DEPARTMENT OF THE INTERIOR

BULLETIN

OF THE

UNITED STATES

GEOLOGICAL SURVEY

No. 167

WASHINGTON
GOVERNMENT PRINTING OFFICE
1900

UNITED STATES GEOLOGICAL SURVEY
CHARLES D. WALCOTT, DIRECTOR

CONTRIBUTIONS TO CHEMISTRY AND MINERALOGY FROM THE LABORATORY OF THE UNITED STATES GEOLOGICAL SURVEY

FRANK W. CLARKE
CHIEF CHEMIST

WASHINGTON
GOVERNMENT PRINTING OFFICE
1900

CONTENTS.

ILLUSTRATIONS.

LETTER OF TRANSMITTAL.

DEPARTMENT OF THE INTERIOR,
UNITED STATES GEOLOGICAL SURVEY.
Washington, D. C., November 4, 1899.

SIR: I submit herewith a manuscript entitled Contributions to Chemistry and Mineralogy from the Laboratory of the United States Geological Survey. I have the honor to request that it be published as a bulletin of the Survey.

Very respectfully,

F. W. CLARKE,
Chief Chemist.

HON. CHARLES D. WALCOTT,
Director United States Geological Survey.

PREFATORY NOTE.

In the following pages there have been brought together a variety of chemical and mineralogical researches, which were carried out in the laboratory of the United States Geological Survey between July 1, 1893, and July 1, 1899. In one sense the bulletin is a continuation of the series represented by Bulletins Nos. 9, 42, 55, 60, 64, 78, 90, and 113; only, unlike them, it reports no miscellaneous analyses. The latter represent by far the larger part of the work done in the laboratory; but most of them are published in other form, in connection with the geological investigations to which they relate. Their repetition here is unnecessary.

F. W. C.

CONTRIBUTIONS TO CHEMISTRY AND MINERALOGY.

EXPERIMENTS RELATIVE TO THE CONSTITUTION OF PECTOLITE, PYROPHYLLITE, CALAMINE, AND ANALCITE.

By F. W. CLARKE and GEORGE STEIGER.

In a series of investigations by Clarke and Schneider, which were carried out in the laboratory of the United States Geological Survey between 1889 and 1892,[1] a number of reactions were examined which shed some light upon the constitution of several natural silicates. The work then begun was unfortunately interrupted for several years; but it is now resumed, with the hope that it may be pushed considerably further.

Two of the reactions studied by Clarke and Schneider were of peculiar interest. First, in the case of talc, it was found that one-fourth of the silica could be liberated by ignition; and that the fraction thus set free was measurable by solution in aqueous sodium carbonate. This reaction suggests that other acid metasilicates may behave in a similar way, and that we perhaps have a means of discrimination between such salts and other compounds which simulate them. In other words, an acid metasilicate may be experimentally distinguished from a pseudometasilicate by the way in which it splits up when ignited. Evidence bearing upon this supposition will be found in the present paper.

The second of the reactions just referred to is that between dry ammonium chloride, at its temperature of dissociation, and various silicates.[2] This involves, in part at least, the action of dry gaseous hydrochloric acid upon the compounds which are studied; and different minerals are very differently attacked. Some are almost completely decomposed, others are affected but slightly; and here again there seems to be a method of diagnosis which deserves further attention. Both reactions suggest the main purpose of the investigation; which is, the fractional analysis of silicates by means of various reagents, in

---

[1] Bull. U. S. Geol. Survey No. 78, p. 11; Bull. No. 90, p. 11; Bull. No. 113, p. 27.

[2] Bull. U. S. Geol. Survey No. 113, p. 34.

order to gain evidence bearing upon their chemical structure. The evidence, at least, is of value, whether the interpretation of it be right or wrong. Each fact helps to the ultimate solution of the central problem, the problem of constitution.

PECTOLITE.

The pectolite which was chosen for examination was the well-known radiated variety from Bergen Hill, New Jersey. The mineral was in long, white needles, and apparently quite pure; but the analysis shows that it contained some carbonate as an impurity. Enough of the material was ground up to furnish a uniform sample for the entire series of experiments, and the work properly began with a complete analysis. The results obtained are as follows:

Analysis.

SiO_2	53.34
Al_2O_3	.33
CaO	33.23
MnO	.45
Na_2O	9.11
Total H_2O	2.97
CO_2	.67
	100.10

Fractional water.

At 105°	0.27
At 180°	.16
At 300°	.22
At redness	2.32
	2.97

All of the water was given off at a barely visible red heat; and the figures show that practically all of it is constitutional, a fact which perhaps hardly needed reverification. The analysis gives the accepted formula for pectolite,

$$HNaCa_2Si_3O_9.$$

Does this represent, as is commonly assumed, a true metasilicate? If it does, we should expect that ignition would split off silica proportional to the acid hydrogen, or one-sixth of the total amount. To answer this question several portions of the pectolite were sharply ignited, to complete dehydration, and then boiled each for fifteen minutes with a solution of sodium carbonate containing 250 grams to the liter. In the extract so obtained the silica was determined; and three experiments gave the following percentages:

	8.96
	8.67
	8.42
Mean,	8.68

One-sixth of the total silica is 8.89 per cent; and the experiments, therefore, justify the original expectation. The belief that pectolite is a metasilicate is effectively confirmed.

Upon the unignited pectolite the sodium carbonate solution has a slow decomposing action, both silica and bases being withdrawn. In two experiments fifteen minutes of boiling extracted 2.07 and 2.55 per cent of silica, and by a treatment lasting four days 4.80 per cent was taken out. With water alone similar results were obtained; the action being so rapid, although relatively slight, that pectolite, moistened, gives an immediate and deep coloration with phenol phthalein. By boiling the powdered pectolite with distilled water alone 1.65 per cent of silica was brought into solution, and the ignited mineral, similarly treated for fifteen minutes, gave 1.78 per cent. The extraction in these cases is really an extraction of alkaline silicate, as the two following experiments prove. In A the unignited pectolite was boiled for fourteen hours with distilled water; and in B the mineral after ignition was subjected to like treatment for four hours. The dissolved matter in each case was determined, with the subjoined results:

	A.	B.
SiO_2	2.98	3.03
CaO	.30	.10
Na_2O	.81	1.50
	4.09	4.63

In A, no simple ratio appears; but in B the extracted silicate approximates very nearly to the salt $Na_2Si_2O_5$. In each instance the ratios vary widely from those of the original mineral, showing that actual decomposition and not a solution of the pectolite as such has occurred.

In the experiments upon pectolite the heating with dry ammonium chloride was omitted, for the data are already given in the original paper by Schneider and Clarke. In their experiments the mineral was thrice heated with ten times its weight of the reagent to above 350°, and then leached out with water. In the solution 20.50 per cent of lime and 6.95 of soda were found, with part of the manganese; showing that a very considerable decomposition had taken place. Possibly, by repeated treatments with ammonium chloride a complete decomposition might be effected, but this question is one upon which it seemed unnecessary to spend further time.

PYROPHYLLITE.

The empirical formula for pyrophyllite, $AlHSi_2O_6$ is apparently that of an acid metasilicate, and the mineral is therefore peculiarly available for fractional analysis. The compact variety from Deep River, North Carolina, was taken for examination, and a uniform sample was prepared. Analysis gave the following results:

SiO_2	64.73
TiO_2	.73
Al_2O_3	29.16
Fe_2O_3	.49
MgO	trace
Ignition	5.35
	100.46

If, now, pyrophyllite is an acid metasilicate it should break up on ignition in accordance with the equation

$$2AlHSi_2O_6 = Al_2Si_3O_9 + SiO_2 + H_2O.$$

That is, one-fourth of the silica, or 16.18 per cent, should be liberated. The mineral itself is very slightly attacked by boiling with the sodium carbonate solution, and in an experiment of this kind only 0.72 per cent of silica was dissolved. Upon ignition under varying circumstances the following data were obtained:

Ignited ten minutes over a Bunsen burner, and then extracted with sodium carbonate solution, 1.51 per cent of SiO_2 dissolved.

Ignited fifteen minutes over a Bunsen burner, 1.89 per cent became soluble.

Ignited ten minutes over a Bunsen burner and then fifteen minutes over the blast, 2.84 per cent of silica was liberated.

These results are of a different order from those given by pectolite and talc, and raise the question whether pyrophyllite, despite its ratios, is a metasilicate at all. So far as the evidence goes, it may with propriety be regarded as a basic salt of the acid $H_2Si_2O_5$, and its formula then becomes

$$Si_2O_5 = Al - OH.$$

This formula is at least as probable as the metasilicate expression, which latter rests upon assumption alone. Still other formulæ, but of greater complexity, are possible; but until we know more of the genesis and chemical relationships of pyrophyllite, speculation concerning them would be unprofitable.

By heating with dry ammonium chloride, pyrophyllite is very slightly attacked. In two experiments it lost in weight 6.17 and 6.30 per cent, respectively. The excess of loss over water is due, as we have proved, to the volatilization of a little ferric and aluminic chloride. The residue of the mineral after this treatment contained no chlorine, so that no chlorhydrin-like body had been formed. The formation of such a compound, the replacement of hydroxyl by chlorine, would, if it could be effected, be a valuable datum toward determining the actual constitution of the species.

CALAMINE.

The simplest constitutional formula for calamine, the one which is generally accepted, represents it as a basic metasilicate, $SiO_3=(ZnOH)_2$. In this the hydrogen is all combined in one way, and so, too, is the zinc. In all other possible formulæ, simple or complex, the hydrogen as well as the zinc must be represented as present in at least two modes of combination; a condition of which, if it exists, some evidence should be attainable. Our experiments upon calamine have had this point in view; and we have sought to ascertain whether water or zinc could be split off in separately recognizable fractions. Our results, in the main, have been negative, and tend toward the support of the usual formula; but the data are not conclusive, although they seem to be worthy of record.

The beautiful white calamine from Franklin Furnace, New Jersey, was selected for study, and gave the subjoined composition:

Analysis.

SiO_2	24.15
Al_2O_3, Fe_2O_3	.19
ZnO	67.55
CaO	.12
H_2O	7.95
	99.96

Fractional water.

At 100°	.27
At 180°	.22
At 250°	.75
At 300°	.88
Incipient red heat	4.46
Full red heat	1.37
	7.95

Here no clear and definite fractionation of the water is recognizable, at least of such a character as to suggest any other than the ordinary formula for calamine.

Upon boiling powdered calamine with water practically nothing went into solution, but by boiling with the solution of sodium carbonate 0.25 per cent of silica was dissolved. After ignition at a red heat, only 0.14 per cent of silica became soluble in sodium carbonate, and after blasting, only 0.24. In these experiments a very little zinc was dissolved also; but there was no evidence that any breaking up of the mineral into distinguishable fractions had occurred. In a hot 10 per cent solution of caustic soda both the fresh and the ignited calamine dissolve almost completely; but boiling with aqueous ammonia seems to leave the mineral practically unattacked. All experiments aiming to extract a definite fraction of zinc while leaving a similar fraction behind resulted negatively.

By heating with dry ammonium chloride, calamine is vigorously attacked, and gains in weight by absorption of chlorine. In two experiments the mineral was intimately mixed with three times its weight of powdered salammoniac and heated in an air bath for several hours to a temperature somewhat over 400°. A large part of the residue was soluble in water, and the percentage of this portion, together with the percentage increase in weight, is given below.

	I.	II.
Gain in weight	27.60	25.78
Soluble in water	53.23	67.13

A conversion of calamine into the chlorhydrin, $SiO_3(ZnCl)_2$ would involve a gain in weight of 15.34 per cent. Complete conversion into $2ZnCl_2 + SiO_2$ implies an increase of 38.14 per cent. The figures given lie between these two; and are indefinite also for the reason that there was volatilization of zinc chloride.

In two more experiments the calamine, mingled with three times and four times its weight of ammonium chloride, respectively, was heated for an hour and a half to bright redness in a combustion tube. The zinc chloride which was formed, volatilized, and was collected by suitable means for determination. It corresponded to 59.6 and 59.0 per cent of the original mineral, calculated as zinc oxide; which indicates a nearly complete decomposition of the calamine into $2ZnCl_2 + SiO_2$. The residue was mainly silica, with a small part of the zinc, about half of the silica being soluble in sodium carbonate solution. Here again no definite fractionation of the mineral could be observed.

Finally the action of dry hydrogen sulphide upon calamine was investigated. The mineral was heated to redness in a current of the gas, and gained perceptibly in weight. The percentage data, reckoned on the original calamine, were as follows, in two experiments:

	I.	II.
Gain in weight	6.00	6.43
SiO_2 soluble in Na_2CO_3	16.45	20.95
Sulphur in residue	....	24.12

Complete conversion of calamine into $2ZnS + SiO_2$ implies a gain in weight of 5.80 per cent; and it is therefore evident from the figures of the second experiment that the limit of change was approached very nearly. The 24.12 of sulphur taken up is quite close to the 26.53 per cent which is required by theory. About eight-ninths of the calamine had undergone complete transformation. Again, no definite fractionation was detected.

The hydrogen sulphide reaction was examined still further with reference to the temperature at which it becomes effective. Even in the cold calamine is slightly attacked by the gas, but its action is unimportant until the temperature of 400° is approximated. Then it becomes vigorous and the reaction goes on rapidly. A few experiments with willemite showed that it also was attacked by hydrogen sulphide, but less vigorously than calamine.

ANALCITE.

Analcite, from many points of view, is a species of peculiar interest, and of late years it has received a great deal of attention. Its formula may be written in various ways, especially as regards the interpretation of its one molecule of water; but evidence too often has yielded before preconceived opinion. Additional evidence is now available, partly from the experiments of Friedel and partly from the data obtained during the present investigation.

The analcite examined by us was in well-developed crystals from Wassons Bluff in Nova Scotia. A uniform sample was prepared as usual, and the analysis given below is contrasted with the theoretical composition required by the accepted empirical formula $NaAlSi_2O_6 H_2O$.

Analysis.

	Found.	Calculated.
SiO_2	57.06	54.55
Al_2O_3	21.48	23.18
Fe_2O_3	.13	....
CaO	.16	....
Na_2O	12.20	14.09
H_2O at 100°	.58	....
H_2O over 100°	8.38	8.18
	99.99	100.00

Fractional water.

At 100°	0.58
At 180°	1.16
At 260°	3.64
At 300°	1.57
Low redness	1.90
Full redness	0.11
Blast	none.
	8.96

The fractional water determinations were made by heating in an air bath to constant weight at each temperature up to 300° and finally over the direct flame. The first fraction, at 100°, is evidently hygroscopic or extraneous water, which can be disregarded. The remainder of the water, 8.38 per cent, belongs to the species. The significance of the analytical figures will be considered later.

Upon boiling the powdered analcite with sodium carbonate solution, 250 grams to the liter as in all the preceding experiments, 0.73 per cent of silica was extracted. After ignition the mineral in two determinations yielded 1.46 and 1.38 per cent respectively. The splitting off of silica is therefore very slight; and one of the formulæ proposed by Doelter,[1] $Na_2Al_2Si_2O_8 + 2H_2SiO_3$, may be set aside as improbable. Metasilicic acid or an acid metasilicate can hardly be present in analcite, although the possibility of a neutral metasilicate, as indicated by the empirical formula, is not excluded. By Doelter's formula one-half of the silica ought to be removable.

Upon heating analcite with dry ammonium chloride results of a remarkable character were obtained. Sodium chloride was formed which could be leached out by water and measured, while ammonia free from chlorine was retained by the residue to a notable and surprisingly stable degree. The experiments in detail were as follows:

A. Analcite, mixed with four times its weight of ammonium chloride was heated for four hours to 350°. There was a gain in weight of 2.18 per cent, and 6.10 per cent of soda, or one-half of the total amount, was converted into NaCl, which was leached out by water, examined as to its purity, and weighed. In the residue 1.20 per cent of silica was extractable by sodium carbonate, showing that no more splitting off had occurred than was previously observed. The gain in weight, as will be seen from subsequent experiments, is due to the fact that all of the NH_4Cl had not been driven off; or else that more water was retained.

B. Analcite was ground up with four times its weight of NH_4Cl, heated for several hours, reground with another fourfold portion of chloride, and heated to 350° for twenty-one hours. Gain in weight, 0.08 per cent; 5.57 per cent of soda was extracted as chloride.

C. Analcite heated to 350° for eight hours, with four times its weight of NH_4Cl. Loss of weight, 0.10 per cent.

---

[1] Neues Jahrb. für Min., 1890, Vol. I, p. 133.

D. Six grams of mineral and 28 of chloride, mixed by thorough grinding, were heated to 350° for fourteen hours; then were reground with 28 grams of fresh NH_4Cl and heated for thirty-five hours. Loss of weight, 0.13 per cent; 5.07 per cent of soda was extracted as chloride, plus 0.14 of ammonium chloride unexpelled; 2.03 per cent of silica was rendered soluble in sodium carbonate.

So far, three facts are noticeable. First, the weight of the mineral after treatment is almost exactly the same as before; showing that gains and losses have balanced each other. Second, little silica has been split off. Third, approximately, but not rigorously, one-half of the soda had been converted into NaCl. In A, it was exactly half; in the other experiments, a little less than half. Furthermore, in the sodium chloride dissolved out there is only a very little ammonium chloride, amounting at most to 0.14 per cent, calculated upon the weight of the original mineral.

In the residue of the analcite after extraction of sodium chloride, abundant ammonia can be detected, with either no chlorine or at most a doubtful trace. If, however, the unleached mineral, still retaining its sodium chloride, be heated strongly, say from 400° up to redness, NH_4Cl is regenerated and given off. Its absence, as such, both from the leach and the residue was repeatedly proved. The ammonia and water retained by the analcite after heating to 350° with ammonium chloride were several times determined; and the following percentages, still reckoned on the original mineral, were found:

	NH_3.	H_2O.
In B	2.03	2.25
In C	2.19	2.00
In D	2.36	1.89
In D	2.35	....
In D	2.06	....
Mean	2.20	2.04

Correcting the ammonia for the 0.14 of NH_4Cl found in D, the mean value becomes 2.15. This permanent ammonia is not given off upon warming the material with caustic soda solution, and is therefore not present as a salt. The determinations of it were made by three distinct methods, and there is no possible doubt as to its presence and character.

The composition of the analcite after the treatment with ammonium chloride may now be considered, with the subjoined combination of the data. The NaCl in A, 11.50 per cent, was in material which had gained 2.18 per cent, and is subject to a correction which reduces the figure to 11.26. In B, C, and D the corresponding correction is so small that it may be neglected. The last column gives the composition of the leached residue, recalculated to 100 per cent, after deduction of NaCl and the soluble silica. The letters refer back to the several experiments, and the little iron is included with the alumina.

	A.	B.	C.	D.	Average.	Residue.
Sol. SiO_2	1.20			2.03	1.61	
Insol. SiO_2				54.96	54.96	62.59
Al_2O_3				21.37	21.37	24.34
CaO				.16	.16	.18
NaCl	11.26	10.50		9.57	10.44	
Na_2O				7.12	7.12	8.11
NH_3		2.03	2.19	2.21	2.15	2.46
H_2O		2.25	2.00	1.89	2.04	2.32
				99.31	99.85	100.00

The analcite residue, like the original mineral, is completely decomposable by aqueous hydrochloric acid. It may be a mixture, but it seems more probable that it is a definite compound, for it approximates in composition to the formula

$$H_2Na_2Al_4Si_8O_{24} . NH_3.$$

This represents a quadrupled analcite formula, in which half of the sodium is replaced by hydrogen, and with NH_3 in place of $4H_2O$ The analytical comparison is as follows:-

	Found.	Calculated.
SiO_2	62.59	61.46
Al_2O_3	24.34	26.12
CaO	.18	
Na_2O	8.11	7.94
H_2O	2.32	2.30
NH_3	2.46	2.18
	100.00	100.00

The agreement is not close, but it is close enough to be suggestive and to indicate the character of the reaction which has taken place. It needs, however, verification by additional experiments upon other preparations, and upon analcite from other sources. In this connection it may be well to reiterate that the substance was prepared by very long heating at 350°, and is therefore stable at that temperature.

An interesting feature of these experiments is their harmony with the researches of G. Friedel,[1] who has shown that the water of zeolites may be replaced by ammonia and other substances, without change of the crystalline structure. In the case of analcite, ammonia was taken up to the extent of 2.04 per cent, or almost exactly the amount found

---

[1] Bull. Soc. Min., Vol. XIX, 1896, p. 94.

in our analcite residue. The great difference between Friedel's method of experimentation and ours renders the agreement all the more striking and sustains our belief that the mineral and the residue are compounds of the same general order. We hope to continue our experiments and to extend our investigations to other zeolites.

If, now, analcite and its derivative, our analcite residue, are analogous compounds, the relation between them is expressed by these formulæ:

Analcite.......................................$Na_4Al_4Si_8O_{24} . 4H_2O$.
Analcite residue...............................$H_2Na_2Al_4Si_8O_{24} . NH_3$.

That is, the minimum molecular weight assignable to analcite is represented by four times its empirical formula. Other interpretations of the evidence are possible, but this appears to be the simplest. The water of analcite, as Friedel has shown, must be regarded as water only, not as hydroxyl, for it can be expelled by heat without destruction of the crystalline nucleus, the anhydrous salt, and is taken up again from moist air. But whatever its mode of union may be, the amount of water corresponds to the simple molecular ratio which is indicated in the formula of the species. One molecule of analcite holds a certain definite number of water molecules, and Friedel's observations are not incompatible with the idea that these are retained with varying degrees of tenacity. This idea is suggested by the various series of fractionation experiments which have been made from time to time by independent workers, even though the data are not by any means concordant. Thus Lepierre[1] found that half the water of analcite was driven off at or below 300°, the other half above 440°. In our own experiments three-fourths were expelled at 300°, the remaining fourth being held up to a much higher but undetermined temperature. In both series the water fractions are representable by fourths, but Friedel's experiments[2] indicate a continuity of loss in weight of quite a dissimilar order. Friedel holds that all of the water fractionations heretofore made upon analcite are fallacious, and that no definite fractions can be identified, a conclusion strongly supported by his own data, even though the proof is not absolutely positive. The most that can be said is that the weight of evidence so far is in favor of Friedel's contention, but that additional investigation is necessary in order to reconcile all discrepancies. The full significance of the water in analcite remains unknown.

