of synthetic aluminium and iron phosphates corresponding to the natural minerals variscite and metavariscite ($AlPO_4.2H_2O$), strengite and phosphosiderite ($FePO_4.2H_2O$), barrandite (Al, Fe)$PO_4.2H_2O$, leucophosphites (K, NH_4)$Fe_2(PO_4)_2(OH).2H_2O$, and taranakites, and also some of the synthetic phosphates, namely $NH_4Fe_3H_8(PO_4)_6.6H_2O$ [empirical formula $(NH_4)_2O.3Fe_2O_3.6P_2O_5.20H_2O$], and the corresponding potassium compound.

The powder diffraction pattern of the salt $NH_4Fe_3H_8(PO_4)_6.6H_2O$ was also recorded by Haseman, but comparison of the two patterns proves them to be completely different.

The products enumerated above were also analysed thermographically.

Frazier and Taylor[60] made optical, X-ray diffraction, and thermographic studies of the artificial taranakites, and the salts $(NH_4)_2.AlH(PO_4)_2.4H_2O$, $NH_4AlPO_4OH.2H_2O$, and $NH_4AlPO_4.OH.3H_2O$ and measured the infrared spectra. Their differential heating curve for ammonium taranakite differed from those obtained by Arlidge et al. and depended on the conditions of the thermographic experiments (in a stream of air or in a stationary atmosphere) and on the dilution of the specimen; on this basis, the authors concluded that thermal analysis is unsuitable for the identification of ammonium phosphatoaluminates.

The ammonium phosphato-ferrates(III) and -aluminates investigated by the present author[53] behaved on heating similarly to the corresponding divalent metal compounds, namely ammonia and water were evolved from the salts in several stages with formation of a series of intermediate compounds, as shown by the changes in the refractive indices and in the colour of the iron compounds. The intermediate compounds were not identified.

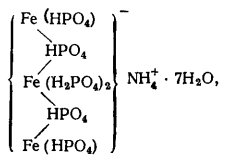
The Structure of Compounds of the Type $a(NH_4)_2O.bR_2O_3.cP_2O_5.nH_2O$

The application of X-ray diffraction and infrared spectroscopy in the study of certain trivalent metal ammonium phosphates isolated in a pure form established the presence of definite groups in these compounds and demonstrated their distribution, and conclusions concerning their structure were arrived at on this basis. As already stated, Smith and Brown[55], having determined by X-ray diffraction the space groups and the density of the compound $2(NH_4)_2O.3Al_2O_3.5P_2O_5.26H_2O$ obtained by Haseman and corresponding to the natural mineral taranakite, found that the formula $(NH_4)_3Al_5H_6(PO_4)_8.18H_2O$ gives a better representation of the properties of this compound.

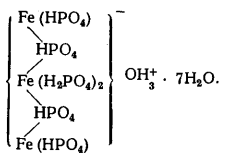
The infrared spectra of taranakite, obtained by Arlidge et al.[62], showed that it contains acid phosphate groups. Arlidge et al. isolated from dilute solutions the compounds $(NH_4, K)_2O.2Fe_2O_3.2P_2O_5.5H_2O$, corresponding to group 4 in Haseman's classification, and found by infrared spectroscopy that they contain the OH and PO_4 groups and water of hydration, which led to their identification with the natural mineral leucophosphite $NH_4Fe_2(PO_4)_2(OH).2H_2O$.

Shishkin and coworkers[63,64], who studied the structure of iron phosphates, established that in some of these part of the water of crystallisation is of the oxonium type. For example, they regard phosphatoferric(III) acid as the oxonium salt $[Fe(HPO_4)_2]^-OH_3^+$, and Weinland's pink salt as an isomorphous compound, and therefore they believe that Weinland's salt is more correctly represented by the formula $[Fe(HPO_4)_2]^-NH_4^+$. They believe that the validity of this formula is confirmed by the fact that two of the hydrogen ions in this salt cannot be substituted by ammonium ions. Furthermore, the compounds $[(Fe(HPO_4)_2]NH_4$ and $[Fe(HPO_4)_2]H_3O$ proved to be very similar in their physical properties (specific gravity, refractive index). It is quite possible that this formula does indeed represent better the structure of the above ammonium phosphatoferrate(III). The possibility of the existence of the complex $[Fe(HPO_4)_2]^-$ in solutions of iron salts in phosphoric acid has been pointed out by Salmon[65].