In order to discuss the constitution of analcite, let us recur to the analysis of the mineral itself. It is at once evident from the comparison made on a preceding page that our sample of the mineral varies notably in composition from the requirements of theory. The silica is 2.5 per cent too high, while alumina and soda are correspondingly low. No probable impurity and no presumable errors of manipulation can

---

[1] Bull. Soc. chimique, Paris, 3d series, Vol. XV, 1896, p. 561.

[2] Bull. Soc. min., Vol. XIX, 1896, p. 363.

account for so great a divergence. If we consult other analyses, as we find them tabulated in manuals like those of Dana and of Hintze, we shall find other cases resembling this, and also examples of variation in the opposite direction, with silica low and an apparent excess of bases. Most analcite gives quite sharply the metasilicate ratios required by the accepted formula; but the variations from it are large enough, common enough, and regular enough to command attention. The analyses are not all covered by the recognized theory, and the apparent irregularities are not fortuitous, but are systematic in character.

One explanation of the seeming anomalies is simple and clear. If analcite, instead of being a metasilicate, is really a mixture of ortho- and trisilicate, then all of the analyses became intelligible. In most cases the two salts are commingled in the normal ratio of one to one; but in our analcite the trisilicate predominates, while in some other samples the orthosalt is in excess. All reduce alike to the simple expression

$$NaAlX.\ H_2O,$$

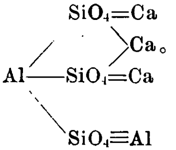
in which X represents $nSiO_4+mSi_3O_8$; a formula which agrees with evidence from various other sources.

For example, analcite may be derived in nature either from albite, $AlNaSi_3O_8$, or nephelite, $AlNaSiO_4$, and, on the other hand, alterations of it into feldspars have been observed. Its closest analogue, leucite, has yielded pseudomorphs of orthoclase and elæolite; while leucite and analcite are mutually convertible each into the other. The evidence of this character, the evidence of relationship between analcite and other species, is varied and abundant, and the simplest conclusion to be drawn from it is that which has been given. Every alteration, every derivation, every variation in the composition of analcite points to the same belief. The consistency of the data can not well be denied.

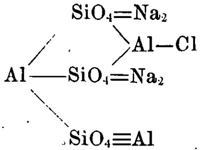
In the case of a normal analcite—that is, one which conforms to the usual empirical formula—the expression which best represents these relations is

$$Al_4Na_4(SiO_4)_2\,(Si_3O_8)_2\,.\,4H_2O;$$

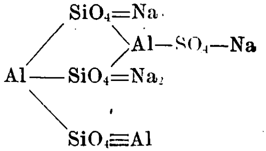
and this accords with the minimum molecular weight as determined by the study of our ammoniated residue. Structurally, this is comparable with the formulæ of garnet, zunyite, sodalite, nosite and leucite; all of which are also isometric in crystallization. The more important of the symbols are as follows:



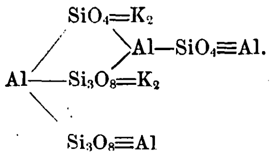
Garnet.



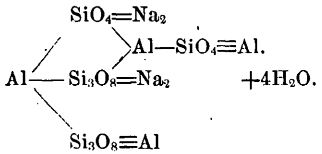
Sodalite.



Nosite.



Leucite.



Analcite.

That is, analcite and leucite become members of the garnet-sodalite group of minerals, and their relations to nephelite, albite, prehnite, natrolite, etc., natural and artificial, are perfectly clear. In analcite there may be admixtures of strictly analogous ortho- or trisilicate molecules; but these remain to be separately discovered.

Now, these formulæ are not ultimate verities to be blindly accepted. They are simply expressions which represent composition and a wide range of established relationships, and which serve a distinct purpose in the correlation of our knowledge. Properly used, with due recognition of their limitations, they are helpful, and suggest possibilities of research; misused, they may become mischievous. They now satisfy all known conditions, and that is a sufficient warrant for their existence.

THE CONSTITUTION OF TOURMALINE.

By F. W. Clarke.

Some years ago, in an extended paper upon the constitution of the silicates,[1] I proposed a formula for tourmaline which seemed to satisfy all known conditions. Recently Penfield and Foote[2] have offered still another interpretation of the analyses, and support their views with a considerable weight of argument. The appearance of their paper has led me to rescrutinize the evidence more in detail than previously, and the result has been to modify my formulæ in some particulars while retaining them in their general form.

According to Penfield and Foote all tourmaline may be represented as salts of the alumino-borosilicic acid $H_{11}Al_3B_2Si_4O_{21}$, in which two hydroxyls are permanently linked to boron, leaving an available valency or basicity of nine. In my formulæ all tourmalines are derived from the similar acid $H_{14}Al_5B_3Si_6O_{31}$, with all of the hydrogen atoms replaceable by bases. Upon bringing the two acids to the common basis of six silicon atoms, they compare as follows:

Penfield and Foote	$H_{16\frac{1}{2}}Al_{4\frac{1}{2}}B_3Si_6O_{31\frac{1}{2}}$
Clarke	$H_{14}Al_5B_3Si_6O_{31}$

Replacing aluminum by hydrogen, in order to show the ultimate acids, these expressions become

Penfield and Foote	$H_{30}B_3Si_6O_{31\frac{1}{2}}$
Clarke	$H_{29}B_3Si_6O_{31}$

The small difference between the empirical formulæ is thus made evident, and it hardly amounts to more than the uncertainties in the analyses. In fact, the trustworthy analyses of tourmaline give ratios lying between and beyond both extremes, as the following formulæ, computed from Riggs's data, show: In these expressions fluorine has been assumed equivalent to hydroxyl.

Pierrepont, black	$H_{28.87}B_{2.93}Si_6O_{30.83}$
Paris, black	$H_{30.73}B_{2.66}Si_6O_{31.35}$
Stony Point, black	$H_{30.23}B_{3.02}Si_6O_{31.65}$
Auburn, colorless	$H_{29.25}B_{2.77}Si_6O_{30.78}$
Brazil, red	$H_{30.79}B_{2.78}Si_6O_{31.56}$
Gouverneur, brown	$H_{28.36}B_{2.95}Si_6O_{30.61}$
Hamburg, brown	$H_{30.93}B_{3.05}Si_6O_{32.14}$

---

[1] Bull. U. S. Geol. Survey No. 125, 1895.

[2] Am. Jour. Sci., 4th series, Vol. VII, 1899, p. 97.

The two analyses by Penfield and Foote, however, conform sharply to their formula, thus:

De Kalb, white	$H_{29.85}B_{3.03}Si_6O_{31.48}$
Haddam Neck, green	$H_{29.98}B_{3.06}Si_6O_{31.59}$

The Gouverneur and Hamburg tourmalines represent the extreme range of variation; a variation which is too large to be safely set aside as due to analytical errors or to impurities in the material analyzed. Some of the formulæ approximate to mine, some to that of Penfield and Foote, and hence it seems probable that neither formula, without some qualification, can safely be taken as final.

In order to be satisfactory, a constitutional formula must fulfill several conditions. First, it must adequately express the composition of the compound in question, covering all of its variations. Second, it must be readily applicable to the full discussion of analyses, so that the different isomorphous salts which are commingled in a mineral species can be separately identified and given reasonable expressions. Finally, it should indicate the relations between a species and the other minerals with which it is allied, or into which it commonly alters. A formula can be fully adopted only when all of these conditions are satisfied. The third condition, which relates to function, is equally important with the other two.

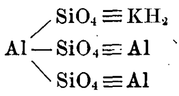
With the tourmalines, the micas seem to be most nearly akin. In each group we have to consider comminglings of isomorphous molecules, and when tourmaline alters, a mica is commonly the product of the reaction. In composition, also, the two groups show an apparent parallelism. With the lithia mica, lepidolite, lithia tourmalines occur; with muscovite and biotite, the common iron tourmaline is associated; and the magnesian tourmalines, which show the minimum of alumina in their composition, are similarly allied to phlogopite. This relationship, if it is real, should be suggested in the formulæ assigned to the several species.

To the commoner micas a simple series of formulæ can be easily given, thus:

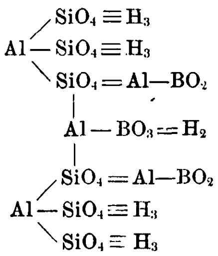
Muscovite	$Al_3(SiO_4)_3KH_2$,
Biotite	$Al_2(SiO_4)_3Mg_2KH$,
Phlogopite	$Al_1(SiO_4)_3Mg_3KH_2$;

and to these types, or mixtures of them, most micas are referable. The variations and exceptions have been considered elsewhere, and need not be discussed here.

With these fundamental molecules the corresponding salts of the tourmaline acid $H_{29}B_3Si_6O_{31}$, or $H_{14}Al_5B_3Si_6O_{31}$ are structurally correlated. The subjoined formulæ are sufficient to make this point clear; and to render the splitting up of tourmaline, its alteration into mica, somewhat intelligible.



Muscovite



The tourmaline acid.

In the acid, two hydrogen atoms are united with the orthoboric group, and twelve with the orthosilicate portion of the nucleus. Hence, to avoid repetition of the structural expression, the formula may be condensed into a linear form, as follows:

$$Al_5(SiO_4)_6(BO_2)_2 \,.\, BO_3H_2 \,.\, H_{12},$$

and this is applicable to the discussion of the analyses. For example, Riggs's analysis of the black magnesium tourmaline from Pierrepont, New York, corresponds to the following molecular mixture:

13. $Al_5(SiO_4)_6(BO_2)_2 \,.\, BO_3Ca \,.\, Mg_4H_4$
7. $Al_5(SiO_4)_6(BO_2)_2 \,.\, BO_3Mg \,.\, Mg_4H_4$
2. $Al_5(SiO_4)_6(BO_2)_2 \,.\, BO_3Na_2 \,.\, Al_2Na_4H_2$

Comparing this with the analysis, and reducing the latter by union of like bases and recalculation to 100 per cent, we have—

	Found.	Reduced.	Calculated.
SiO_2	35.61	37.19	37.05
B_2O_3	10.15	10.51	10.80
Al_2O_3	25.29	27.10	27.19
Fe_2O_3	.44		
TiO_2	.55		
CaO	3.31	3.45	3.40
FeO	8.19	16.31	16.28
MgO	11.07		
Na_2O	1.51	1.72	1.74
K_2O	.20		
H_2O	3.34	3.72	3.54
F	.27		
	99.93	100.00	100.00

The result is evidently satisfactory. In dealing with titanium I have followed Penfield, regarding it as really Ti_2O_3 and equivalent to alumina. The fluorine is treated as replacing hydroxyl, and is, therefore, united with the water. It is possible, however, that fluorine may sometimes replace the group BO_2, an equivalency which is strongly indicated in the cappelenite group of minerals.

The brown tourmaline from Gouverneur, New York, as analyzed by Riggs, also reduces to a similar mixture of molecules, and its composition may be written thus:

5. $Al_5(SiO_4)_6(BO_2)_2 . BO_3Ca . Mg_4H_4$,
3. $Al_5(SiO_4)_6(BO_2)_2 . BO_3Mg . Mg_4H_4$,
2. $Al_5(SiO_4)_6(BO_2)_2 . BO_3NaH . Al_2Na_2H_4$;

and the comparison between analysis and theory is as follows:

	Found.	Reduced.	Calculated.
SiO_2	37.39	37.54	37.32
B_2O_3	10.73	10.76	10.88
Al_2O_3	27.79	28.72	28.53
Fe_2O_3	.10		
TiO_2	1.19		
FeO	.64		
MgO	14.09	14.51	14.52
CaO	2.78	2.79	2.90
Na_2O	1.72	1.83	1.93
K_2O	.16		
H_2O	3.83	3.85	3.92
	100.42	100.00	100.00

By consolidating lime with magnesia the expressions for both tourmalines might be simplified; but in other cases this would not be warranted. In some tourmalines calcium seems rather to replace sodium, or else the group NaH, a probability which will appear later. In these two tourmalines the theoretical silicon-oxygen ratio Si_6O_{31} is assumed, in accordance with my original formula. We may now consider the cases in which that ratio is exceeded, with more or less approach to the formula proposed by Penfield and Foote. This condition is easily satisfied by regarding one of the component salts of tourmaline as slightly basic, containing the bivalent group $=Al-O-H$ or $=Al-F$ as an essential factor. With this assumption, which recognizes the equivalency of hydroxyl and fluorine, the analyses reduce to the general type indicated in the two preceding examples. For instance, the white tourmaline from De Kalb, New York, has the following composition:

10. $Al_5(SiO_4)_6(BO_2)_2 . BO_3(AlOH) . Mg_4H_4$.
20. $Al_5(SiO_4)_6(BO_2)_2 . BO_3Ca . Mg_4H_4$.
3. $Al_5(SiO_4)_6(BO_2)_2 . BO_3Na_2 . Al_3Na_3$.

For comparison the analyses by Penfield and Foote and by Riggs are available. In this case the minute quantities of titanium are ignored.

	Found.		Reduced.			Calculated.
	P. and F.	Riggs.	P. and F.	Riggs.	Mean	
SiO_2	36.72	36.88	36.56	36.81	36.69	36.79
TiO_2	.05	.12	....	....	....	....
B_2O_3	10.81	10.58	10.76	10.56	10.66	10.74
Al_2O_3	29.68	28.87	29.55	28.81	29.18	29.07
FeO	.22	.52				
MgO	14.92	14.53	14.97	14.79	14.88	14.86
CaO	3.49	3.70	3.47	3.69	3.58	3.48
Na_2O	1.26	1.39	1.28	1.50	1.39	1.44
K_2O	.05	.18				
H_2O	2.98	3.56	3.41	3.84	3.62	3.62
F	.93	.50				
	101.11	100.83	100.00	100.00	100.00	100.00

The dark brown tourmalines from Orford, New Hampshire, and Monroe, Connecticut, as analyzed by Riggs, also reduced to similar form, and approximate to the mixture

15. $Al_5(SiO_4)_6(BO_2)_2 . BO_3(AlOH) . Mg_4H_4$,
6. $Al_5(SiO_4)_6(BO_2)_2 . BO_3Ca . Mg_4H_4$,
8. $Al_5(SiO_4)_6(BO_2)_2 . BO_3NaH . Al_3Na_2H$,

with the comparison as follows:

	Found.		Reduced.		Calculated.
	Orford.	Monroe.	Orford.	Monroe.	
SiO_2	36.66	36.41	36.96	37.34	36.84
B_2O_3	10.07	9.65	10.16	9.89	10.74
Al_2O_3	32.84	31.27	33.28	33.13	33.11
TiO_2	.23	1.61			
FeO	2.50	3.80			
MgO	10.35	9.47	11.84	11.88	11.85
CaO	1.35	.98	1.36	1.00	1.19
Na_2O	2.42	2.68	2.58	2.88	2.62
K_2O	.22	.21			
H_2O	3.78	3.79	3.82	3.88	3.65
	100.42	99.87	100.00	100.00	100.00

Here the divergence between the composition as found and as calculated is evidently due to the low determinations of boric acid in the analyses. Still the comparison is close.

Between the magnesium tourmalines and the iron tourmalines the closest analogy exists, and the identity of type is absolute. Taking, except when otherwise specified, the analyses by Riggs, all the iron tourmalines reduce to mixtures of the following isomorphous molecules:

A. $Al_5(SiO_4)_6(BO_2)_2 . BO_3(AlOH) . Fe_4H_4,$
B. $Al_5(SiO_4)_6(BO_2)_2 . BO_3Ca . Fe_4H_4,$
C. $Al_5(SiO_4)_6(BO_2)_2 . BO_3NaH . Al_3NaH_2,$
D. $Al_5(SiO_4)_6(BO_2)_2 . BO_3NaH . Al_3Na_2H,$
E. $Al_5(SiO_4)_6(BO_2)_2 . BO_3NaH . Al_3Na_3.$

Molecules C, D, and E are evidently identical, except in the varying replacements of sodium by hydrogen. A and B are similarly alike, so that actually only two fundamental compounds are assumed. From the commoner iron tourmalines lime is practically if not quite absent; and these may be interpreted very nearly as mixtures of A and C, such as A_8C_5, A_7C_5, etc. If we take the minute quantities of lime into account, the black tourmalines from Brazil and from Stony Point, North Carolina, correspond to $A_{13}B_2C_9$; that from Auburn, Maine, to $A_{35}B_2C_{27}$, and that from Paris, Maine, to $A_{10}B_1C_9$. It will be noticed that the molecule A is in excess of the other two, a condition which fits the analyses, but which is incompatible with the formula proposed by Penfield and Foote. To satisfy the latter the number of A molecules should be exactly equal to B + C, giving the ratio Si_4O_{21} or $Si_6O_{31\frac{1}{2}}$. The analyses in question are as follows:

	Brazil.	Stony Point.	Auburn.	Paris.
SiO_2	34.63	35.56	34.99	35.03
B_2O_3	9.63	10.40	9.63	9.02
TiO_2	....	.55	....	....
Al_2O_3	32.70	33.38	33.96	34.44
Fe_2O_3	.31	....	....	1.13
FeO	13.69	8.49	14.23	12.10
MnO	.12	.04	.06	.08
MgO	2.13	5.44	1.01	1.81
CaO	.33	.53	.15	.24
Li_2O	.08	trace	....	.07
Na_2O	2.11	2.16	2.01	2.03
K_2O	.24	.24	.34	.25
H_2O	3.49	3.63	3.62	3.69
F	.06	....	....	....
	99.52	100.42	100.00	99.89

The reduced analyses and their comparison with the calculated composition is as follows:

	Found. Stony Point.	Found. Brazil.	Calculated. $A_{13}B_2C_9$.	Found. Auburn.	Calculated. $A_{35}B_2C_{27}$.	Found. Paris.	Calculated. $A_{10}B_1C_9$.
SiO_2	34.10	34.26	34.27	34.75	34.48	34.70	34.62
B_2O_3	9.98	9.54	9.99	9.56	10.06	8.94	10.10
Al_2O_3	32.37	32.54	32.36	33.73	33.28	34.82	33.60
FeO	17.33	17.45	17.14	15.99	15.95	15.30	15.23
CaO	.52	.33	.45	.15	.17	.25	.27
Na_2O	2.22	2.40	2.22	2.23	2.50	2.33	2.67
H_2O	3.48	3.48	3.57	3.59	3.56	3.66	3.51
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Here again the agreements between analysis and theory are as close as could be reasonably expected. The same thing is true of the black tourmalines from Haddam Neck, Connecticut, and Nantic Gulf. Using letters to represent the several molecules, as above, the Haddam mineral is sharply represented by $A_4B_1D_2$, and that from Nantic Gulf by $A_6B_7C_3E_1$. Here is the comparison:

	Haddam Neck.			Nantic Gulf.		
	Found.	Reduced.	Calculated.	Found.	Reduced.	Calculated.
SiO_2	34.95	33.78	33.67	35.34	33.34	33.60
B_2O_3	9.92	9.60	9.82	10.45	9.86	9.80
TiO_2	.57	30.74	30.67	.40	29.01	28.84
Al_2O_3	31.11			30.49		
Fe_2O_3	.50			....		
FeO	11.87	19.31	19.24	8.22	20.46	20.55
MnO	.09			trace		
MgO	4.45			7.76		
CaO	.81	.78	.75	2.32	2.19	2.15
Na_2O	2.22	2.30	2.48	1.76	1.74	1.70
K_2O	.24			.15		
H_2O	3.62	3.49	3.37	3.60	3.40	3.36
	100.35	100.00	100.00	100.49	100.00	100.00

To the lithia tourmalines, as analyzed by Riggs, a similar set of formulæ apply, although the comparison between fact and theory is not quite so close as in the preceding cases. The red tourmalines from Brazil and from Rumford, Maine, are very nearly represented by the expression

$$Al_5(SiO_4)_6(BO_2)_2 \,.\, BO_3R'H \,.\, Al_3R'H_2;$$

with Li : Na approximately as 5 : 4. The slight deficiency in the alkalies is made up by the presence of small amounts of calcium, iron, and manganese, but the ratio $Al_8 : Si_6$ is very clear. The green tourmalines are all lower in alumina, and range downward toward the iron end of the series; and like the latter are representable as mixtures of the following molecular types:

A. $Al_5(SiO_4)_6(BO_2)_2 . BO_3(AlOH) . Fe_4H_4.$
B. $Al_5(SiO_4)_6(BO_2)_2 . BO_3Ca . Fe_4H_4.$
C. $Al_5(SiO_4)_6(BO_2)_2 . BO_3LiH . Al_2Li_2H_4.$
D. $Al_5(SiO_4)_6(BO_2)_2 . BO_3NaH . Al_3NaH_2.$
E. $Al_5(SiO_4)_6(BO_2)_2 . BO_3H_2 . Al_3NaH_2.$

Thus the dark, opaque green tourmaline from Rumford, Maine, is a molecular mixture corresponding to $A_6B_2C_7D_{14}E_5$; the similar mineral from Auburn is $A_8B_1C_8D_{17}$; the light green from Auburn, $A_2CB_{310}D_8E_{12}$, and the nearly colorless from Auburn, $A_1B_5C_{20}D_{10}E_{35}$. From Brazil the dark green is $A_2B_1C_6D_8$, and the light green is $A_1B_2C_9D_8E_5$. The complexity of these expressions is only apparent, not real, as a study of the original type formulæ will show. They compare with the reduced analyses as follows:

	Rumford.		Auburn, dark.		Auburn, medium.	
	Found.	Calculated.	Found.	Calculated.	Found.	Calculated.
SiO_2	36.68	36.69	36.37	36.45	37.95	37.52
B_2O_3	10.26	10.69	9.98	10.63	10.57	10.94
Al_2O_3	38.26	37.74	36.89	37.21	38.11	39.02
FeO	6.78	6.90	7.94	7.72	4.47	4.28
CaO	.34	.34	.17	.16	.50	.50
Na_2O	3.12	3.07	3.19	3.14	2.58	2.58
Li_2O	.95	.94	1.06	1.07	1.35	1.35
H_2O	3.61	3.63	4.40	3.62	4.47	3.81
	100.00	100.00	100.00	100.00	100.00	100.00

	Auburn, pale.		Brazil, dark.		Brazil, light.	
	Found.	Calculated.	Found.	Calculated.	Found.	Calculated.
SiO_2	38.25	37.92	37.24	37.14	37.49	37.64
B_2O_3	10.30	11.05	9.95	10.83	10.32	10.97
Al_2O_3	39.92	40.17	38.66	38.07	39.86	39.04
FeO	2.75	2.56	5.49	5.24	3.74	3.61
CaO	.43	.49	.39	.35	.49	.46
Na_2O	2.55	2.53	2.90	3.01	2.59	2.76
Li_2O	1.34	1.34	1.63	1.64	1.71	1.69
H_2O	4.46	3.94	3.74	3.72	3.80	3.83
	100.00	100.00	100.00	100.00	100.00	100.00

In these cases the low boric acid of the analyses and the uncertainties as to the significance of the water determinations account for the chief variations between observation and theory. There is another complication also, due to the fact that alternative expressions are possible between which it is very difficult to decide. In the tourmaline from Haddam Neck, Connecticut, analyzed by Penfield and Foote, a somewhat different commingling of molecules seems to be necessary, partly on account of the higher proportion of lime in the mineral and partly on account of the fluorine. This tourmaline also admits of various alternatives in formulation, but it agrees well with the molecular mixture—

3. $Al_5(SiO_4)_6(BO_2)_2 . BO_3Ca . Fe_4H_4$,
10. $Al_5(SiO_4)_6(BO_2)_2 . BO_3(AlOH) . Al_2Li_2H_4$,
1. $Al_5(SiO_4)_6(BO_2)_2 . BO_3Ca . Al_3NaH_2$,
6. $Al_5(SiO_4)_6(BO_2)_2 . BO_3NaH . Al_3NaH_2$;

in which Ca is equivalent to a replacement of NaH. This mixture, with the group AlOH proportional to fluorine, gives a good comparison between analysis and theory, thus:

	Found.	Reduced.	Calculated.
SiO_2	36.96	36.75	36.86
B_2O_3	11.00	10.94	10.74
TiO_2	.03		
Al_2O_3	39.56	39.35	39.44
FeO	2.14	4.35	4.43
MnO	2.00		
MgO	.15		
CaO	1.28	1.27	1.15
Na_2O	2.10	2.09	2.07
Li_2O	1.64	1.63	1.54
H_2O	3.10	3.62	3.77
F	1.13		
	101.09	100.00	100.00

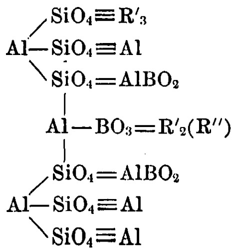
The theoretical amount of fluorine needed to replace hydroxyl in the assumed group, AlOH, is 0.97 per cent. Altogether, the comparison is fairly satisfactory.

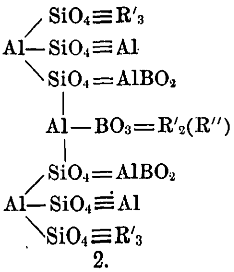
One analysis by Riggs, that of the magnesium tourmaline from Hamburg, New Jersey, I have omitted from my discussion. In that tourmaline there are variations which I can not readily account for, unless by assuming the presence in it of a molecule

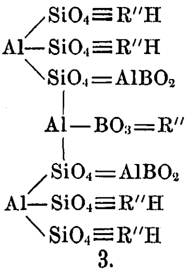
$$Al_5(SiO_4)_6(BO_2)_2 . BO_3R'_2 . R''_6.$$

Such a molecule, written structurally, exhibits affinities to garnet rather than to the micas; and I prefer to await further evidence before committing myself to any definite formulation in this instance. As for the analyses published by Jannasch and Kalb, they fit in well with those of Riggs, and are amenable to the same treatment.

At first glance some of the formulæ which I have proposed may seem to be complex; but they are all of the same type, and can be reduced to a few general expressions, as follows:


1.


2.


3.

These formulæ cover all of the established variations in the composition of tourmaline; they render the various replacements or isomorphous admixtures intelligible, and they indicate the directions into which the species commonly alters. There is one objection to them, namely, that one of the end products contains no alkali metal, and no alkali-free tourmaline is known. The same objection applies to the Penfield-Foote formula, as will be seen by anyone who attempts to apply it in the discussion of the iron tourmalines. Under either system of formulation the existence in tourmaline of alkali-free salts must be assumed.

One further possible advantage in the proposed formulæ remains to be pointed out. All of the chemists who of late years have discussed the composition of tourmaline agree in adopting the ratio between silicon and boron of 2 : 1, or $4SiO_2 : B_2O_3$. And yet many of the analyses vary from this ratio to an extent which may not be due to experimental errors. For example, from among Riggs's analyses the following cases show large variations, the boron being too low. I give the silica and boric oxide as determined, the boric oxide as calculated from the silica by the accepted ratio, and the amount of variation between the two.

	SiO_2.	B_2O_3 found.	B_2O_3 calculated.	Difference.
Rumford, red	38.07	9.99	11.10	—1.11
Paris, black	35.03	9.02	10.22	—1.20
Monroe, brown	36.41	9.65	10.62	—0.97
Brazil, green	36.91	9.87	10.76	—0.89
Auburn, colorless	38.14	10.25	11.12	—0.87

In the analyses by Jannasch and Kalb the following examples are very striking:

	SiO_2.	B_2O_3 found.	B_2O_3, calculated.	Difference.
Snarun	35.64	9.93	10.40	—1.47
Mursinka	34.88	8.94	10.17	—1.23
Buckworth	35.50	8.34	10.35	—2.01
Brazil	37.05	9.09	10.81	—1.72

It would hardly be wise to dismiss these variations as due to errors, especially when the summation of the analyses is good and the analysts are known to be trustworthy. Such errors on the part of either Jannasch or Riggs would be almost incredible, and I am therefore inclined to believe that the analyses are good, and that we should seek a cause for the variations. In my scheme of formulation the bivalent group of atoms $=Al-BO_2$ occurs. Replace this in part by the similar groups $=Al-OH$ and $=Al-F$, and the variations are accounted for. This supposition satisfies the analyses completely, and covers the ground. It is in accord with all the evidence, even though its validity may not be definitely proved. By its application to the discussion of the analyses the divergencies between the calculated composition and the composition as found can be notably diminished.

But although the formulæ which I have adopted serve to express the composition of all tourmalines, they still leave room for alternatives. Penfield and Foote, as well as myself, assume that tourmaline is a mixed salt containing distinct boric and silicic radicles. Future investigation may prove that it is really derived from a complex boro-silicic acid, as yet unknown; and the same conception may be true of other species, such as axinite, datolite, danburite, cappelenite, etc. A series of boro-silicic acids is theoretically conceivable; and until this question has been considered, the constitution of all the minerals above mentioned must be regarded as unsettled.

THE COLORIMETRIC ESTIMATION OF SMALL AMOUNTS OF CHROMIUM, WITH SPECIAL REFERENCE TO THE ANALYSIS OF ROCKS AND ORES.

By W. F. HILLEBRAND.

INTRODUCTION.

In the analysis of a number of highly titaniferous magnetites containing chromium, phosphorus, and vanadium, the satisfactory separation of all these bodies in a form fit for separate determinations became a serious problem. The method of T. Fischer[1]—digestion of the precipitated lead salts with a strong solution of potassium carbonate—appears to offer the long-needed satisfactory quantitative separation of arsenic, phosphorus, chromium, tungsten, and molybdenum from vanadium, the normal lead meta-vanadate remaining quite unattacked, according to the author, while the other lead salts are wholly decomposed, but the applicability of this method to the separation of the minute amounts often found in rocks and ores has not been tested. The time required is considerable, hence it was desirable to devise a more rapid way for determining both chromium and vanadium without resorting to this separation. That this object has been measurably achieved, with certain limitations as to vanadium, the work thus far done seems to indicate. The present paper will deal only with the rapid estimation of chromium either in absence or presence of any or all of the elements above mentioned.

In view of the high coloring power of the chromates, it is surprising that so little use has been made of this property as the basis for a quantitative method for the estimation of chromium. A search through some of the more important text-books has revealed no reference to such a method, although L. de Koningh[2] has successfully applied it in the analysis of articles of food. Yet the results attainable by colorimetric comparisons of dilute alkaline solutions of unknown strength with those of a known standard leave little to be desired in point of quantitative accuracy.

---

[1] Inaugural Dissertation, Rostock, 1894.

[2] Nederl. Tijdsch. voor Pharmacie, Chemie, en Toxicologie, 1889, p. 257.

As with colorimetric methods in general this one gives better results with small than with large percentages of chromium, yet it can be applied in the latter cases with very fairly satisfactory results by making a larger number of consecutive comparisons with the same solution.

OUTLINE OF METHOD.

The chromium is brought into a measured volume of solution as monochromate rendered alkaline by sodium carbonate, and the whole or a portion of this solution is then compared with a definite amount of a somewhat stronger standard, likewise made alkaline with sodium carbonate. The latter is diluted with water till both seem to be exactly alike in color, when a simple calculation gives the amount of chromium sought. The actual comparison takes little time, and any number of repetitions can be made if desired in order to secure greater accuracy from the mean of a large number of observations. The preparation of the solution to be tested offers nothing novel, but certain precautions have to be observed therein as well as in the color comparisons which will be touched upon later.

TESTING OF METHOD BY COMPARISON OF STANDARD SOLUTIONS.

Two standard solutions were prepared by dissolving 0.25525 and 0.5105 gram potassium chromate in 1 liter of water made alkaline by a little sodium carbonate, each cubic centimeter then corresponding respectively to 0.1 and 0.2 milligram chromic oxide, in which latter form chromium is usually reported in rocks and ores. Definite amounts of one of the standards were then diluted with varying amounts of water in a tall, square glass vessel with exactly parallel sides. Into an exact duplicate of this vessel 5 cubic centimeters or more of the standard were introduced from a burette and diluted with water from another burette till exact agreement seemed to be reached on looking through the glasses horizontally.

In the following tables are recorded all observations without regard to the sequence in which they were made. No greater pains were taken to get exact agreement of color than are ordinarily observed in our routine titanium estimations, which are carried out in a precisely similar manner, so that the results may be taken to represent everyday work without extreme precautions. In only two cases can the observations be considered really bad, viz, the third comparison of No. 6 and the first of No. 16.

TABLE I.

[Ten cubic centimeters standard represent 1 milligram chromic oxide.]

No.	Test solution.		Comparison standard.		Contents as chromic oxide.	Chromic oxide found.	Chromic oxide present.	Error.	Chromic oxide found.
	Standard.	Diluted with water.	Cubic centimeters.	H_2O added.					
	c. c.	*c. c.*		*c. c.*	*Mgs.*	*Mgs.*	*Mgs.*	*Mgs.*	*Per cent.*
1	[a]10	[a] 90	5	44.00	0.5	0.98	1	—0.02	98.0
2	[b]20	[b] 80	5	21.00	.5	1.92	2	— .08	96.0
3	40	60	10	14.60	1.0	4.06	4	+ .06	101.5
4	40	60	9.7	14.25	.97	4.05	4	+ .05	101.2
			10	13.95	1.0	4.17	4	+ .17	104.4
			10	14.30	1.0	4.11	4	+ .11	102.9
			10	14.20	1.0	4.13	4	+ .13	103.3
5	40	60	10	14.65	1.0	4.05	4	+ .05	101.4
			10	15.65	1.0	3.90	4	— .10	97.5
6	40	60	10	15.25	1.0	3.96	4	— .04	99.0
			10	14.30	1.0	4.11	4	+ .11	102.9
			10	13.15	1.0	4.32	4	+ .32	108.0
			10	14.75	1.0	4.04	4	+ .04	101.0
			20	29.50	2.0	4.04	4	+ .04	101.0
7	50	50	10	9.75	1.0	5.06	5	+ .06	101.2
8	50	50	10	10.00	1.0	5.00	5	.00	100.0
9	60	40	10	7.20	1.0	5.81	6	— .19	96.7
10	75	25	20	6.65	2.0	7.505	7.5	+ .005	100.1
			20	6.60	2.0	7.519	7.5	+ .019	100.2
			10	3.15	1.0	7.605	7.5	+ .105	101.4
			15	4.70	1.5	7.610	7.5	+ .11	101.5
11	10	10	10	10.15	1.0	0.992	1	— .008	99.2
			20	19.75	2.0	1.006	1	— .006	100.6
12	10	11	10	10.60	1.0	1.02	1	+ .02	102.0
13	14.2	26.9	10	18.60	1.0	1.43	1.42	+ .01	100.7
			20	35.70	2.0	1.47	1.42	+ .05	103.5
14	15	24.35	10	16.55	1.0	1.48	1.5	— .02	98.7
15	16	20	10	13.30	1.0	1.54	1.6	— .06	96.2
			20	24.30	2.0	1.63	1.6	+ .03	101.9
16	31.9	20.6	10.5	8.10	1.05	2.96	3.19	— .23	92.8
			20.5	14.20	2.05	3.10	3.19	— .09	97.2
17	62.05	22.3	20	7.00	2.0	6.25	6.205	+ .45	100.7
			40	12.00	4.0	6.49	6.205	+ .285	104.6

Mean percentage found, 100.5.

[a] Color in this dilution too faint.

[b] Limit of dilution for clear distinction of color in a thickness of 3.3 cm.

TABLE II.

[Varying amounts of standard No. 2 (1 c. c. = 0.2 mg. Cr_2O_3) diluted till of the same concentration as standard No. 1.]

No.	Standard.			Chromic oxide found per 100 c. c.	Chromic oxide present in 100 c. c.	Error.	Chromic oxide found.
	Cubic centimeters.	Water added.	Contents as chromic oxide.				
		c. c.	*Mgs.*	*Mgs.*	*Mgs.*	*Mg.*	*Per cent.*
18	5	5.2	1	9.80	10	—0.2	98.0
19	10	9.95	2	10.02	10	+.02	100.2
20	15	15.8	3	9.74	10	—.26	97.4
21	20	20.0	4	10.00	10	.00	100.0
22	30	29.5	5	10.08	10	+.08	100.8

Mean percentage found, 99.3; grand mean, 100.36.

The first table and the grand mean show an apparent personal tendency toward slightly high results, though it is possible that this is due to a slight difference in the internal dimensions of the two glasses, the same one always having been used for the standard solution. If this is so, a long series of tests with glasses reversed should give a general mean slightly below 100.

TESTING THE METHOD ON ORES AND ROCKS.

In order to prove the value of the method in rock analysis, varying amounts of the standard solution were evaporated in a large crucible with 5 grams of an iron ore carrying phosphorus and vanadium, and fused with 20 grams of sodium carbonate and 3 grams sodium nitrate. The aqueous extract, after reduction of manganese by methyl or ethyl alcohol, was nearly neutralized by nitric acid and evaporated to secure approximate separation of silica and alumina. As a precautionary measure, since a little chromium is usually carried down, the precipitate was ignited, silica was removed by hydrofluoric and sulphuric acids, the residue was fused with sodium carbonate, and alumina again separated as before. To the combined filtrate was added mercurous nitrate, and the slightly washed copious precipitate of phosphate, chromate, vanadate, and carbonate of mercury was ignited with the paper in a platinum crucible, which can be done without much fear of loss or of injury to the crucible. The residue was then fused with a little sodium carbonate, extracted with water, filtered into a graduated flask and made up to 50 or 100 cubic centimeters, according to the intensity of the color, and compared with the standard. A similar operation was carried out with a silicate rock. Table III shows the results.

TABLE III.

No.		Chromic oxide added.	Chromic oxide found.
		Milligrams.	*Milligrams.*
I.	Five grams iron ore	7.03	7.18
		....	7.20
		....	7.25
		....	7.21
II.	Five grams iron ore	2.99	3.08
		....	3.13
III.	Two grams silicate	1.6	1.53
		....	1.57
		....	1.59

When the percentage of chromic oxide in an ore or mineral is more than about 0.2 per cent, and vanadium has not also to be estimated, much time may be spared by at once taking the color of the original extract from the sodium carbonate fusion after insuring complete reduction and removal of manganese, and perhaps concentrating. But if the chromium is much less than this amount, and especially if several grams of powder have been operated on, it becomes difficult or impossible to obtain a filtrate of sufficiently small bulk to show a decided color. Therefore, in such cases, and when vanadium is likewise to be estimated, it is necessary to precipitate as above with mercurous nitrate in order to eventually have a small bulk of sufficiently colored solution. Even then, for very minute amounts, it is necessary to use Nessler tubes exactly as in ammonia estimations.

If niter has been used in the fusion and the crucible has been attacked by it, a yellow color of the filtrate may be due to dissolved platinum, but neither the proportion of niter nor the temperature of the blast should ever be high enough to permit the crucible to be attacked.

THE COLORIMETRIC APPARATUS AND ITS USE.

The glasses employed were of approximately square section, about 12 centimeters high and 3.3 centimeters inside measurement, with exactly parallel sides, and of course as nearly alike as they could be obtained. One pair of opposite sides of each should be blackened. With glasses of the thickness mentioned it is generally advisable to use from 5 to 10 cubic centimeters of standard at a time and to so regulate the strength of the solution to be tested that it shall contain more than 2 milligrams chromic oxide in 100 cubic centimeters, which is about the limit of distinct visibility in a thickness of 3.3 centimeters.

In order to exclude the effect of side light in this and other similar methods (titanium, for instance), it is very convenient to have a simple light box that can be easily held in one hand, about 35 centimeter long and 13 to 14 centimeter square, painted black inside and out and with one end closed by a piece of ground glass, the other open. For a space equal to the width of the glasses the cover is removed at the top next the glass end to permit of the insertion of the glasses, side by side, in such a way that no light shall penetrate around their sides or between them. A stiffly sliding, black cardboard shutter is movable up and down immediately back of the glasses, so that all light can be cut off except that which comes through the liquid.

Precautions of this kind are necessary if accurate results are to be counted on. Except for mere traces this simple combination of glasses and darkened box insures greater accuracy and rapidity of work than Nessler tubes and is preferable likewise, so far as my own experience goes, to expensive instruments like the colorimeter of Soleil-Duboscq, etc. The glasses should, of course, have exactly parallel sides and equal diameters, though they may perhaps be made with advantage rather narrow in one direction to permit of using smaller bulks of liquid.

In making the color comparisons the box is best held close to a window, so as to get a full, strong light. The condition of the light seems to make an appreciable difference in the accuracy of the comparisons, all of which were made by daylight.

ACCURACY OF RESULTS.

Especially for comparatively and very small amounts of chromium the method gives exact results, better than can ordinarily be hoped for from any gravimetric method, considering the fact that as a rule other substances are present which it is extremely difficult to remove completely.

A few comparisons between colorimetric and gravimetric determinations of chromium in a few rocks are here given to show the order of agreement, the former having been made several months and even years after the latter:

Gravimetric.	Colorimetric.
Per cent.	*Per cent.*
trace	0.018
0.05	.051
.14	.12
.08	.083
trace	.013
none	.0086
none	.0067

The outcome was somewhat of a surprise, for it was scarcely to be expected that the long and laborious gravimetric separations should have resulted so well as they are shown to have done. It should be mentioned that for the gravimetric tests but 1 or 2 grams at most were used, which accounts for the reported absence of chromium in two instances, this report being based on the lack of color in the aqueous extract of the alkaline fusion after removal of manganese.

No experiments have been made with high percentages, but the tables give with certainty the degree of accuracy even then attainable. Whether the chromic oxide to be estimated is 0.1 per cent or 100 per cent, the percentage result is the same, provided the dilution is alike in each case. For instance, if 99.5 per cent is found in a total solution of 100 cubic centimeters containing 0.01 gram chromic oxide, the same percentage holds if the total volume were 10 liters holding 1 gram chromic oxide.

It is probably inadvisable to increase the strength of the standard much above that of No. 2 above, containing 0.2 milligram chromic oxide in form of potassium chromate to the cubic centimeter.

No tests have been made with other alkaline solutions than sodium carbonate, in order to ascertain if there is a difference in the color intensities for like dilution, nor is it probably important to do so.

VOLUMETRIC ESTIMATION OF VANADIUM IN PRESENCE OF SMALL AMOUNTS OF CHROMIUM, WITH SPECIAL REFERENCE TO THE ANALYSIS OF ROCKS AND ORES.

By W. F. HILLEBRAND.

OUTLINE AND LIMITATIONS OF THE METHOD.

When chromium and vanadium occur together and the former has been estimated colorimetrically as detailed in the preceding paper, the vanadium can in many instances be at once estimated without separating from the chromium by the well-known method of titration with potassium permanganate in sulphuric acid solution after reduction by sulphurous acid and expulsion of all excess of the latter.

The application of the method is subject to one limitation—the chromium must not be present above a certain moderate amount. This limitation is due to the considerable amount of permanganate required to produce a clear transition tint when titrating in a hot solution, as is necessary with vanadium. In a cold solution of chromic sulphate much less permanganate is needed to produce the peculiar blackish tint without a shade of green, which affords a sure indication of excess of permanganate, but in a hot and especially a boiling solution the oxidation of the chromium[1] itself takes place so rapidly that a very large excess of the reagent may be added before a pronounced end-reaction is obtained. Nevertheless, as will be shown, quite satisfactory determinations of as little as 1 or 2 milligrams of vanadium pentoxide can be made in presence of as much as 30 milligrams of chromic oxide.

Inasmuch as chromium is almost never a prominent constituent of the clays, coals, iron ores, and rocks in which vanadium has been thus far reported, the method promises to be of great advantage in rock and ore analysis, where these elements probably frequently occur together, generally with phosphorus and sometimes arsenic. It is not directly applicable in presence of molybdenum, and arsenic must first be removed by hydrogen sulphide if present.