The second of Weinland's salts, with the empirical formula $(NH_4)_2O.3Fe_2O_3.6P_2O_5.22H_2O$, Shishkin and coworkers represent as follows:



believing it to be isomorphous with the phosphate $3Fe_2O_3.6P_2O_5.25H_2O$ or



The review of the literature data shows that, despite the fact that metal ammonium phosphates are already used in various branches of the national economy, their properties and specially their structure have been investigated quite inadequately.

The structure of certain trivalent metal compounds, formed in the reaction between fertilizers and soils, has been investigated more completely using new research techniques (X-ray diffraction, the crystal-optical method, infrared spectroscopy). These studies were stimulated by the requirements of the technology of fertilizers and agrochemistry: the manufacture of new types of fertilizers and the endeavour to improve their efficacy. As already stated, many of these compounds have been prepared artificially from dilute solutions containing aluminium or ferric phosphates and ammonium phosphate. In this concentration range compounds with the same composition and properties were not always obtained.

The situation is even less clear in the range of high concentrations. Among all the compounds obtained, only the existence of the salt $NH_4Fe(HPO_4)_2$ has been firmly established. The information about all other compounds is contradictory.

On the other hand, the divalent metal compounds are readily precipitated from both dilute and concentrated solutions in the form of crystalline salts having definite composition, but here too very little is so far known about their structure; the available information is insufficient for the solution of a number of problems associated with their properties.

In technological processes involving the synthesis of metal ammonium phosphates it is desirable to carry out the precipitation from concentrated solutions and therefore compounds precipitated in this concentration range are of great practical interest. The synthesis of iron ammonium phosphate has already been achieved in the USSR and the synthesis of a fire-resistent agent based on ammonium phosphato-aluminate and -ferrate(III) is being introduced. The necessity to use in the manufacture of fertilizers low-grade phosphorites containing a considerable amount of iron and aluminium has also stimulated the expansion of studies in this field.

The development of studies on the application of a number of metal ammonium phosphates as slowly hydrolysable complex fertilizers containing both macro- and micro-elements and the development of synthetic methods for these compounds are of considerable interest.

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Separation of Rare-earth Elements† by Electrolysis at a Mercury Cathode

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The review deals with the questions of the mechanism of the reduction of rare-earth elements at a stationary mercury cathode and the conditions of their electrochemical deposition and separation, and of their extraction by alkali metal amalgams, are described and discussed. Examples of the separation of almost all the rare-earth elements at a mercury cathode are quoted. The bibliography incorporates 103 references.

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I. INTRODUCTION

Among the methods for the separation of rare-earth elements available at the present time the most widely used are fractionation based on the gradual variation of the solubility or basicity of rare-earth compounds, ion-exchange and partition chromatography, extraction methods, and electrolysis at a mercury cathode. The last makes it possible, in particular, to separate comparatively readily large amounts of one rare earth from very small amounts of other adjacent elements and can be used in most cases where the separation of large amounts of a rare earth by ion-exchange or fractionation methods involves considerable difficulties.

† Lanthanides is the term used at present in Western literature (Ed.of Translation).

At the present time a large amount of data on the separation of rare earth at a stationary mercury cathode has accumulated. However, unfortunately studies on electrolysis with a mercury cathode for the separation of rare-earth elements has not been reviewed so far. Some information is given in the review of Ryabchikov and Terent'eva[1].

II. APPLICATION OF THE MERCURY CATHODE

The method of the electrolytic reduction of rare-earth elements developed as a result of several studies carried out with different aims. In 1906 Matignon[2] isolated samarium(II) sulphate and in 1911 Urbain and Burion[3] isolated for the first time a europium(II) compound. In