---

[1] Storer, through Gmelin-Kraut, Vol. II, pt, 2, p. 290.

TESTING THE METHOD.

A solution of sodium vanadate was prepared by fusing 0.937 gram of pure vanadium pentoxide with sodium carbonate and diluting to 1 liter. Each cubic centimeter contained 0.000937 gram vanadium pentoxide. Of this, sufficient amounts were mixed with varying volumes of a standard solution of potassium chromate. After in some cases determining chromium colorimetrically, sulphuric acid was added, sulphur dioxide gas[1] introduced for a few moments, and the excess of the latter expelled by boiling in a rapid current of carbon dioxide, without which its complete expulsion is difficult. When cooled to from 70°–80° C. the titration was made with very dilute solution of permanganate corresponding to about 1 milligram vanadium pentoxide to the cubic centimeter as calculated from its equivalent in iron. By repeating the reduction and boiling, any number of check tests can be rapidly made in the same solution. The solutions ranged in bulk from 50 to 200 cubic centimeters according to the amounts of chromium added.

With the larger chromium contents the differences in the quantity of permanganate used, according as titration was effected at practically boiling temperature or a somewhat reduced one, were very apparent. In one case, at nearly boiling heat, 10 milligrams of chromic oxide were largely oxidized to chromium trioxide, as shown by the change of color from dark green to yellow. Even at 70°–80° with this amount of chromium the results for vanadium will be too high unless the precaution is taken to ascertain the needed correction by adding permanganate to an equal bulk of hot chromic sulphate solution containing approximately the same amount of chromium. When this is done, however, the results are satisfactory even when as much as 30 milligrams of chromic oxide are present and only 1 or 2 milligrams of vanadium pentoxide.

The following tables contain the results of a considerable number of tests, those in Table II being tabulated separately in order to show the degree of accuracy attainable with a large excess of chromium by applying the correction above mentioned and also the amount of this correction.

---

[1] The direct use of a solution of sulphur dioxide or of an alkaline sulphite is inadmissible unless these have been freshly prepared, since after a lapse of time they contain other oxidizable bodies than sulphurous acid or a sulphite. The sulphur dioxide is best obtained as wanted by heating a flask containing a solution of sulphur dioxide, or of a sulphite to which sulphuric acid has been added

TABLE I.—*Test determinations of vanadium in presence of chromium.*

No.	Chromic oxide.	Vanadium pentoxide.	Vanadium pentoxide found.	Error.
	Milligrams.	*Milligrams.*	*Milligrams.*	*Milligrams.*
1	1	9.37	9.22	—0.15
2	1	0.94	1.04	+ .10
			.98	+ .04
3	1.5	5.25	5.49	+ .24
			5.43	+ .19
4	2	5.62	5.5	— .12
			5.5	— .12
5	3	4.68	4.78	+ .10
			4.78	+ .10
			4.83	+ .15
6	3	5.62	5.58	— .04
			5.58	— .04
7	3.5	18.74	18.89	+ .15
			18.97	+ .23
8	6	5.6	6.1	+ .50
9	6	4.68	4.78	+ .10
10	6	5.62	5.58	— .04
11	10	5.62	5.58	— .04
12	10	23.52	23.81	+ .29
			23.71	+ .19
13	10	46.85	46.98	+ .13
			47.20	+ .35
14	25	23.52	23.65	+ .13
			23.75	+ .23
15	87.5	23.52	23.71	+ .19

TABLE II.—*Application of degree of correction for larger amounts of chromium, obtained by adding potassium permanganate to an equal bulk of solution containing a like amount of chromic sulphate.*

No.	Chromic oxide.	Vanadium pentoxide.	Vanadium pentoxide found.		Error.	Volume of solution.
			Uncorrected.	Corrected.		
	Mgs.	*Mgs.*	*Mgs.*	*Mgs.*	*Mg.*	*c.c.*
16	20	0.94	1.59	0.99	+0.05	50–100
17	20	1.87	2.69	2.09	+ .22	50–100
			2.39	1.79	— .08	
			2.59	1.99	+ .12	
18	20	18.74	19.4	18.73	— .01	50–100
			19.3	18.63	— .11	
			19.3	18.63	— .11	
19	30	1.87	2.99	2.14	+ .27	[a] 100
			2.79	1.94	+ .07	
			2.79	1.94	+ .07	
			2.69	1.84	— .03	
			2.69	1.84	— .03	
20	30	1.87	2.69	1.79	— .08	200
			2.89	2.09	+ .22	
			2.89	2.09	+ .22	
			2.79	1.89	+ .12	
21	62	46.85	48.60	47.60	+ .75	200

[a] About.

In spite of the fact that the correction in most of the trials of this last table represents a large proportion of the permanganate used, the results must be considered satisfactory in view of the small amount of vanadium present, and they show that the method in competent hands after a little experience affords trustworthy figures.

TESTING THE METHOD ON ROCKS AND ORES.

The following table shows its availability for rocks and ores. Known amounts of both chromium and vanadium were added to an iron ore and to a silicate, both free from arsenic, which were then fused with sodium carbonate and nitrate and further treated as follows: After extracting with water and reducing manganese by alcohol, the silica and alumina were mostly removed by nearly neutralizing with nitric acid and evaporating to near dryness. The washed precipitate was ignited and treated with hydrofluoric and sulphuric acids, the residue fused with sodium carbonate, since it frequently contains a little chromium, and again nearly neutralized, etc. To the combined and slightly alkaline filtrates was added mercurous nitrate, the precipitate of phosphate, vanadate, chromate, and carbonate was ignited in platinum, fused with a little sodium carbonate, leached with water, and filtered into a small graduated flask. After colorimetric determination of the chromium, sulphuric acid was added, both chromium and vanadium were reduced by sulphur dioxide gas, and the titration carried out as described.

TABLE III.—*Test determinations of vanadium added to rocks and ores in presence of chromium.*

No.	Chromic oxide.	Vanadium pentoxide.	Vanadium pentoxide.	
			Found.	Error.
	Mgs.	*Mgs.*	*Mgs.*	*Mg.*
*a*22	7	6.76	6.81	+0.05
			6.48	— .28
			6.43	— .33
			6.37	— .37
*a*23	3	3	3.08	+ .08
			3.13	+ .13
			3.03	+ .03
			3.08	+ .08
*b*24	1.6	1.87	1.86	— .01
			1.97	+ .10
			2.07	+ .20
			1.86	— .01

a Five grams iron ore. *b* Two grams silicate.

These and other experiments show that by taking not over 5 grams of ore or rock, vanadium, if present to the extent of 0.01 or 0.02 per cent, can be readily estimated by exercising reasonable care in all the operations. Absolute confirmation of its presence can be easily obtained by evaporating and igniting the solution to remove excess of sulphuric acid, taking up with a few drops of dilute nitric acid, and adding to the solution in a test tube a drop or two of hydrogen peroxide. In this way positive or negative assurance as to the presence of vanadium is given when the result of titration alone might be uncertain. Addition of ether at the same time affords a simultaneous test for chromium by its blue color, and this might, perhaps, be made use of, if necessary, to remove all or the greater part of the chromium prior to titration of the vanadium, since the oxidation product of the latter does not dissolve in the ether.

It is even possible that the dark-brown color produced by hydrogen peroxide might be utilized for an exact colorimetric method for estimating vanadium.

DISTRIBUTION AND QUANTITATIVE OCCURRENCE OF VANADIUM AND MOLYBDENUM IN ROCKS OF THE UNITED STATES.

By W. F. HILLEBRAND.

Aside from its well-known mineral combinations, vanadium has long been known to occur in magnetites and other iron ores. Hayes in 1875 reported its occurrence in a great variety of rocks and ores. Quoting from Thorpe's Dictionary of Chemistry: "It is said to be diffused with titanium through all primitive granite rocks (Dieulafait) and has been found by Deville in bauxite, rutile, and many other minerals, and by Bechi and others in the ashes of plants and in argillaceous limestones, schists, and sands * * * ." It is further reported to comprise as V_2O_5 0.02–0.07 per cent of many French clays, 0.02–0.03 per cent of some basalts, 0.24 per cent of a coal of unknown origin and 0.45 per cent of one from Peru, amounting to 38.5 per cent and 38 per cent of the ash, and noted respectively by Mourlot and Torrico y Meca. Doubtless many other instances of its occurrence have been noted.

In Table I following is shown its quantitative occurrence and distribution in a large number and variety of igneous rocks of the United States arranged according to their silica contents; and in Table II the same data are given for a few of the component minerals separated from some of these rocks, while Table III shows its presence in metamorphosed and secondary rocks by a few examples of roofing slates and schists and especially by two composite samples representing 253 sandstone and 498 building limestones. These last two afford positive proof of its general distribution through rocks of those classes. Incidentally some information has been acquired as to molybdenum. Owing to lack of entire certainty as to its condition of oxidation, the vanadium is tabulated in terms of both V_2O_5 and V_2O_3, a point which will be reverted to later on. With very few exceptions the amount of each sample taken for analysis was 5 grams. The reagents used were carefully tested and found free from vanadium and molybdenum. Except Nos. 38, 39, 47, 52, and 53, by Dr. H. N. Stokes, all determinations are by myself.

TABLE I.—*Igneous rocks.*

No.	Name and locality of occurrence.	SiO_2.	V_2O_5=V_2O_3.		Mo.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
1	Melilite-nepheline-basalt, Uvalde County, Tex.	38	0.054	0.045	
2	Nephelinite, Uvalde County, Tex	40	.042	.035	
3	Saxonite, Douglas County, Oreg	41.5	none	none	
4	Diorite, Cecil County, Md	44	.062	.052	none
5	Gabbro, Adirondack region, N. Y	45	.02	.017	
6	Plagioclase-basalt, Uvalde County, Tex	46	.048	.04	
7	Amphibole-gabbro, Alpine County, Cal	46	.046	.038	none
8	Plagioclase-gneiss, Amador County, Cal	46.5	.033	.027	
9	Diorite, Mitchell County, N. C	47	.05	.042	
10	Porphyry, La Plata County, Colo	47	[a] .06	[a] .05	
11	Amphibole-gabbro, Tuolumne County, Cal	47	.024	.02	none
12	Orthoclase-bearing basalt, Uvalde County, Tex	48?	.048	.04	
13	Orthoclase-bearing basalt, Uvalde County, Tex	48	.02	.017	
14	Norite, Cecil County, Md	48	.023	.019	
15	Gabbro, Union County, Tenn	48	.038	.032	
16	Gabbro, Douglas Island, Alaska	48	.055	.046	none
17	Nepheline-basanite, Colfax County, N. Mex	48.5	.044	.037	
18	Olivine-basalt, Kruzof Island, Alaska	49.5	.054	.045	none
19	Diabase, Mount Ascutney, Vt	49.5	.034	.028	
20	Phonolite, Cripple Creek, Colo	50	.033	.027	
21	Syenite-lamprophyre, Prowers County, Colo	50.5	.04	.033	
22	Augite-andesite-porphyry, Electric Peak, Wyo.	50.5	.045	.038	
23	Pyroxenic gneiss, Calaveras County, Cal	51.5	.10	.083	none
24	Labradorite-porphyrite, Michigamme iron district, Mich	52.5	.048	.04	
25	Pyroxenite, Cecil County, Md	53	.04	.034	none
26	Orendite, Sweetwater County, Wyo	54	.022	.018	
27	Andesite, El Paso County, Colo	54?	.018	.015	trace?
28	Nepheline-syenite, El Paso County, Colo	54.5	.022	.018	trace?
29	Diorite, Butte and Plumas counties, Cal	54.5	.037	.031	none
30	Quartz-diorite, Cecil County, Md	55	.043	.036	none
31	Diorite, La Plata County, Colo	55.5	.038	.032	
32	Camptonite? San Miguel County, Colo	55.5	(b)	(b)	
33	Phonolite, Colfax County, N. Mex	56	trace	trace	
34	Augite-bronzite-andesite, Unga Island, Alaska.	56.5	.046	.038	none
35	Andesite, El Paso County, Colo	57 ?	.025	.021	trace?
36	Spilosite, Michigamme iron district, Mich	58	.03	.025	none
37	Hornblende-granite, Cecil County, Md	58.5	.022	.018	none
38	Latite, Tintic district, Utah	60	.007	.006	none
39	Monzonite, Tintic district, Utah	60	.024	.02	trace
40	Diorite-porphyry La Plata Mountains, Colo	60.5	.02	.017	
41	Trachyte-andesite tuff, Tuolumne County, Cal	62.5	.017	.014	
42	Diorite, Douglas Island, Alaska	63	[a] .012	[a] .01	none
43	Rhyolite, San Miguel County, Colo	64.5	.004	.003	trace
44	Syenite, Mount Ascutney, Vt	65.5	trace?	trace?	
45	Quartz-mica-diorite, Tuolumne County, Cal	65.5	.013	.011	trace
46	Quartz-monzonite, Calaveras County, Cal	67	.014	.012	trace
47	Rhyolite, Tintic district, Utah	69	.009	.008	none
48	Quartz-diorite, Amador County, Cal	69.5	.005	.004	trace
49	Trachyte, Highland County, Va	69.5	trace?	trace?	
50	Biotite-granite, Amador County, Cal	70.5	trace	trace	trace
51	Rhyolite, Crater Lake, Oreg	71	.004	.003	ft. tr.
52	Monzonite (altered), Tintic district, Utah	71	.021	.017	none
53	Rhyolite (quartz-porphyry), Tintic district, Utah	71.5	.016	.013	none
54	Rock between rhyolite and dacite, Sutter County, Cal	71.5	trace	trace	
55	Syenite-porphyry, Mount Ascutney, Vt	73	none	none	
56	Granite-porphyry, Mount Ascutney, Vt	73.5	none	none	
57	Granite, Union County, Tenn	76.5	none	none	

[a] Approximate.

[b] Lost, but considerable.

TABLE II.—*Component minerals from certain of the above igneous rocks.*

No.	Name and source.	SiO_2.	V_2O_5	$= V_2O_3$.	Mo.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
7^a	Amphibole from 7	(?)	0.075	0.062	none
11^a	Amphibole from 11	46	.044	.037	none
21^a	Pyroxene from 21	51.5	.043	.036	
23^a	Biotite from 23	36.5	.153	.127	none
29^a	Amphibole from 29	50	.08	.066	
45^a	Biotite from 45	(?)	.057	.048	none
46^a	Biotite from 46	35.5	.08	.066	

TABLE III.—*Miscellaneous.*

No.	Name and locality of occurrence.	SiO_2.	V_2O_5	$= V_2O_3$.	Mo.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
58	Epidotic schist, Mitchell County, N. C	48	0.057	0.047	
59	Quartz-schist, Madera County, Cal	79	trace	trace	
60	Serpentine, Connecticut Valley, Mass	38.5	none	none	
61	Sea-green roofing slate, West Pawlet, Vt	68	.017	.017	
62	Two red roofing slates (equal parts), Washington County, N. Y	67 56	.008	.007	
63	253 sandstones	78.5	.003	.003	
64	498 building limestones	14	.004	.004	

Of the igneous rocks specimens were so selected as to represent not only many widely separated localities, but also numerous varieties from the least siliceous up to those high in silica, in order to ascertain whether a preconceived opinion that the vanadium accompanied chiefly the less siliceous rocks was well founded or not. The choice was, however, confined largely to those rocks analyzed in this laboratory within the past three or four years of which a supply of powder remained after the original analyses had been completed, and hence the list is perhaps not fully representative. Nevertheless it permits of drawing certain conclusions, the chief of which is that the vanadium predominates in the less siliceous igneous rocks and is absent, or nearly so, in those high in silica. The inference, based on the existence of the mineral roscoelite, classed as a vanadium mica, at once suggests itself, that the ultimate source of the vanadium may be one or more of the heavier silicates such as the biotites, pyroxenes, and amphiboles, and a few tests on all the available mineral separation products lend strong support to this view. For instance, the amphibole-gabbros 7 and 11 show 0.038 per cent and 0.02 per cent V_2O_3, while the amphiboles 7^a and 11^a separated from them give 0.062 per cent and 0.037 per cent; the pyroxenic gneiss 23 shows 0.083 per cent against 0.127 from its contained biotite 23^a; the diorite 29 with 0.031 per cent contains an amphibole 29^a with 0.066 per cent; from 0.011 per cent in the quartz-mica-diorite 45 and 0.012 per cent in the quartz-monzonite 46 the percentages rise to 0.048 and 0.066 in their separated biotites 45[a] and 46[a]. The pyroxene 21[a] shows, however, practically the same amount as its mother rock, the syenite-lamprophyre 21.

In most of these cases, notably the last one, the vanadium in the separated mineral is not sufficiently in excess of that in the rock from which it was taken to account for all of that found in the latter. Hence, if the determinations are correct it must also be a constituent of some other mineral than the one analyzed. In roscoelite the trivalent condition of vanadium corresponding to the oxide V_2O_3 is now recognized as probable, although Roscoe's analysis reports V_2O_5 and Genth's an oxide intermediate between V_2O_3 and V_2O_5. This assumption seems to be necessary if the mineral is to be regarded as a mica, and it is then doubtless the equivalent of trivalent iron or aluminum. It would then be natural to look for it in the aluminous or ferric silicates of igneous rocks, certain biotites, pyroxenes, and hornblendes, and its absence in such minerals as serpentine and chrysolite, as shown by analyses 3 and 60, appears natural enough.

Few and inconclusive as the above comparisons are, they seem to favor strongly this view as to the source of the vanadium, and in a measure are confirmatory of the observation of Hayes (Proc. Am. Acad. Arts Sci., Vol. X, 1875, p. 294), who rather indefinitely associates it with phosphorus and proto-salts of iron and manganese, which are usually more prominent components of basic than of acid rocks.

We are probably justified by the evidence in tabulating the vanadium as V_2O_3 in analyses of igneous and some metamorphic rocks which have undergone little or no oxidation, but with sandstones, clays, limestones, etc., which are of more or less decided secondary origin, this is probably not the case. The probabilities are there largely in favor of its acid character and the existence of various vanadates of calcium, iron, aluminum, etc., in which case it should appear in analytical tables as V_2O_5.[1]

---

[1] In the regular course of analysis vanadium will be weighed with alumina, iron, titanium, etc., since it is precipitated by both ammonia and sodium acetate in presence of those and other metals, hence the alumina percentages in nearly all rock analyses heretofore made are subject to correction for the vanadium the rock may have held. This correction is of course to be made in terms of V_2O_5 and not of V_2O_3.

All determinations of iron are likewise affected by its presence, whether as V_2O_5 or V_2O_3. As V_2O_3 it will make the FeO appear too high in the proportion V_2O_3 : 4FeO, or 150.8 : 288, an error which becomes appreciable in some of the basic rocks and amounts to 0.25 per cent in the biotite 23[a]. As V_2O_5 the FeO will not be affected, but in either condition the Fe_2O_3 will need correction and to a different extent, according as the titration of iron is made after reduction by hydrogen sulphide or by hydrogen. If the former is used, as should always be the case in presence of titanium, the vanadium is reduced by it to V_2O_4, which in its action on permanganate is equivalent to 2 molecules of FeO representing 1 of Fe_2O_3, or only one-half as great as the influence on the FeO titration of the same vanadium as V_2O_3. An example will make this clear:

Found 2.50 per cent apparent FeO in a rock containing 0.13 per cent V_2O_3.
Deduct 0.25 per cent FeO, equivalent in its action on $KMnO_4$ to 0.13 per cent V_2O_3.
Leaving 2.25 per cent FeO corrected.
Found 5 per cent apparent total iron as Fe_2O_3 in the same rock.
Deduct 0.14 per cent Fe_2O_3, corresponding to 0.13 per cent V_2O_3.
Leaving 4.86 per cent corrected total iron as Fe_2O_3.
Deduct 2.50 per cent Fe_2O_3, equivalent to 2.25 per cent FeO.
Leaving 2.36 per cent Fe_2O_3 in the rock.

Failure to correct for the vanadium in both cases would have made the figures for FeO and Fe_2O_3, respectively, 2.50 and 2.22 instead of 2.25 and 2.36 as shown above.

It was not until the greater part of the above tests had been finished that any careful attempt was made to identify molybdenum as well as vanadium. From the evidence gathered during the latter part of the work it would seem that molybdenum, when it does occur, is a much less important constituent quantitatively than vanadium, and that unlike the latter it accompanies the more acid rocks. Molybdenite is a well-known accessory constituent of some granites, etc., but in the above instances its amount was extremely small and no hint was obtained as to its state of combination.

CHEMICAL METHOD EMPLOYED.

In conclusion it is proper to outline the method by which the foregoing tests were carried out, and to indicate the precautions that must be observed in order to insure good results.

Quite a number of workers have busied themselves with the problem of vanadium estimation in ores and rocks, particularly magnetites and other iron ores, and the methods used have been often diverse in parts if not altogether. There is nothing absolutely novel in the following except that chromium and vanadium when together need not be separated, but are determined, the former colorimetrically, the latter volumetrically, in the same solution as detailed elsewhere (p. 44).

Five grams of the rock are thoroughly fused over the blast with 20 of sodium carbonate and 3 of sodium nitrate. After extracting with water and reducing manganese with alcohol it is probably quite unnecessary, if the fusion has been thorough, to remelt the residue as above, though for magnetites and other ores containing larger amounts of vanadium than any of these rocks, this may be necessary, as Edo Claassen has shown.[1] The aqueous extract is next nearly neutralized by nitric acid, the amount to be used having been conveniently ascertained by a blank test with exactly 20 grams of sodium carbonate, etc., and the solution is evaporated to approximate dryness. Care should be taken to avoid overrunning neutrality because of the reducing action of the nitrous acid set free from the nitrite, but when chromium is present it has been my experience that some of this will invariably be retained by the precipitated silica and alumina, though only in one case have I observed a retention of vanadium, it being then large. The use of ammonium nitrate instead of nitric acid for converting the sodium carbonate into nitrate did not seem to lessen the amount of chromium retained by the silica and alumina.

As a precautionary measure, therefore, and always when chromium was to be estimated also, the silica and alumina precipitate was evaporated with hydrofluoric and sulphuric acids, the residue fused with a little sodium carbonate and the aqueous extract again nearly neutral-

---

[1] Am. Chem. Jour., Vol. VIII, p. 437.

ized with nitric acid and boiled for a few moments, the filtrate being added to the main one.

Mercurous nitrate was now added to the alkaline solution in some quantity so as to obtain a precipitate of considerable bulk containing chromium, vanadium, molybdenum, tungsten, phosphorus, and arsenic, should all happen to be in the rock, and also an excess of mercurous carbonate to take up any acidity resulting from the decomposition of the mercurous nitrate. Precipitating in a slightly alkaline instead of a neutral solution renders the addition of precipitated mercuric oxide unnecessary for correcting this acidity. If the alkalinity, as shown by the formation of an unduly large precipitate, should have been too great, it may be reduced by careful addition of nitric acid until an added drop of mercurous nitrate no longer produces a cloud.

After heating and filtering, the precipitate is ignited in a platinum crucible after drying and removing from the paper to obviate any chance of loss of molybdenum and of injury to the crucible by reduction of phosphorus or arsenic. The residue is fused with a very little sodium carbonate, leached with water, and the solution, if colored yellow, filtered into a graduated flask of 25 cubic centimeters or more capacity. The chromium is then estimated accurately in a few minutes by comparing with a standard alkaline solution of potassium monochromate (p. 37). Then, or earlier in absence of chromium, sulphuric acid is added in slight excess and molybdenum and arsenic together with occasional traces of platinum are precipitated by hydrogen sulphide, preferably in a small pressure bottle.[1] If the color of the precipitate indicates absence of arsenic, the filter with its contents is carefully ignited in porcelain and the delicate sulphuric acid test for molybdenum is applied.

The filtrate, in bulk from 25 to 100 cubic centimeters, is boiled in a current of carbon dioxide to expel hydrogen sulphide, and titrated at a temperature of 70–80° C. with a very dilute solution of permanganate representing about one milligram of V_2O_5 per cubic centimeter as calculated from the iron strength of the permanganate, one molecule of V_2O_5 being indicated for each one of Fe_2O_3. One or two checks are always to be made by reducing again in a current of sulphur dioxide gas, boiling this out in a current of carbon dioxide again, and repeating the titration.

As shown in a previous paper (p. 45), the presence of even thirty times as much Cr_2O_3 as V_2O_5 does not prevent a satisfactory determination of the vanadium if the precautions therein given are observed, provided there is present not less than one-half to 1 milligram of V_2O_5 in absolute amount. In absence of chromium less than half a milligram can be readily estimated. The phosphoric acid almost invariably present does not affect the result.

---

[1] From a sulphuric solution the separation of molybdenum by hydrogen sulphide is much more rapid and satisfactory than from a hydrochloric solution.

In case the volume of permanganate used is so small as to make doubtful the presence of vanadium, it is necessary to apply a qualitative test which is best made as follows: The solution is evaporated and heated to expel excess of sulphuric acid, the residue is taken up with 2 or 3 cubic centimeters of water and a drop or two of dilute nitric acid, and a couple of drops of hydrogen peroxide are added. A characteristic brownish tint indicates vanadium. Unless the greater part of the free sulphuric acid has been removed the appearance of this color is sometimes not immediate and pronounced, hence the above precaution.

The above is a surer test to apply than the following: Reduce the bulk to about 10 cubic centimeters, add ammonia in excess and introduce hydrogen sulphide to saturation. The beautiful cherry-red color of vanadium in ammonium sulphide solution is much more intense than that caused by hydrogen peroxide in acid solution, but the action of ammonia is to precipitate part or all of the vanadium with the chromium or aluminum that may be present or with the manganese used in titrating, and ammonium sulphide is unable to extract the vanadium wholly from these combinations. Usually, however, the solution will show some coloration, and addition of an acid precipitates brown vanadium sulphide, which can be collected, ignited, and further tested if desired.

SUMMARY OF RESULTS.

Vanadium occurs in quite appreciable amounts in the more basic igneous and metamorphic rocks, up to 0.08 per cent or more of V_2O_3, but seems to be absent or nearly so from the highly siliceous ones. The limited evidence thus far obtained points to the heavy ferric-aluminous silicates as its source—the biotites, pyroxenes, amphiboles. As opportunities offer further evidence will be accumulated and it is hoped that other chemists will lend their aid.

Limestones and sandstones appear to contain very small amounts of vanadium, as shown by analyses of a composite sample of each, aggregating over 700 different occurrences.

From the few tests of molybdenum it appears as if this element were confined to the more siliceous rocks. It is present in no observed case in amount sufficient for quantitative measurement when operating on 5 grams of material.

NOTE.—Since the above was written a few tests have been made on minerals of which powdered samples were at hand. A phlogopite from Burgess, Canada, gave 0.007 per cent V_2O_3. Mica from Laurel Hill, Georgia, gave 0.026 per cent V_2O_3. Protovermiculite from Magnet Cove, Arkansas, gave 0.04 per cent V_2O_3. Hallite from Chester County, Pennsylvania, gave 0.01 per cent V_2O_3. Jeffersonite from Franklin Furnace, New Jersey, gave none, and a nonferruginous amphibole from St. Lawrence County, New York, gave a faint trace.

WARNING AGAINST THE USE OF FLUORIFEROUS HYDROGEN PEROXIDE IN ESTIMATING TITANIUM.

By W. F. HILLEBRAND.

Dunnington[1] has pointed out a source of error to be guarded against in estimating titanium in rocks and minerals by Weller's method, due, as he believes, to the partial reversion, in certain cases, of ordinary titanic to meta-titanic acid, which does not afford a yellow color with hydrogen peroxide. It remains for me to indicate another source of error in the possible presence of fluorine in the hydrogen peroxide.

For two years the colorimetric method has given reasonable satisfaction in this laboratory, but recently a new lot of hydrogen peroxide was purchased of a different brand from that hitherto used, and after a time it was noticed that the results obtained were in some instances far too high, and that no two determinations agreed.

It is known that hydrogen peroxide does not produce a yellow color in titanium solutions carrying hydrofluoric acid or fluorides, and moreover the addition of even a drop of the dilute acid to an already peroxidized titanium solution weakens the color. For this reason it is necessary to take the greatest care to insure the complete expulsion of all fluorine when dissolving rocks or minerals by means of hydrofluoric and sulphuric acids prior to the colorimetric estimation. A drop of hydrofluosilicic acid acts similarly, but the latter reagent can not be made to completely discharge the color even if added in great excess.

This, however, was not suspected as the cause of our trouble until, on referring to the circular of one of the leading makers of hydrogen peroxide in this country, whose product has always given satisfactory results in titanium work, it was found that among the various acids enumerated as usually to be found in the commercial article, hydrofluroic acid appears. Talbot and Moody, in the Technology Quarterly, v. 123, mention hydrofluosilicic acid as of frequent occurrence in the peroxide manufactured a few years ago. On examining the suspected peroxide by neutralizing with fixed alkali, evaporating to dryness, and heating with strong sulphuric acid, fluorine was detected by the odor of the acid evolved and by its action on glass.

It is therefore imperative to use only hydrogen peroxide which is free from fluorine in estimating titanium, for its presence may utterly vitiate the results, even if only 2 or 3 cubic centimeters of the peroxide are employed.

---

[1] Jour. Am. Chem. Soc., Vol. XIII, p. 210.

MINERALOGICAL NOTES.

By W. F. HILLEBRAND.

1. CALAVERITE FROM CRIPPLE CREEK, COLORADO.

The occurrence of tellurium in the ores of the mining district of Cripple Creek, Colorado, has been known from an early day in the as yet brief industrial history of that region. That it was, in part at least, associated with gold was likewise known from the observance of a crystallized gold-tellurium mineral. Although the ores of the district are chiefly gold carriers, they contain also a little silver, and since recognized silver minerals had not been observed, or at most only in minute amount, it seemed probable that the silver was associated with the gold in the tellurium compound. Indeed, Mr. R. Pearce, of Denver, came to the conclusion, from analyses of oxidized and unoxidized ores,[1] that this mineral was sylvanite, and he says: "Sylvanite itself appeared in little silver-white specks disseminated through a mass of greenish rhyolite." Notwithstanding that F. C. Knight[2] has identified calaverite by analysis and that sylvanite has not been identified by positive chemical and crystallographical tests, the evidence of Mr. Pearce as to its presence, in some portions of the district at least, is entitled to consideration.

The telluride examined by me was collected by R. A. F. Penrose, jr., who procured his material from three different mines in order to ascertain whether it was of constant or varying composition, or, in fact, whether there might not be more than one specific compound. That the composition does vary within narrow limits the analyses show; but there is no reason apparent for assuming the existence of more than one species in the ores of these particular mines.

The material from the Prince Albert mine, the first received, was with little trouble brought into an almost ideal condition of purity. It was in part apparently fairly well crystallized, but the measurements made by Prof. S. L. Penfield, of New Haven, are unfortunately not decisive as to the system of crystallization, as shown by his notes at the close of this paper. The specific gravity of this material was 8.91 at 24° C., which becomes 9 when corrected for a small admixture of silico-ferruginous gangue of assumed specific gravity 2.70 (probably

---

[1] Proc. Colorado Sci. Soc., Vol. V, 1894, pp. 5, 11.

[2] Ibid., Vol. V, 1894, p. 70.

low). The other samples were imperfectly crystallized and held too much foreign matter of uncertain composition to make specific gravity determinations of any value.

	I. Prince Albert mine.	II. Raven mine.	III. C. O. D. mine.
Tellurium (Te)	57.27	47.69	53.89
Gold (Au)	38.95	33.93	39.31
Silver (Ag)	3.21	1.47	.85
Insoluble	.33	5.80	.91
Ferric oxide (Fe_2O_3)	[a] .12		
Iron (Fe)		5.41	1.67
Sulphur (S)		[b] 6.17	1.58 (2.96 FeS_2)
Manganese (Mn)			[c] .23
Calcium (Ca)			.51
Magnesium (Mg)			.10
Oxygen, fluorine, and soluble silica by difference			[d] .95
	99.88	100.47	100.00

[a] This was included with the insoluble matter in arriving at the corrected density.
[b] Calculated from the Fe to make FeS_2.
[c] As MnO_2?
[d] A part of the calcium found in solution was derived from fluorite, which likewise constituted some of the insoluble matter in this instance.

Selenium has been reported in the oxidized ores of the district,[1] but it could not be detected in the amount of mineral taken for the above analyses.

Excluding everything but gold, silver, and tellurium and recalculating to 100, the following comparison is obtained:

	I.		II.		III.	
	Per cent.	Ratio.	Per cent.	Ratio.	Per cent.	Ratio.
Te	57.60	2.01	57.40	2.05	57.30	2.09
Au	39.17	1.00	40.83	1.00	41.80	1.00
Ag	3.23		1.77		.90	
	100.00		100.00		100.00	

The ratio here obtaining is that for sylvanite and calaverite, but the very low percentage of silver shows that the mineral is calaverite. Indeed the first analysis agrees almost exactly with Genth's analyses

---

[1] F. C. Knight, Proc. Colorado Sci. Soc., Vol. V, 1894, p. 68.

of the species. Interesting is the slight variation in the ratio between gold and silver, and the very low percentage of silver in the mineral from the C. O. D. and Raven mines. Calaverite, the lowest silver carrier of the gold-silver tellurides, has not heretofore been known to carry less than 3 per cent of silver.

The pyrognostic characteristics of the mineral from the Prince Albert mine were essentially those ascribed to calaverite. In the closed tube it fuses, giving a white coating near the assay, and a globular gray coating just above, which latter by strong heat can be in part driven higher up, leaving the glass covered with the same white fused coating as lower down. This latter is yellow while hot. On charcoal the mineral fuses with a green flame, giving a white coating and similar fumes, and leaving a yellow bead. The color is pale bronze-yellow, in powder greenish gray. The hardness is not less than and perhaps a little over 3. Specific gravity, as given above, 9.

The identity of the telluride occurring at Cripple Creek, which in oxidizing gives free gold and oxidized tellurium compounds,[1] seems thus satisfactorily established, but unless there is another richer in silver, as believed by Pearce, the mode of occurrence of the silver in some of the ores is still in large part unaccounted for. It may be derived from a very rich argentiferous tetrahedrite of which Professor Penrose submitted a small specimen for identification. This carries over 11 per cent of silver, but is said to be excessively scarce and therefore hardly to be considered in this connection, unless indeed this should have been the original source of most of the silver and later have suffered oxidation to a great extent whereby the silver has become more evenly distributed throughout the ore.

Professor Penfield has kindly contributed the following notes on the crystallography of the mineral:

> The crystals of calaverite which were examined were developed with prismatic habit, but the prismatic zone was striated to such an extent that it was impossible to identify a single face in the zone, and on the reflecting goniometer almost an unbroken band of signals was obtained in a revolution of 360°. Owing to oscillatory combinations the crystals were also much distorted, so that they did not present regular cross sections.
>
> The prisms were attached so that doubly terminated ones were not observed, while the faces at the free end were small and developed with so little symmetry that after a study of a number of crystals it was found impossible to determine with certainty the system of crystallization.
>
> The crystals do not exhibit the perfect cleavage ascribed to sylvanite and krennerite, but are similar to the former in some of their angles. When placed in position to show their relation to sylvanite they have their prismatic development parallel to the *b* axis. One crystal, which owing to its development was more carefully measured than any of the others, was apparently a twin about 101, and showed

---

[1] From tests made by myself on a number of specimens collected by Professor Penrose the combination seems to be chiefly if not altogether with iron, but whether as tellurite or tellurate could not be ascertained. Knight (loc. cit., p. 69), however, has shown that the combination, in some cases at least, is a tellurite, approximating to the formula $2(Fe_2O_3, 2TeO_2)+H_2O$.

at the end the forms 111 and 110. The measurements compared with the corresponding ones of sylvanite are as follows:

		Sylvanite.
111∧(111) over twinning plane	93° 35′	94° 30′
110∧(110) over twinning plane	35 2	34 43
110∧111	36 35	37 3
110∧111 in twin crystal	36 33	37 3

Other forms which were measured could not be referred to the sylvanite axes, and it seems probable from their development and lack of symmetry that the crystals are triclinic; but no satisfaction was obtained after a long and careful study of the limited supply of material on hand.

In conclusion therefore it may be stated that the crystals are probably triclinic, but near sylvanite in angles and axial ratio.

NOTE.—Since the foregoing work was completed additional analyses of Cripple Creek tellurides have been made by Profs. A. H. Chester[1] and W. H. Hobbs.[2] From the crystallographic data they were able to obtain it would appear that neither of the minerals examined by them can be identical with calaverite, though both possess the same general formula MTe_2, in which, however, the ratio of gold to silver was not at all alike. The analysis of that one, which by its crystallographic features was identified as krennerite, has even less silver than the specimens of calaverite from the C. O. D. mine, while goldschmidtite, showing crystallographic relations with sylvanite, contains 8.95 per cent Ag to only 31.41 per cent Au, thus supporting, in a measure, Mr. Pearce's belief in the existence at Cripple Creek of a telluride much richer in silver than calaverite.

2. TELLURIDES FROM CALIFORNIA.

In a suite of tellurides from the Mother Lode region in California, collected by Mr. F. L. Ransome, of the United States Geological Survey, I have been able to identify a nickel telluride (melonite?), a mercury telluride (coloradoite?), besides petzite and hessite.

MELONITE?.

Several specimens from the old Stanislaus mine,[3] the original source of Genth's melonite[4] (Ni_2Te_3?), but now included with the Melones and

---

[1] On krennerite from Cripple Creek, Colorado. Am. Jour. Sci., 4th series, Vol. V, 1898, p. 375.

[2] Goldschmidtite, a new mineral. Am. Jour. Sci., 4th series, Vol. VII, 1899, p. 357.

[3] Mr. Ransome has kindly furnished the following notes: This mine is situated on the south slope of Carson Hill, Calaveras County, just above Robinsons Ferry, and has not been worked for several years. There is no prominent vein at this point, the ore being very irregularly distributed, and occurring in small, nearly horizontal, stringers in dark clay slates of Carboniferous age, with nearly vertical dip. This mine has long been known as a source of interesting tellurides, and Dana, in the sixth edition of his System of Mineralogy, cites petzite, calaverite, melonite, and altaite as occurring here. The other ore minerals are pyrite and galena, the latter in small quantities. The ore-bearing stringers are filled with quartz, or a mixture of quartz and calcite as a gangue. The rich masses of tellurides appear, however, to be usually associated with calcite (or dolomite). The melonite of specimen No. 16, shows at least one perfect cleavage, resembling in the thinness of the resulting laminæ the cleavage of the micas. The cleavage faces are usually somewhat curved, and possess a splendent metallic luster. The cleavage can best be detected by carefully scraping thin folia from such a brilliant surface with a sharp knife point. The color of the cleavage faces is pale bronze yellow.

[4] Long *o*, accented (mel-ǫ-nite).

other claims under the name Melones mine, showed plainly a nickel telluride of reddish-white cast, of color like that of bismuth,[1] thickly scattered in grains, and showing pronounced cleavage and a brilliant luster. A concentrate was prepared by the aid of cadmium-boro-tungstate solution, and this was then laboriously hand picked by the aid of a powerful glass. There was certainly more than one foreign mineral present, but identification was not possible except as to a little gold and petzite. The chief impurity was a silver mineral, presumably hessite. If so, the analyses seem to indicate also native tellurium. A perfectly pure article could not be extracted because of difficulty in sometimes distinguishing the foreign minerals from the one sought, but it was hoped that an analysis of both the selected and rejected portions would permit of calculating the composition of the nickel mineral with considerable certainty on the reasonable assumption that no impurity had been removed in relative excess over the other or others.

The analyses below represent the composition of (*a*) the rejected, (*b*) the original, and (*c*) the selected material. Analysis *b* is given chiefly because of the cobalt determination, the nickel being probably a little high. Although but 0.22 and 0.13 grams, respectively, were available for the analyses *a* and *c* the data are believed to be more trustworthy on the whole than those of *b*, hence the figures under *d* have been obtained by calculation based on *c* and *a* only, after reducing them to 100. Under *e* is shown the theoretical composition of $NiTe_2$. Small amounts of iron, traces of copper, and perhaps one or two other elements are omitted, besides the three-fourths to 2 per cent of gold and petzite that remained unattacked by cold dilute nitric acid, in which the nickel mineral is readily soluble.

The specific gravity of *b* at 22.5 was 7.72, which is probably higher than the true density of the pure nickel telluride.

Analyses of melonite.

	a	*b*	*c*	*d*	*e* $NiTe_2$.
Te	75.29	77.72	80.75	81.40	81.29
Ni	15.71	17.16	18.31	18.60	18.71
Co		.10			
Ag	8.44	5.09	.86	....	....
	99.44	100.07	99.92	100.00	100.00

---

[1] Under a lens, and to the unaided eye in certain lights, the color appears more bronze yellow.

If hessite and native tellurium constitute the foreign admixture the mineralogical composition of *a* and *c* is shown to be as follows:

	a	*c*
$NiTe_2$	84.44	97.89
Hessite	13.51	1.38
Tellurium	2.05	.73
	100.00	100.00

There is here indicated a considerable selective separation of the foreign minerals, since the relative proportions of tellurium and hessite are very different in the two mixtures, but the amounts operated on were so small that a very slight actual error in a determination might give rise to this change in the relative proportions of impurities without affecting materially the ratios found for the components of the nickel telluride. The three analyses taken together point unmistakably to $NiTe_2$ as the formula for the latter mineral. The question then arises, Is this Genth's melonite, or is it a new mineral? Genth found:

Te	73.43
Ni	20.98
Ag	4.08
Pb	.72
	99.21

from which, after deducting hessite, altaite, and free tellurium, he deduces the formula Ni_2Te_3, requiring Te 76.49 and Ni 23 51.

The difference between his and my own analyses is too great to admit of bringing them into accordance, yet I am indisposed to believe that two minerals are represented, for both occurrence and appearance are opposed to such a view. The present mineral is from the same source as Genth's. Its physical characteristics, so far as ascertainable, coincide with those of melonite, and it is called melonite by the people at the mine. Melonite was considered by Genth to be hexagonal on the strength of its eminent cleavage and the observation of a single microscopic 6-sided plate. Mineralogically a hexagonal form in the pyrite group, assuming this mineral to belong there, is not to be looked for, but the evidence in favor of hexagonal crystallization is too meager to permit this to be used as an argument one way or another.

COLORADOITE?

One small specimen from the Norwegian mine showed in dolomite, petzite, hessite, and a mercury telluride. Superficially the latter was not to be distinguished from the accompanying petzite and hessite, and it was in insufficient amount to admit of analysis for the determination of its formula. It however gave the tests noted by Genth for the original coloradoite from Colorado, and in addition the following characteristic may be noted: On heating with strong nitric acid it becomes coated with a white insoluble salt of mercury, which retards further action of the acid.

It is, in all probability, coloradoite, and if so this is its second known locality of occurrence, though I have been informed that a mercury telluride has recently been found in western Australia.

PETZITE.

One specimen of petzite from the Norwegian mine gave such an abundance of pure material that an analysis seemed desirable. The results were as follows:

Au	25.16	1.98	1.00
Ag	41.87		3.04
Te	33.21	1.00	
Se	trace		
Mo	.08		
	100.32		

Approximate specific gravity at 23° C., 8.925. The molybdenum may exist as sulphide. The ratios lead almost exactly to the formula Au_2Te, 3 Ag_2Te.

3. HESSITE FROM MEXICO.

As an addition to the foregoing work may be given an analysis of hessite from a new locality—San Sebastian, Jalisco, Mexico—the material having been received from Mr. Frederic Chisolm:

Ag	61.16
Te	36.11
Pb	1.90
S. Fe. Zn	[a].83
	100.00
Specific gravity at 26° C	8.24

[a] Difference.

4. COVELLITE AND ENARGITE FROM MONTANA.

The only important occurrence of covellite in this country is at Butte, Montana, where it occurs in splendid indigo-blue masses. Specimens from the East Greyrock mine, collected by Mr. George W. Tower, formerly of the United States Geological Survey, gave almost the theoretical composition as shown below. Specific gravity at 26° C., 4.76, uncorrected for impurities.

An analysis of enargite collected by Mr. Tower in the Rarus mine, at Butte, is also given.

Analysis of covellite.

Cu	66.06	
S	33.87	
Fe	.14	$=.30\ FeS_2$
Insol	.11	
	100.18	

Ratio Cu : S as 1 : 1.01.

Analysis of enargite.

Cu	48.67
Fe	.33
Zn	.10
As	17.91
Sb	1.76
S	31.44
Insol	.11
	100.32

5. TYSONITE AND BASTNÄSITE.

These minerals formed a single fine specimen half as large as the fist, without crystal faces, from Cheyenne Mountain, near Pikes Peak, Colorado. The bastnäsite covered one side of the tysonite to the depth of an inch. The line of demarcation between the two minerals was sharp, but examination of their sections by Mr. H. W. Turner showed the tysonite to be permeated by stringers of bastnäsite along numerous cracks and that occasional grains of the latter were embedded in the tysonite, which accounts for the CO_2 shown in the tysonite analysis. Attached to the tysonite at portions of its surface were other white and brownish alteration products derived from it, as shown by qualitative tests. The tysonite was evidently the remnant of a single large crystal, since, according to Mr. Turner, all parts had the same optical orientation. Mr. Turner further found the optical properties of both minerals, so far as determinable, to agree with those given in Dana's Mineralogy, and the index of refraction of the bastnäsite to be greater than that of the tysonite. He likewise noted in both minerals minute colored inclusions, indeterminable and very trifling in amount, and also in the tysonite "numerous minute angular cavities in which there is a liquid, often with gas bubble. Minute, clear, cuboidal crystals, apparently isometric, were also noted in some of these cavities."

The composition of the minerals was found to be as given by Allen and Comstock, with the exception that the ratios of cerium oxide to the oxides of the lanthanum group are not quite the same. The formulæ are not thereby affected.

Cerium was separated from the lanthanum group oxides by two precipitations by potassium hydroxide followed by long introduction of chlorine. After recovery of the earths remaining in solution, they were again subjected to this treatment to be certain of having all the cerium. In one case a small portion was thus recovered. The cerium was most carefully examined for thorium and traces of what appeared to be thoria were found. The other earths were wholly precipitable by potassium sulphate with exception of traces of what may be oxides of the yttrium group. Approximate molecular weight determinations of the combined oxides of these two groups were made, and they show an appreciable difference, which may, however, be due to the uncertainty of the method. It may be mentioned that on ignition of the sulphates of these earths they acted like the old didymium in that they lost exactly two-thirds of their SO_3 on ignition over the full flame of the Bunsen burner, a fact which would seem to exclude the presence of lanthanum. Their solutions were pink and gave pronounced absorption spectra. The ignited oxides freed from cerium were a dull, dirty brown, which became nearly white on blasting and acquired a distinct bluish cast on ignition in hydrogen. No appreciable reduction in weight followed heating in hydrogen. The material saved is at the disposal of anyone desiring to examine these earths spectroscopically.

Owing to the great difficulty in effecting complete decomposition of the minerals by sulphuric acid at a single treatment, the fluorine was obtained in condition for estimation by fusing with potassium carbonate after mixing with silica in the proportion of 0.6 gram mineral to 1 gram silica.

Fragments of tysonite when held in the blast gave a distinct crimson flame showing the lithium red line, but an alkali determination failed to reveal more than a trace of this element.

Of the bastnäsite very little pure material could be separated, and it was therefore impossible to place with certainty all the loss shown by the analysis, but a portion of it is to be charged to the oxides of the lanthanum group because of an accident.

Specific gravity of the bastnäsite 5.12 at 27° C. and of the tysonite 6.10 at 28° C., which becomes 6.14 when corrected for 2.65 per cent of bastnäsite.

Analysis of tysonite.

Ce_2O_3	[a] 42.89
La group	[b] 39.31
F	[c] 28.71
CO_2	.53
CaO	.18
Fe_2O_3	.11
Na_2O (with traces K_2O and Li_2O)	[d] .30
	112.03
Less O for F	12.08
	99.95

[a] 0.13 per cent ThO_2?
[b] At. w. 139.7; includes 0.21 per cent soluble in K_2SO_4.
[c] Mean of 28.86 and 28.56.
[d] Approximate.

Analysis of bastnäsite.

Ce_2O_3	[a] 37.71
La group (slight loss)	[b] 36.29
F	7.83
CO_2	[c] 20.03
Fe_2O_3	.22
Na_2O (with traces K_2O and Li_2O)	.18
H_2O	.08
	102.34
Less O for F	3.30
	99.04

[a] Mean of 37.73 and 37.69; includes .10 per cent ThO_2?
[b] At. w. 141; includes .09 per cent soluble in K_2SO_4.
[c] Mean of 19.94 and 20.11.

Neglecting the last three constituents in each case, the ratios become for

Bastnäsite	$R : F, CO_3 = 1 : 2.94$
Tysonite	$R : F, CO_3 = 1 : 3.05$

which ratio for tysonite is not changed by allowing for admixed bastnäsite.

The above direct fluorine determinations fully establish the hitherto assumed formulas $R''' F_3'$ for tysonite and $R''' (F' CO_3'')$ for bastnäsite.

6. PROSOPITE.

Early in 1896 Mr. George F. Kunz sent for examination a beautiful pale green mineral from Utah, supposed to be identical with the green variscite called by him utahlite in Mineral Resources of the United States, 1894, page 602. Under a recent date Mr. Kunz writes that Mr. T. H. Beck, of Provo, Utah, found the mineral "in 1895, in the Dugway mining district, Tooele County. It was found in a low range of hills about 5 miles long, surrounded by a desert on an arid region occurring as flat rock, associated with fluorite, native silver, slate, and trachytic rock (?), containing decomposed pyrite in which there was present a little free gold."

Unexpectedly this was found to be the hydrous aluminum-calcium fluoride prosopite, mixed with some quartz and probably fluorite, and colored by a small amount of some copper salt. A new and interesting occurrence for this very rare mineral is thus afforded.

The material as prepared for analysis after separation by a heavy solution proved to be still far from pure; quartz grains in amount from 1 to 2 per cent were left undissolved after complete conversion of the fluorides into sulphates, and presumably considerably more had been removed by the escaping fluorine. The total amount of quartz was not determined, and the material at hand did not suffice for attempts at more complete purification, so that the conclusions drawn from the analysis, while extremely probable, are not to be taken as altogether proven.

The specific gravity of the mineral as analyzed was 2.87 at 21° C. and the hardness about 4.5, both agreeing with the constants for prosopite. Furthermore, but little of the water (1.25 per cent) was expelled by several hours heating at 280° C. Analysis gave:

Al	20.08
Ca	17.55
Mg	trace
K	.12
Na	.32
Cu	.17
F	28.00
H_2O	14.24
Quartz and oxygen	19.52
	100.00

Neglecting copper, alkalies, and the oxygen calculated for their oxides, and assuming the water to exist entirely as hydroxyl, the following not very satisfactory atomic ratios result:

Al	.7407	2
Ca	.4380	1.18
F	1.4690	8.23
Hydroxyl	1.5808	

which become

Al	.7407	2
Ca	.3712	1
F	1.3354	7.87
Hydroxyl	1.5808	

if enough calcium and its equivalent in fluorine are subtracted to make the ratio Al : Ca exactly 2 : 1, on the not improbable assumption that fluorite is present as an admixture, an assumption that had to be made also for the Colorado prosopite in order to bring it into close agreement with Brandl's formula.

There is now a deficiency in the acidic radicals. The figures for Al, Ca, and H_2O are undoubtedly very nearly correct, while the fluorine may well be a half per cent low, having been determined by the Berzelian method, owing to the difficulty of securing complete decomposition of the fine powder by a single treatment with sulphuric acid. Let it be permitted to balance the basic and acidic radicals by raising the fluorine, and to figure the ideal percentages on this basis. These become of interest when compared with the corresponding figures for prosopite from Altenberg and Pikes Peak as given below:

	Altenberg.	Pikes Peak.	Utah.
Al	23.37	22.02	22.74
Ca	16.19	17.28	16.85
F	35.01	33.18	29.95
H_2O	12.41	13.46	16.12
O	12.58	13.41	14.34
	....	....	100.00

If the assumptions made in the foregoing are justified, the Utah mineral is prosopite, and further evidence is afforded of the correctness of the view established by Penfield that fluorine and hydroxyl can mutually replace each other in many mineral species, for their relative proportions differ materially in the prosopite from the three known localities. The correctness of the formula as applied to the Colorado and Utah prosopite is, however, predicated, as said, on the unproven assumption that the material analyzed contains some admixed fluorite.

7. JEFFERSONITE.

Two brown substances associated with franklinite and other zinc minerals from Franklin Furnace, New Jersey, so alike in appearance as to have been taken for the same mineral species, were received from Mr. George L. English. One was a little duller than the other and proved to be a mixture of several minerals, according to Mr. F. L. Ransome of the U. S. Geological Survey, largely pseudomorphic after some micaceous mineral. From Professor Clarke's calculations, based on the following analysis, it might be a mixture of a calcium-aluminum garnet, troostite, and limonite. SiO_2 32.09, Al_2O_3 11.12, Fe_2O_3 5.16, MnO 15.85, ZnO 16.89, CaO 15.65, H_2O 2.15, MgO and alk. 1.12; total 100.00.

The other was of a richer and deeper brown, and showed such a pronounced cleavage or parting in one direction as to produce a lamellar structure. The luster was brilliant on these cleavage surfaces. Other directions of cleavage were apparent. The hardness was about 5.5 and the density 3.39 at 21.5° C. Before the blowpipe a fragment fused with difficulty to a light-colored blebby glass. Analysis gave:

SiO_2	51.70
Al_2O_3	.36
Fe_2O_3	.37
MnO	7.43
ZnO	3.31
CaO	23.68
MgO	12.57
Na_2O	.12
K_2O	trace
H_2O	.65
	100.19

TiO_2, FeO, P_2O_5 absent.

Neglecting the sesquioxides, alkalies, and water, this leads to the ratio $SiO_2 : RO = 1 : 1.02$, and the formula is that of a metasilicate $R''SiO_3$. According to Mr. English, the material submitted by him had been pronounced by Professor Penfield on the basis of qualitative tests to be jeffersonite, a manganese-zinc pyroxene, a statement supported by the analysis above given, although neither the color of the mineral nor its quantitative composition agree with the hitherto published data. In Dana's Mineralogy the color is given as "greenish black, on the exposed surface chocolate brown," the density as 3.36 on page 358, but 3.63 on page 360. The discoverers of the species, Keating and Vanuxem, give 3.50–3.55 for the density and 4.5 for the hardness. The present mineral presents all the evidences of being fresh and unaltered, yet it is brown throughout, and its analysis furnishes figures widely at variance with those of Herrmann and of Pisani, but giving a better metasilicate ratio than either of their analyses. Notwithstanding these discrepancies, there is no reason for ascribing to the mineral a new subspecies name. The analysis is chiefly valuable as showing a wide range of composition for the mineral.

8. ANORTHITE AND EPIDOTE.

In specimens collected by T. F. Lamb at Phippsburg, Maine, these two minerals occur under unusual circumstances. The mass of the material is a highly metamorphosed contact limestone, carrying an abundance of cinnamon garnet and occasionally a green pyroxene. Now and then there is embedded in the masses of garnet a dark-gray mineral, nearly black in some specimens, in brilliant plates which nowise suggest epidote. Epidote, however, it proved to be, as shown by the subjoined partial analysis, and as verified by Mr. J. S. Diller under the microscope. The anorthite, also determined optically by Mr. Diller, and analytically by Mr. George Steiger, is associated sometimes with the epidote and sometimes in coarse crystals only with the garnet. The analyses are as follows:

	Epidote.	Anorthite.
SiO_2	38.54	45.62
Al_2O_3	28.39	35.29
Fe_2O_3	6.89	....
FeO	.50	....
CaO	24.12	17.31
MgO	trace	....
Ignition	2.26	....
	100.70	98.22

In some ways the epidote resembles axinite, a mineral which has long been recorded as found at Phippsburg. Is the supposed axinite really epidote?

9. ROSCOELITE.

The rare mineral roscoelite has greatly needed reexamination, in order to reconcile the discrepancies between the analyses of Roscoe and Genth and to establish a satisfactory formula for this supposed vanadium mica. To the kindness of Mr. G. W. Kimble, of Placerville, California, I am indebted, through Mr. H. W. Turner, for specimens from the Stockslager mine, from which a limited amount of fairly pure material was picked out. This was then laboriously purified by the aid of Thoulet's solution, the result being a very nearly pure product weighing only 1.2 grams and having, after drying at 100° C., a density of 2.97 at 20° C.

Notwithstanding the small amount, it was possible by the exercise of care to make fairly satisfactory analyses.

With regard to the methods employed little need be said except as to the determination of the condition of the vanadium. For this purpose decomposition was effected by rather dilute H_2SO_4 in sealed tubes, the greatest care being taken to expel every trace of air from the powder and acid, and to seal the tube during passage of a current of CO_2. Otherwise it is impossible to prevent oxidation of a considerable part of the V_2O_3. In one case, unfortunately, the air could not have been fully expelled, for the solution after decomposition was blue instead of green and much less oxygen was required in titration than when the color was green.

The contents of the tube, still warm, were poured into fairly hot freshly boiled water and titrated rapidly. Iron and vanadium were then reduced by H_2S gas, the latter boiled out in a current of CO_2, and titration repeated on the hot liquid. The solution was then boiled with ammonia, the precipitate fused with Na_2CO_3, leached with water, and the residue again fused with Na_2CO_3 and leached to remove the last of the vanadium. This residue was then fused with $KHSO_4$,[1] dissolved in dilute H_2SO_4, boiled first with H_2S and then in a current of CO_2, and the liquid titrated for total iron. The solution held titanium which was then estimated colorimetrically.

The first of the titration results gave the effect of all iron, assuming its existence as FeO, and of all vanadium that might exist in a lower state of oxidation than V_2O_5. The second gave all iron as FeO and all vanadium as V_2O_4. Deduct from both the figure for FeO and the remainder gives that for vanadium. In this way two very concordant results were obtained for total vanadium as V_2O_4, which were supplemented by tests on portions used for other constituents, but only one was obtained for the vanadium as it exists in the mineral, a second being vitiated by evident oxidation during decomposition in the tube. As a check, however, a fresh sample of unpurified mineral was similarly treated, and it was found that fully nine-tenths of the vanadium existed as V_2O_3, a result confirming the single test on the purified material which showed 93.5 per cent as V_2O_3. It is not impossible that slight oxidation had taken place even in these cases, and I feel justified in assuming with Genth that the vanadium should be considered wholly as V_2O_3.

In the other portions analyzed the vanadium was likewise titrated in V_2O_4 condition, but only after separation from iron, titanium, and aluminum by fusion with Na_2CO_3, extraction with water and separation of dissolved alumina by ammonium carbonate. A second fusion of the residue and of the precipitated alumina was necessary in order to extract all the vanadium. These numerous manipulations render the figures for Al_2O_3 perhaps the least trustworthy of all, but the average given is probably not far from correct.

The iron is assumed to be present as FeO; and the titanium to belong to a foreign mineral, since a test on unpurified material gave much more, namely, 1.50 per cent TiO_2, without accompanying increase in FeO, which latter observation seems to exclude ilmenite as the source of the titanium.

Both the iron and magnesium are supposed to belong to the roscoe-

---

[1] Any slight trace of vanadium remaining will impart a bright yellow color to the cold $KHSO_4$ fusion, a test which proved useful more than once during the analysis.

lite, since they were found by Genth in nearly the same amounts and no recognizable iron or magnesium minerals were noticed in the purified powder.

For comparison, the mean of Roscoe's analyses and that one of Genth's considered by himself to be his best are also given in the table below.

Very marked differences are apparent in the three analyses by different chemists. If titanium was present in the material analyzed by Genth and Roscoe, as is very probable, their high results for alumina are in great part at least accounted for. It is inconceivable how Genth obtained his value for water by ignition, since the mineral oxidizes when heated in air. In fact the oxidation in one of my own analyses, after allowing for loss of water as ascertained by direct weight, was almost what theory requires for the oxidation of V_2O_3 to V_2O_5 and of FeO to Fe_2O_3, or 5.14 per cent instead of 5.27 per cent. It may fairly be assumed that his water was weighed directly after expulsion by ignition of the powder. Roscoe's figures for water, if not for moisture, must be affected by error, probably arising from the unsuspected oxidation of vanadium.

Analyses of roscoelite.

	Hillebrand.						Genth.	Roscoe.	
Amount used.....	0.3000*g*.	0.2531*g*.	0.2635*g*.	[a]0.1560*g*	0.2038*g*.	Mean.			
SiO_2	45.30	45.04	....	....	....	45.17	47.69	SiO_2	41.25
TiO_2	.77	....	.77	....	.80	.78	....	V_2O_5	[b]28.60
V_2O_3	23.90	24.00	....	24.09	24.06	24.01	20.56	Al_2O_3	14.14
Al_2O_3	....	11.74	11.34	....	....	11.54	14.10	Fe_2O_3	1.13
FeO	1.59	....	....	1.65	1.57	1.60	1.67	Mn_2O_3	1.15
MgO	1.64	....	....	....	....	1.64	2.00	CaO	.61
K_2O	....	10.41	10.32	....	....	10.37	7.59	MgO	2.01
Na_2O	....	.13	none	....	....	.06	.17	K_2O	8.56
Li_2O	....	ft. tr.	....	....	....	ft. tr.	trace	Na_2O	.82
								Water	1.08
H_2O below 105° C.	.40	....	....	....	....	.40	....	Moisture .	2.27
H_2O 105-280° C ...	.17	....	4.29	....	....	.17	4.96 ign.		
H_2O above 280°C..	....	....		....	....	4.12			
Fl	....	....	....	....	....	none	....		
						99.86	98.76		101.62

---

[a] 4.94 per cent oxygen used for complete oxidation instead of 5.27 needed for all V as V_2O_3 and Fe as FeO.

[b] Equivalent to 23.59 per cent V_2O_3.

From the column of means of my own analyses the following ratios are obtainable:

SiO_2	.753
V_2O_3	.159
Al_2O_3	.113
FeO	.022
MgO	.041
K_2O	.110
H_2O	.229

The entire absence of manganese and of calcium in my own and Genth's samples tends to confirm the suspicion that Roscoe's material was far from pure. It is to be remarked, however, that my figures for vanadium agree quite closely with his and differ widely from Genth's.

Discrepancies of this kind are not necessarily to be ascribed to faulty analyses. It is well enough known that in any one species of mica various molecules must sometimes be assumed to exist in different proportions, and the general formula for such a species can only be arrived at by comparison of a series of analyses of different varieties. Hence, in view of the lack of any simple ratios, the deduction of a definite and final formula from my data is not justifiable. Further analyses are needed of new and very pure material from other locations, even if these be not far removed from the source of the present material. Nevertheless, in the hands of an expert very unpromising data may often be made to afford positive indications, and that this is true in the present case the following discussion by Prof. F. W. Clarke clearly shows:

CHEMICAL CONSTITUTION OF ROSCOELITE, BY F. W. CLARKE.

The ratios given in the foregoing new analysis, used directly, lead to the following empirical formula for roscoelite:

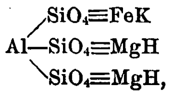
$$H_{458}K_{220}Fe_{22}Mg_{41}Al_{226}V_{318}Si_{753}O_{2724}.$$

Here H to K and Mg to Fe are as 2 to 1. Between O and Si, however, the ratio is not simple, and lies below the orthosilicate and above the trisilicate proportion. Since in many micas the groups SiO_4 and Si_3O_8 are replaceable, that suggestion may be followed out here; and then the formula reduces to

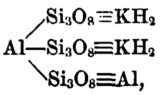
$$R'_{678}R''_{63}Al_{226}V_{318}(SiO_4)_{536}(Si_3O_8)_{71}.$$

From this expression, applying Clarke's mica theory, the mineral may be regarded as a molecular mixture of the three compounds

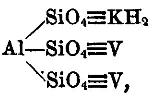
1.



2.



3.



in the ratio 21:22:159, or nearly 1:1:8. Upon reducing the analysis to 100 per cent, after throwing out the TiO_2 and the water lost below 280° as extraneous, we get the following comparison between the results found and the theoretical composition:

	Found.	Reduced.	Calculated.
SiO_2	45.17	45.88	45.52
TiO_2	.78	....	....
V_2O_3	24.01	24.39	24.64
Al_2O_3	11.54	11.73	11.62
MgO	1.64	1.66	1.72
FeO	1.60	1.63	1.55
K_2O	10.37	10.53	10.81
H_2O, 280°—	.57	....	....
H_2O, 280°+	4.12	4.18	4.14
	99.80	100.00	100.00

This comparison, based on the ratio 21:22:159, is as satisfactory as could be expected.

Of these component molecules the first represents the normal phlogopite type, the second is a trisilicate alkaline biotite, and the third, which forms 74.5 per cent of the whole mass, is a muscovite in which two-thirds of the aluminum have been replaced by vanadium—in short, a vanadium muscovite. Ordinary muscovite is $Al_3(SiO_4)_3KH_2$, and whether a corresponding $V_3(SiO_4)_3KH_2$ exists can be determined only by analyses of roscoelite from other localities, and so learning its range of variation. That vanadium may replace aluminum is shown by the fact that Piccini has prepared true vanadium alums. That roscoelite is essentially a vanadium muscovite seems to be fairly well established. As for the molecule $Al_2(Si_3O_8)_3K_2H_4$, its existence is indicated in some other micas, and in Simmler's "helvetan" it seems to be the dominant molecule.

NOTE.—A full discussion of the mode of occurrence of roscoelite, with historical data relative to the species, is given by Mr. H. W. Turner in the American Journal of Science, 4th series, Vol. VII, June, 1899, p. 455.

10. MARIPOSITE.

Samples of the peculiar micaceous mineral named mariposite by Silliman were collected at the Josephine mine, Bear Valley, Mariposa County, California, by H. W. Turner in 1894.[1] According to Turner it resembles talc optically, but chemically it appears to be one of the ill-defined substances known, for want of a more precise name, as pinite. Two varieties were analyzed—one white, the other green, but neither analysis leads to any definite formula. The data are as follows:

---

[1] Occurrence described by Turner in Am. Jour. Sci., 3d series, Vol. XLIX, 1895, p. 377.

	Green.	White.
SiO_2	55.35	56.79
TiO_2	.18	25.29
Al_2O_3	25.62	
Cr_2O_3	.18	none
Fe_2O_3	.63	1.59
FeO	.92	
CaO	.07	.07
MgO	3.25	3.29
K_2O	9.29	8.92
$(NaLi)_2O$	.12	[a] .17
H_2O	4.52	4.72
	100.13	100.84
Sp. gr	2.817,29°.5	2.787,28°.5

[a] Contains some K_2O.

No water was lost below 300°. The reaction for lithia was very strong. The color of the green mariposite is evidently due to chromium.

11. TWO SULPHATES FROM MONTANA.

Mr. W. H. Weed collected in the St. Paul mine, near Whitehall, Montana, a magnificent specimen of a compact soluble fibrous sulphate, supposed to be melanterite. It seemed to be a filling between fragments of broken rock. Outwardly it was white from dehydration, but at some depth the unaltered green mineral was to be found. This had the following composition:

Al_2O_3	4.34
FeO	9.04
NiO	.03
MnO	2.62
ZnO	1.06
CuO	.05
CaO	.09
MgO	3.07
Na_2O	.07?
SO_3	21.88
Cl, CO_2	none
H_2O	48.84
Insol	.16
	99.25

Of the water, 10 per cent escaped in twenty-four hours over sulphuric acid and only 0.4 per cent more in another like period, but a total of 14.4 per cent after ten days' uninterrupted exposure. The water thus lost is very slightly reabsorbed on exposure to air.

From calculations by Prof. F. W. Clarke the substance may be regarded as a mixture of alunogen or the halotrichite group, with salts of the melanterite group, the empirical formula being nearly

$$(Fe, Mn)_4(Zn, Mg)_2Al_2 (SO_4)_9 . 65 H_2O.$$

The outer white zone of the specimen contained only 39.62 per cent of water.

The second sulphate examined was a beautiful sky-blue stalactite from the Anaconda mine at Butte, collected by Mr. G. W. Tower. Its composition was as follows:

CuO	9.32
FeO	.18
MgO	.08
Al_2O_3	10.67
SO_3	35.05
P_2O_5	1.13
As_2O_5	.07
H_2O	43.44
Insol	.06
	100.00

The stalactite was of some size, and was most readily soluble in cold water, the solution giving a strong acid reaction. The calculated ratio is strongly acid, showing either a mixture of highly acid salts or of normal salts with free acids.

ON THE CHLORONITRIDES OF PHOSPHORUS AND THE METAPHOSPHIMIC ACIDS.

By H. N. STOKES

I. ON TRI- AND TETRAPHOSPHONITRILIC CHLORIDES.[1]

"Chlorophosphuret of nitrogen" (Chlorphosphorstickstoff) was discovered in 1832 by Liebig,[2] while attempting to prepare amides of phosphoric acid by acting on phosphorus pentachloride with gaseous ammonia and with ammonium chloride. Analysis[3] led to the formula $P_3N_2Cl_5$, and he observed that the compound could be distilled with steam or boiled with acids or alkalies without appreciable decomposition—properties unique in a phosphorus-chlorine compound.

Liebig did not pursue the subject much further, but at his suggestion Gladstone[4] in 1849 continued the study of the phosphorus-nitrogen compounds and, incidentally, of chloro-phosphuret of nitrogen. In his papers on this body[5] Gladstone detailed a method of preparation from phosphorus pentachloride and ammonium chloride, and pointed out some of its properties—among them its decomposition in aqueous ether or by alcoholic alkalies into hydrochloric acid and a nitrogenous compound, deutazophosphoric acid. Gladstone adopted Liebig's formula, $P_3N_2Cl_5$. The correctness of this was disputed on theoretical grounds by Laurent[6] and Gerhardt,[7] and the formula $PNCl_2$ suggested. At a later date Gladstone and Holmes[8] revised the work of the former and adopted Laurent and Gerhardt's formula, at the same time showing, on the basis of the vapor density, that it must be tripled: $P_3N_3Cl_6$.

---

[1] The following work was begun in the laboratory of the School of Pharmacy, Northwestern University, Chicago, and continued in the laboratory of the United States Geological Survey. I wish to express my sincere thanks to Prof. J. H. Long, of the former institution, for his kindness in permitting me to work in his laboratory.

[2] Liebig-Wöhler, Briefwechsel, Vol. I, p. 63; Ann. Chem. (Liebig), Vol. XI, 1834, p. 146.

[3] The part of Wöhler in this investigation seems to have consisted merely in making the analyses for Liebig.

[4] Quart. Jour. Chem. Soc. London, Vol. II, 1850, p. 121.

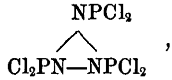
[5] Ibid., Vol. III, pp. 135, 353; Ann. Chem. (Liebig), Vol. LXXVI, p. 74; Vol. LXXVII, p. 314.

[6] Compt. rend., Vol. XXXI, 1850, p. 356, and Compt. rend. des Trav. de Chimie, 1850, p. 387.

[7] Compt. rend. des Trav. de Chimie, 1851, p. 30; Ann. Chim. Phys. [3], Vol. XVIII, p. 204, note.

[8] Jour. Chem. Soc. London, [2], Vol. II, 1864, p. 225.

Later, Wichelhaus[1] confirmed the results of Gladstone and Holmes, and suggested the structural formula



,

and A. W. Hofmann[2] and Couldridge[3] added some further observations.

By distilling under diminished pressure the reaction product of phosphorus pentachloride and ammonia gas Besson[4] obtained a substance of the composition $PNCl_2$, which he describes as "un corps solide donnent par sublimation des cristaux très réfringents, fusibles à 106°." The low melting point would indicate a body other than $P_3N_3Cl_6$ (melting point 114°), but as the latter is the chief volatile product formed under ordinary circumstances it may be regarded as an open question whether Besson's compound is identical with Liebig's.

Finally, White[5] and Gilpin[6] observed it as a secondary product of the action of phosphorus pentachloride on acid ammonium orthosulphobenzoate, doubtless originating in the action of the ammonia.

None of these investigations have thrown much light on the constitution of the chlorophosphuret or on its relation to other phosphorus compounds.

My attention being called to this substance while engaged in studying the amides of phosphoric acid, I have prepared it in large quantity with a view to further investigation. Although the experiments have not progressed far enough to establish any definite constitutional formula, they show that the chlorophosphuret is by no means as intractable as has been supposed, and that it is one of an homologous series of compounds having the general formula $(PNCl_2)_x$, which are the chlorides of an homologous series of acids $(PNO_2H_2)_x$, the metaphosphimic acids. From the reaction product of phosphorus pentachloride and ammonium chloride I have thus far isolated the body $(PNCl_2)_4$, which almost equals $(PNCl_2)_3$ in stability, and which yields, on saponification, an acid $(PNO_2H_2)_4$, also an extremely stable substance. A further product of the reaction is a stable, oily chloride $(PNCl_2)_x$ of high, but as yet unknown, molecular weight. I have also obtained from Liebig's chlorophosphuret the corresponding acid $(PNO_2H_2)_3$, an intermediate chlorhydrine $P_3N_3Cl_4O_2H_2$, and a chloramide $P_3N_3Cl_4(NH_2)_2$. The object of the present paper is mainly to describe the preparation and properties of the chlorides, the consideration of the acids being deferred to a later occasion.

Nomenclature.—In view of the large number of phosphorus-nitrogen compounds actually known or theoretically possible, it is desirable to have a more definite nomenclature than has thus far been used. I

---

[1] Ber. Deutsch. chem. Gesell., Berlin, Vol. III, 1870, p. 163.

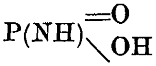
[2] Ibid. Vol. XVII, 1884, p. 1910.

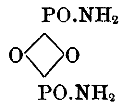
[3] Jour. Chem. Soc. London, Vol. LIII, 1888, p. 398.

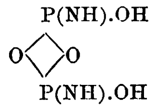
[4] Compt. rend., Vol. CXIV, 1892, pp. 1264, 1480.

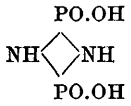
[5] Dissertation, Baltimore, 1891, p. 13.

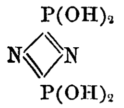
[6] Dissertation, Baltimore, 1892, pp. 7, 16.

have proposed[1] to reserve the name amido-orthophosphoric acid for the ortho acid in which one hydroxyl is replaced by the amido group, and to call the isomeric form $P(NH)(OH)_3$ orthophosphimic acid. By analogy an acid  $P(NH)\begin{smallmatrix}=O\\ \diagdown OH\end{smallmatrix}$ might be named metaphosphimic acid. Corresponding to the polymeric metaphosphoric acids we may imagine an homologous series of metaphosphimic acids, but for each of these several forms would be possible, according as the polymerization is effected by means of oxygen or of nitrogen atoms, assuming them to be otherwise built on the same general type. For example, an acid of the formula $P_2N_2O_4H_4$, with cyclic structure, might have any of the following constitutional formulas, omitting mixed forms:


(a)
Dimetaphosphoryl amide.


(b)
——


(c)
Dimetaphosphimic acid.


(d)
Diphosphonitrilic acid.

(a) and (b) represent the amide of a dimetaphosphoric acid with its desmotropic form; (c) and (d) represent the two forms of an acid isomeric with the former, but not directly derivable from a dimetaphosphoric acid. In the former class, phosphorus is united by means of oxygen; in the latter, by nitrogen. (b) and (c) are polymers of (PO) (NH) (OH) while (d) is a polymer of an acid $N \equiv P(OH)_2$, which we may call phosphonitrilic acid. Acids of the type (c) I call x-metaphosphimic acids, and those of the type (d), x-phosphonitrilic acids.[2]

In the chlorides $P_3N_3Cl_6$ and $P_4N_4Cl_8$, phosphorus must be united by means of nitrogen[3] (in the absence of oxygen); hence also in all probability in the acids derived from them. The direct replacement of chlorine by hydroxyl would result in phosphonitrilic acids, but as the type (c) is equally plausible, in the absence of definite experimental grounds, I call them, provisionally, metaphosphimic acids. For the chlorides themselves, instead of the old term chlorophosphuret of nitrogen, which is no longer characteristic, the more definite names tri- and tetraphosphonitrilic chloride may be used.

EXPERIMENTAL PART.

Preparation of the chlorides.—The theoretical yield of triphosphonitrilic chloride is 55.5 per cent of the phosphorus pentachloride; in reality, it falls far below this, no matter what process may be employed, and at best is but a by-product. Gladstone[4] states the yield as

---

[1] Am. Chem. Jour., Vol. XVI, p. 124, note.

[2] x = mono-, di-, tri-, etc.

[3] Unless we assume P to be joined to P, and N to N, a view which is not supported by their general behavior.

[4] Quart. Jour. Chem. Soc. London, Vol. III, p. 135; Ann. Chem. (Liebig), Vol. LXXVI, p. 76.

about 6 per cent of the pentachloride (11 per cent of the theoretical), when 1 molecular weight is distilled with 8 molecular weights ammonium chloride. Couldridge[1] obtained by a similar method a maximum yield of 10 per cent of the pentachloride (18 per cent of the theoretical). As a large excess of ammonium chloride is used, much "phospham" is formed. A modification by Gladstone and Holmes,[2] consisting in acting on the pentachloride with mercuric chloramide, gave no better results.

I made numerous experiments in sealed tubes at 200°–260°, using sal ammoniac and pentachloride in theoretical proportions. In this case there is no formation of "phospham," but the yield of the desired body is not increased—in fact, seems to be even less than by distilling with an excess of ammonium chloride from an open retort. What results is a mixture of chloronitrides, largely crystalline, but of various degrees of solubility and stability toward water, of which but a very small portion is volatile with steam. A study of this mixture would, in all probability, lead to the discovery of other members of the series $(PNCl_2)_x$.

I finally adopted a slight modification of Gladstone's original method: A mixture (which need not be very intimate) of 1 part pentachloride and 2 parts dry ammonium chloride is rapidly heated in a tubulated retort (one-third filled) fitted to a receiver containing water, which is connected with one or two Woulff's bottles, with water, to condense the small portions carried over with the escaping hydrochloric acid. The water in the receiver should be gently agitated occasionally in order to break up the crust forming on the surface. When the decomposition is about half finished the heating is interrupted and the hard cake of phospham and sal ammoniac turned over with a rod inserted through the tubulure; this is necessary, as it is so poor a conductor that the bottom of the retort melts before the upper portions of the cake are affected. Heating must not be continued too long, because the subliming ammonium chloride acts on the chlorides condensed in the neck of the retort. After cooling, the substances condensed in the neck are removed by scraping and injecting hot water through the tubulure. The yield varies considerably, according to the quantity of mixture taken; the less the amount, the greater the yield. I have obtained as high as 11.5 per cent. Practically it is not desirable to push this too far, and I have obtained the most satisfactory results by distilling 200 grams of mixture at a time. The proportion of ammonium chloride should not be less than 2 parts; otherwise much pentachloride sublimes unchanged. The distillate, after washing with water, is by no means pure triphosphonitrilic chloride; it is a mixture of chlorides, of which about one-half is quite stable toward cold water, but decomposed on distilling with steam. During this operation nearly all the triphosphonitrilic chloride, $P_3N_3Cl_6$, is deposited as a hard crust in the con-

---

[1] Jour. Chem. Soc. London, Vol. LIII, p. 399.

[2] Ibid. [2], Vol. II, p. 227.

denser. Distillation is continued only as long as much substance passes over; during the later stages large needles—mainly the new chloride, $P_4N_4Cl_8$—slowly collect in the condenser. There remain in the flask, besides a strongly acid liquid, a little solid material, consisting partly of phospham, partly of the crystalline acid ammonium tetrametaphosphimate, $P_4N_4O_8H_6(NH_4)_2$, and a considerable amount of oil, which solidifies, on cooling, to a crystalline cake of the compound $P_4N_4Cl_8$, impregnated with an oil of the same empirical composition.

The distillate, consisting of triphosphonitrilic chloride, mixed with about 5 per cent of tetraphosphonitrilic chloride, is dried, and an approximate separation effected by systematic recrystallization from benzene. This solvent has proved the most satisfactory, because the chlorides, in benzene solution, are scarcely affected by water, and no care need be taken to exclude it completely; aqueous ether, on the contrary, acts with considerable ease. The triphosphonitrilic chloride is pure after three or four recrystallizations, the tetraphosphonitrilic chloride accumulating in the mother liquors, the residues from which are again subjected to distillation with steam, the substance remaining in the flask being added to the first residue.

Apart from its influence on the melting point, the presence of very small quantities of the new body in the triphosphonitrilic chloride is readily detected by dissolving in alcohol-free ether and agitating for several hours with a little water, the tetraphosphonitrilic chloride being indicated by the formation in the water of microscopic needles of the difficultly soluble tetrametaphosphimic acid.

The residue from the distillation with steam is sucked out, whereby most of the oily chloride runs through with the water, and may be collected. The substance is then dried, the tetraphosphonitrilic chloride extracted with benzene and purified by several recrystallizations from this solvent. The residue left by the benzene, treated with dilute ammonia, leaves amorphous substances, and gives up tetrametaphosphimic acid, which is thrown down, on acidifying, as its acid ammonium salt. It may be mentioned here that the affinity of this acid for ammonia is such that its acid salt remains undecomposed even in large excess of hot 10 per cent nitric acid.

The yield of pure chlorides (from 9 kilograms of phosphorus pentachloride) was $P_3N_3Cl_6$, 6.9 per cent of the pentachloride, $P_4N_4Cl_8$, 0.76 per cent of the pentachloride, of which 0.42 per cent was obtained from the residue and 0.34 per cent from the crude steam distillate; these are respectively 12.4 and 1.4 per cent of the theoretical. A further small amount of tetraphosphonitrilic chloride was decomposed during distillation and, in part, recovered as tetrametaphosphimic acid. The yield of oily chloride was not determined, but it was approximately 1 per cent of the pentachloride.

It is not easy to give a reason for the relatively much higher yield of the triple phosphonitrilic chloride. Doubtless more of the quadruple compound is formed than is actually obtained, which, because of its less volatility, fails to distill over before it is attacked by the ammonium chloride, and I have also mentioned the simultaneous formation of large quantities of chlorides, unacted on by cold, but decomposed by boiling water. Still, it seems that there is some cause leading to the predominant formation and greater stability of this body, perhaps analogous to that acting in the case of the aromatic hydrocarbons. The proof that $P_3N_3Cl_6$ is a cyclic compound has not been found, but the occurrence of the number 6 in each case (C_6 and P_3N_3) is possibly more than a mere coincidence. Tetraphosphonitrilic chloride is also possessed of great stability, but I have observed, in various connections, that its chlorine is less firmly held than in the triple compound. The reverse appears to be true of the derived acids, $P_4N_4O_8H_8$ being more stable than $P_3N_3O_6H_6$.

Analytical methods.—The analysis of these bodies presents no difficulty. The chlorides, which volatilize on heating, are gently warmed with dilute alcoholic soda or potash. In this solution chlorine is directly determined as silver chloride; phosphorus is determined after evaporating off the alcohol, either by fusing the residue with sodium carbonate or by boiling for one or two hours with strong sulphuric acid, either of which converts it wholly into phosphoric acid. Nitrogen is determined as ammonia after acidifying the saponification product with hydrochloric acid, evaporating the alcohol, and boiling the residue with strong sulphuric acid. Experiment showed that no ammonia is evolved during saponification. In the case of the acids and other nonvolatile derivatives, the alcoholic saponification is omitted and the substance decomposed either by boiling with concentrated sulphuric acid, or fusing with sodium carbonate, the precaution being taken in the latter case first to moisten the mixture in the crucible. Owing to the strong reducing action of the imido group at high temperatures, these substances can not be fused alone in platinum without risk to the crucible. This is true even of the salts, which should give pyro- or metaphosphates on ignition.

The chlorides.—As triphosphonitrilic chloride has been the object of previous investigation, and as I have begun several lines of investigation with the object of explaining its nature and relations, I state here only a few incidental observations.

This chloride, as was early observed, has great crystallizing power. The rhombic crystals have been measured by Miller[1] and by Groth.[2] When pure it tends to form large, thick prisms. I have obtained these (from benzene) as much as 8 centimeters long and 2 centimeters wide, their further growth being hindered only by the size of the flask. When impure, it tends to form rhombic or 6-sided plates. It fuses at 114° (corr.), while the quadruple chloride, $P_4N_4Cl_8$, fuses at 123.5° (corr.), but a

---

[1] Jour. Chem. Soc. London [2], Vol. II, p. 227.

[2] Ber. Deutsch chem. Gesell., Berlin, Vol. III, p. 166.

mixture of equal parts is liquid below 90°. The corrected boiling point is 256.5° at 760 millimeters pressure. Besides the solvents elsewhere mentioned (for some of which quantitative data are given below), warm glacial acetic acid dissolves it readily. On boiling this solution with zinc dust some phosphuretted hydrogen is evolved. Hot concentrated sulphuric acid dissolves it easily. On boiling, some is decomposed, but the greater part distills off unaltered. The rather pleasant aromatic odor of its vapor has long been known. Although this is by no means irritating, inhaling it in any considerable amount is likely to be followed in two or three hours by alarming difficulty in breathing, succeeded by persistent irritation of the air passages. This insidious property renders care necessary in working with it in large quantities or for extended periods, all the more as the nose is the best instrument for detecting it.

A vapor-density determination by Victor Meyer's method at 360° in dry hydrogen gave 12.35 (calculated 12.01). The volatilization is complete, but on long boiling in air a little solid substance is deposited. Ethyl bromide and sodium are without action on the ethereal solution. Brombenzene and sodium acts slowly on the ether or benzene solution, forming a mixture of brownish amorphous organic substances, in part soluble, in part insoluble in ether, in which only a portion of the chlorine is replaced. No smooth reaction could be obtained.

Zinc ethyl, as observed by Couldridge,[1] is without action at ordinary temperature. On heating together in a sealed tube a violent reaction occurs, accompanied by liberation of gas and carbonization. If the zinc ethyl be diluted with 2 volumes benzene, a mixture of complex addition products is formed on heating, which are left on evaporating as a no longer soluble white vitreous mass, containing zinc, phosphorus, nitrogen, chlorine, and ethyl. This is decomposed by caustic potash, which liberates a mixture of oily bases of a disagreeable, sweetish odor, which are for the greater part decomposed on distillation, and which dissolve in cold water, and are thrown out on warming. These are slowly decomposed, on heating with hydrochloric acid, into ammonia and what appear to be highly complex phosphinic acids, containing nitrogen. At 170° considerable quantities of combustible gases, and of mono-, di-, and triethyl phosphine are formed by the action of zinc ethyl, in addition to a small amount of a crystalline basic substance containing nitrogen, and showing much the same properties as the oily substances alluded to. The yield was very minute.

Action of water on triphosphonitrilic chloride.—By decomposing chlorophosphuret of nitrogen with aqueous ether,[2] or with alcoholic alkalies,[3] Gladstone obtained a substance which he named deutazophosphoric

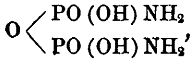
---

[1] Jour. Chem. Soc. London, Vol. LIII, p. 398.

[2] Quart. Jour. Chem. Soc. London, Vol. III, pp. 135, 354; Ann. Chem. (Liebig), Vol. LXXVI, p. 79; Vol. LXXVII, p. 315.

[3] Jour. Chem. Soc. London, [2], Vol. II, p. 231.

acid. He afterwards obtained this in larger quantity by treating phosphorus oxychloride with dry ammonia, and assigned to it the formula



$$O\begin{cases} PO\,(OH)\,NH_2 \\ PO\,(OH)\,NH_2 \end{cases}\!,$$

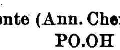
and the name pyrophosphodiamic acid. The formation of such an acid can only be due to a deep decomposition of the molecule.

Although unacted on by water alone or by anhydrous ether alone, I have found that a smooth decomposition is easily effected by dissolving the chlorophosphuret in alcohol-free ether, and shaking this solution a long time with water, whereby intimate contact is effected. The final products are hydrochloric acid and an acid in which the chlorine is wholly replaced by oxygen and hydrogen, without further change. I have named this substance, $P_3N_3O_6H_6$, *trimetaphosphimic acid.*[1] If the water contain bases or acetates in solution, the salts are directly obtained. As the acid will be described in a separate section, I mention here only that it is extremely soluble and totally devoid of crystallizing power, but forms some salts of characteristic crystalline form, and has a strong tendency to form double salts, one of these, $P_3N_3O_6H_3NaBa$, giving especially fine crystals.

As intermediate products, chlorhydrines have been observed. Theoretically, five of these are possible, one of which I have isolated, namely:

Triphosphonitrilic tetrachlorhydrine, $P_3N_3Cl_4O_2H_2$.—One part triphosphonitrilic chloride is dissolved in 10 parts alcohol-free ether, and the solution agitated with about one-third its volume of water for six to eight hours, best by means of a small turbine. The water then contains hydrochloric acid and trimetaphosphimic acid, and the ether contains the chlorhydrines and unchanged chloride. The ether is dried over calcium chloride, and the greater part distilled off in the water bath, the latter portions being removed at ordinary temperature by a current of dry air. The residue consists of unchanged chloride, the chlorhydrine in question, and small quantities of others. The greater part of the chloride is removed by a little benzene, and the residual chlorhydrine well washed with carbon disulphide. The yield depends somewhat on the time the water has acted, but as there is a continuous conversion of chloride into chlorhydrine, and of the latter into trimetaphosphimic acid, the amount present at any one time is not great. Under the above conditions it was about 10 per cent of the theoretical, fully one-half the chloride being recovered.

---

[1] According to Mente (Ann. Chem. (Liebig), Vol. CCXLVIII, pp. 241, 244), Gladstone's pyrophosphodiamic acid is really  $NH\langle\begin{smallmatrix} PO.OH \\ PO.OH \end{smallmatrix}\rangle NH$, *i. e.*, dimetaphosphimic acid, which has the same empirical composition as trimetaphosphimic acid. Mente did not obtain his acid from triphosphonitrilic chloride, but from phosphorus oxychloride, and it is not clear that it is really identical with Gladstone's acid from chlorophosphuret of nitrogen. The independent existence and stability of the tetra-acid affords a presumption that other members of the series can exist also.

Analysis gave:

	Calculated for $P_3N_3Cl_4O_2H_2$.	Found.		
		1.	2.	3.
P	29.94		30.00	30.04
N	13.54		13.74	
Cl	45.59	45.38	48.18	48.37

2. P : N : Cl = 3 : 3.03 : 4.20. 3. P : Cl = 3 : 4.23.

1, 2, and 3 represent different preparations, 1 having been further purified by recrystallizing from benzene.

The chlorhydrine forms a white sandy powder, consisting of well-defined microscopic prisms. It is very difficultly soluble in boiling benzene, and is insoluble in benzine and in carbon disulphide. With the latter it shows a peculiar behavior. Its refractive index is such that it nearly vanishes and apparently dissolves when brought into the disulphide; on decanting the liquid the moist powder shows beautiful iridescence. Alcohol dissolves it easily and in ether it is much more soluble than the original chloride, the presence of a trace of ether vapor causing it to liquefy instantly. Water dissolves it somewhat slowly, but abundantly, the solution containing hydrochloric acid and trimetaphosphimic acid, the latter being left on rapid evaporation on the water bath or in vacuo, as a transparent, easily soluble, gummy residue. From the aqueous solution of the chlorhydrine, salts of trimetaphosphimic acid were directly prepared and analyzed. The chlorhydrine is quite stable in the air at ordinary temperature,[1] but on heating at 100° it slowly increases in weight through absorption of moisture, undergoing decomposition with formation of ammonium chloride. It shows no definite melting point, but, on rapid heating, liquefies imperfectly, gives off hydrochloric acid, and leaves a mixture of amorphous substances of different degrees of solubility in water.

Other chlorhydrines, partly crystalline, appear to be formed simultaneously, but in relatively small amount, and their isolation is attended with difficulties. Whether the 2 chlorine atoms removed are associated with the same or with different phosphorus atoms remains to be determined.

Triphosphonitrilic chloramide, $P_3N_3Cl_4(NH_2)_2$.—The tendency to the formation of stable bodies in which one-third of the chlorine is substituted, observed in the case of the chlorhydrine, appears if triphosphonitrilic chloride be acted on in ether solution by ammonia. Gaseous ammonia may be used, but this is by no means necessary, aqueous ammonia producing the same result. If the chloride be dissolved in ether and

---

[1] On keeping for several months, a slight formation of ammonium salts was observed.

shaken a short time with 10 per cent ammonia, but one amide appears to be formed. As soon as a few drops of the ether solution leave, on evaporation, a residue completely soluble in hot water, indicating complete transformation of the chloride, it is dried over calcium chloride and allowed to evaporate spontaneously, whereby a substance crystallizing in needles is deposited. The product, which appeared homogeneous on microscopic examination, was directly analyzed.

	Calculated for $P_3N_3Cl_4(NH_2)_2$.	Found.
P	30.12	29.51
N	22.72	21.98
Cl	45.86	44.83

P:N:Cl=3:4.94:3.98.

The yield was 67 per cent of the theoretical, some of the chloride having been further decomposed and dissolved by the ammonia.

Triphosphonitrilic chloramide is quite soluble in ether, and less soluble in hot benzene, from which it crystallizes in long tufts of delicate hairs. It is easily soluble in alcohol, and from the concentrated alcoholic solution it is precipitated by water. Its stability toward water is striking; cold water dissolves it slightly, and, on rapid evaporation, even on the water bath, much is deposited unaltered; it can even be recrystallized from hot water, though with much decomposition, in needles or short prisms. Its stability in aqueous solution is further indicated by the failure of silver nitrate to give a precipitate except on boiling. Aqueous ammonia has but little action in the cold. On heating its aqueous solution, ammonium chloride and a sirupy acid result. Cold dilute acids have no marked solvent action. It undergoes change gradually at ordinary temperature, and rapidly on heating, without fusing, ammonium chloride and an infusible white substance being the products in the latter case.

Couldridge,[1] by acting on fused triphosphonitrilic chloride with gaseous ammonia, obtained a substance which he regarded as phospham. Both Couldridge and A. W. Hofmann[2] express the opinion that phospham has the composition expressed by the formula $P_3N_3(NH)_3$. I regard this as too sweeping. Apart from the fact that its composition varies with the mode of preparation,[3] it is likely that the true phospham is a mixture of an homologous series of imides $(PN.NH)_x$, derivable from the homologous phosphonitrilic chlorides $(PNCl_2)_x$.

Tetraphosphonitrilic chloride, $P_4N_4Cl_8$.—The new chlorophosphuret of

---

[1] Jour. Chem. Soc. London, Vol. LIII, p. 398.

[2] Ber. Deutsch. chem. Gesell., Berlin, Vol. XVII, p. 1911.

[3] Salzmann: Ber. Deutsch. chem. Gesell., Berlin, Vol. VII, p. 494.

nitrogen, prepared as above described, gave the following results on analysis:

	Calculated for $P_4N_4Cl_8$.	Found.	
		1.	2.
P	26.77	26.89	27.00
N	12.11	12.35	12.36
Cl	61.12	61.17	61.28

1. P:N:Cl=1:1.01:1.99. 2. P:N:Cl=1:1.01:1.99.
1 and 2 represent different preparations.

The vapor density, determined by Victor Meyer's method, in dry hydrogen at 360°, was:

	Calculated for $P_4N_4Cl_8$.	Found.
Density	16.03	16.20

I am indebted to Mr. B. H. Hite, of the Johns Hopkins University, for a series of determinations of the molecular weight by the ebullioscopic method. The following is his statement of the results:

Solvent: Benzene. Molecular elevation, 26.7.

Substance $(PNCl_2)_x$.

Grams solvent.	Grams substance.	Concentration.	Elevation (degrees).	Molecular weight found.	Percentage variation from 464.
37.618	1.1620	3.09	0.177	466	+0.4
37.618	1.4820	3.94	.227	463	— .2
37.987	1.1107	2.92	.167	467	+ .7

These results agree well with the quadruple formula.

The following table gives some of the constants compared with those of $P_3N_3Cl_6$.

	$P_3N_3Cl_6$.	$P_4N_4Cl_8$.
Specific gravity	a 1.98	b 2.18
Melting point (corrected)	114°	123.5°
Boiling point (760 mm. pressure; thermometer wholly in vapor), degrees	256.5	328.5
100 parts ether at 20° dissolve	46.5	12.3
100 parts benzene at 20° dissolve	57.4	20.9

a Gladstone. b At $\frac{24°}{24°}$

Tetraphosphonitrilic chloride forms colorless, brittle prisms, not easily wet by water, and therefore having a strong tendency to float. Superficially, these are not always to be distinguished from those of triphosphonitrilic chloride, but in a general way it may be said that they tend to be much smaller, and are to be measured by millimeters rather than centimeters, and that they tend to vary toward an acicular rather than a tabular form. In alcohol and in benzene it is much less soluble than $P_3N_3Cl_6$. Hot concentrated sulphuric acid dissolves it, and, on boiling, much hydrochloric acid is evolved, but some of the substance sublimes out unchanged. It may be recrystallized from glacial acetic acid; on boiling this solution with zinc dust a little hydrogen phosphide is given off, and the solution contains ammonia. It is noticeably volatile at its fusing point, its vapor having an odor suggesting, but perceptibly differing from, that of triphosphonitrilic chloride, and less aromatic. The fused substance solidifies to a mass of nearly parallel needles, while triphosphonitrilic chloride gives transparent plates. As mentioned above, its volatility with steam is comparatively slight. If boiled for some time in contact with air, a minute amount of substance is formed, which swells enormously to a clear gelatinous mass in benzene. Alcohol converts it slowly into an oily ether, which aqueous ammonia, on warming, saponifies to tetrametaphosphimic acid.

Action of water on tetraphosphonitrilic chloride.—In its chemical behavior it resembles triphosphonitrilic chloride. It is scarcely acted on by boiling water, yet on prolonged boiling a minute amount of tetrametaphosphimic acid is formed; aqueous fixed alkalies are without perceptible action, while alcoholic alkalies decompose it easily, but the product is mainly something else than tetrametaphosphimic acid.

A smooth decomposition is effected by dissolving in ether and shaking protractedly with water. The first products of this action consist of chlorhydrines, which remain dissolved in the ether, are crystalline, and readily soluble in cold water, from which solution tetrametaphosphimic acid is rapidly deposited in the form of thick needles; the same acid is the final product of the action of water on the ether solution. The action of water proceeds rather more rapidly than in case of triphosphonitrilic chloride, but many days are required for complete decomposition. The small amount of material at present in my possession made it unadvisable to attempt to isolate any of the chlorhydrines, of which seven are theoretically possible.

Tetrametaphosphimic acid, $P_4N_4O_8H_8 + 2H_2O$, will be described in a separate section. It may be remarked here preliminarily that it has highly characteristic properties, is highly crystalline, very difficultly soluble in cold water, and much less soluble in dilute acids; that it readily decomposes soluble chlorides, nitrates, and sulphates, and gives three series of salts, in which, respectively, one-fourth, one half, and all the hydrogen is replaced by metal; many of these show characteristic forms. The free acid far surpasses the metaphosphoric acids in stability, and may be boiled for hours with nitric acid or aqua regia without much decomposition.

Tetraphosphonitrilic chloride is readily extracted from its ethereal solution by aqueous ammonia, the ammoniacal solution giving tetrametaphosphimic acid on warming with hydrochloric acid. No clear evidence of the formation of chloramides has yet been observed.

Oily phosphonitrilic chloride.—This substance, obtained from the residues as above stated, is possibly a mixture. It is scarcely volatile without decomposition, not volatile with steam, and not acted on by water, except in ethereal solution, when a moderately soluble phosphimic acid is slowly formed, which crystallizes in needles, and decomposes on warming with water into tetrametaphosphimic acid and ammonium phosphate. The analysis gave:

	Calculated for $(PNCl_2)_x$.	Found.
P	26.77	26.73
N	12.11	12.09
Cl	61.12	61.89

P : N : Cl = 1 : 1 : 2.03.

2. ON TRIMETAPHOSPHIMIC ACID AND ITS DECOMPOSITION PRODUCTS.

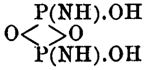
In the preceding section of this paper I mentioned, by way of preliminary notice, that Liebig's chloronitride, $P_3N_3Cl_6$, by appropriate treatment gives an acid, $P_3N_3O_6H_6$, to which I gave the name trimetaphosphimic acid. The object of the present section is to describe in detail the properties and decomposition products of this, the third member of the metaphosphimic-acid series.

In the preliminary notice a metaphosphimic acid was defined as a metaphosphoric acid $(PO_3H)_n$, in which one-third of the oxygen is replaced by an equivalent of imide groups, NH, i. e., $(PNO_2H_2)_n$. It was further pointed out that for each acid of this formula, with the exception of the simplest, at least four forms are theoretically possible, two of which are direct substitution products of the corresponding metaphosphoric acid, containing a nucleus consisting of phosphorus atoms united by oxygen, the other two belonging to a different type, in which the phosphorus atoms are united by nitrogen. This was illustrated by the acid, $P_2N_2O_6H_6$, none of the forms of which, it is true, are as yet known with certainty:

$$O\left<\begin{matrix}PO.NH_2\\ PO.NH_2\end{matrix}\right>O$$

(*a*)

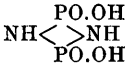
Dimetaphosphoryl amide.



$$O\left<\begin{matrix}P(NH).OH\\ P(NH).OH\end{matrix}\right>O$$

(*b*)

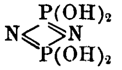
———



$$NH\left<\begin{matrix}PO.OH\\ PO.OH\end{matrix}\right>NH$$

(*c*)

Dimetaphosphimic acid.

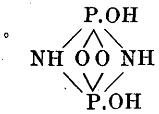


$$N\left<\begin{matrix}P(OH)_2\\ P(OH)_2\end{matrix}\right>N$$

(*d*)

Diphosphonitrilic acid.

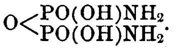
A fifth form might be added:



containing at the same time both the metaphosphoric and the metaphosphimic nucleus.

Schiff[1] described a body to which he gave the name phosphaminsæure, formed by acting on phosphorus pentoxide with dry ammonia, and which, according to his analyses, has the formula PNO_2H_2.[2] According to Gladstone and Holmes,[3] Schiff's acid is probably a mixture of pyrophosphodiamic and metaphosphoric acids. As Schiff failed to publish nitrogen determinations for his salts, it still remains a question whether a metaphosphimic acid can be produced in this way.

Gladstone, who was the first to devote much attention to phosphorus chloronitride, obtained from it by the action of aqueous ether and of alcoholic alkalies[4] an acid which he first called deutazophosphoric acid and later pyrophosphodiamic acid, and to which he gave the formula $P_2N_2O_5H_6$, regarding it as the diamide of pyrophosphoric acid.[5]



$$O\begin{matrix}\diagup PO(OH)NH_2 \\ \diagdown PO(OH)NH_2\end{matrix}.$$

While I am not prepared to deny positively the correctness of the formula deduced by Gladstone, and to assert that no such acid can be obtained in this way from phosphorus chloronitride, yet the facts as stated by him are capable of another interpretation, namely, that his acid is not the diamide of pyrophosphoric acid, but trimetaphosphimic acid.

It will be seen that

$$\underset{\text{Pyrophosphodiamate,}}{P_2N_2O_5H_4M'_2} = P_2N_2O_4H_2M'_2 + H_2O,$$

the latter being identical in empirical composition with $P_3N_3O_6H_3M'_3 + 1\frac{1}{2}H_2O$, i. e., a trimetaphosphimate with $1\frac{1}{2}H_2O$. Hence the latter, if containing this amount of water, might be mistaken for a pyrophosphodiamate. The only salts made by Gladstone directly from the chloride, $P_3N_3Cl_6$, were the silver and barium salts; the others were made from a supposed pyrophosphodiamate obtained from phosphorus oxychloride and ammonia, and there is no proof in Gladstone's papers of the identity of the acids from both sources. His figures for the

---

[1] Ann. Chem. (Liebig), Vol. CIII, 1887, p. 168.

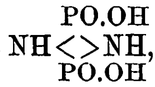
[2] I have elsewhere pointed out (Amer. Chem. Jour., Vol. XV, p. 198) that Schiff's acid has been erroneously described in some of the reference books as amidophosphoric acid, a body which I was the first to obtain.

[3] Jour. Chem. Soc. London, [2], Vol. II, pp. 229, 233, 235.

[4] Quart. Jour. Chem. Soc. London, Vol. III, pp. 135, 354; Ann. Chem. (Liebig), Vol. LXXVI, p. 79; Vol. LXXVII, p. 315; Jour. Chem. Soc. London, [2], Vol. II, p. 231.

[5] Jour. Chem. Soc. London, [2], Vol. VI, p. 69.

barium salt were, as he admits, not satisfactory, while the analyses of the silver salt were made with a crude preparation, for the purity of which there is no guaranty. I have myself found that barium trimetaphosphimate varies considerably in composition, contains water, and is hygroscopic. Sodium trimetaphosphimate is the only well-defined substance I have been able to obtain by decomposing the chloronitride by alcoholic soda, and the salt is so characteristic as hardly to be mistaken. It seems quite possible, therefore, that Gladstone actually had crude trimetaphosphimic acid in hand and failed to recognize its true nature only because of the unfortunate selection of salts which are amorphous, hydrated, and difficult to obtain pure.

In a paper of much later date Mente[1] described several acids obtained by the successive action of ammonium carbamate and water on phosphorus oxychloride. Among them is one to which he gave the name diimidodiphosphoric acid and the formula  $\mathrm{NH}<\genfrac{}{}{0pt}{}{\mathrm{PO.OH}}{\mathrm{PO.OH}}>\mathrm{NH}$, and which he regards as identical with Gladstone's pyrophosphodiamic acid. If Mente's formula is correct, it is the second or dimetaphosphimic acid. I have been unable to repeat Mente's work, and his data are too meager to admit of a positive conclusion, either as to its molecular weight or even its empirical composition, but it appears not to be identical with trimetaphosphimic acid.

Constitution of trimetaphosphimic acid.—Although trimetaphosphimic acid is an uncrystallizable and unstable body, it forms stable salts, several of which crystallize in characteristic forms. Three atoms of hydrogen are replaceable by alkali metals, while silver is able to replace either 3 or 6. The following are the most noteworthy:

$P_3N_3O_6H_3Na_3+4H_2O$—Rhombic prisms.
$P_3N_3O_6H_3Na_3+H_2O$—Slender prisms.
$P_3N_3O_6H_3(NH_4)_3+H_2O$—Scales.
$P_3N_3O_6H_3NaBa+1\frac{1}{2}H_2O$—Rhombohedra.
$P_3N_3O_6H_3Ag_3$—Monoclinic prisms.
$PN_3O_6Ag_6$—Two forms, white and red.

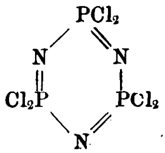
The first, third, and fifth serve to identify the acid. The tertiary silver salt, being anhydrous and easily obtained pure, establishes its empirical formula. Those salts which contain water of crystallization do not lose it completely at any temperature short of decomposition, leaving open the question whether the acid may not have the formula $P_3N_3O_7H_8$.

The constitution of trimetaphosphimic acid depends on that of the chloronitride $P_3N_3Cl_6$. The structural formula of the latter has not yet been definitely established, but the following data are available. It is reasonably certain that in the chloronitride phosphorus atoms are united by nitrogen atoms. Its formation from phosphorus pentachlo-

---

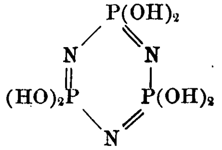
[1] Ann. Chem. (Liebig), Vol. CCXLVII, 1888, pp. 239, 244.

ride and ammonia is best explained on this assumption, as is its decomposition into orthophosphoric acid and ammonia. If phosphorus were united to phosphorus and nitrogen to nitrogen, the formation of reducing phosphoric acids or of hydrazine might be expected. Neither is it likely that chlorine is united to nitrogen, for in this case hydroxylamine might be expected to result. Several structural formulas are possible which meet this requirement, the simplest being that in which the nucleus consists of a symmetrical ring of 3 phosphorus and 3 nitrogen atoms:



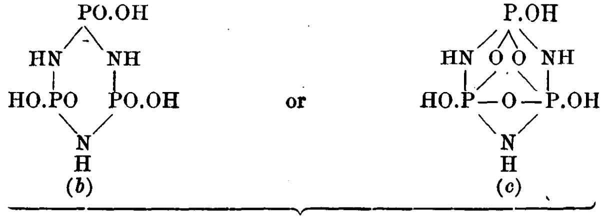
or a similar one with diagonal or "centric" union.

Direct replacement of chlorine by hydroxyl would then give



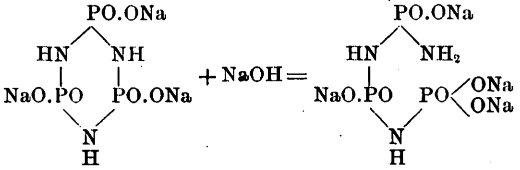
(a)
Triphosphonitrilic acid.

The labile nature of the hydrogen atoms in nitrogenous bodies, as observed in many organic compounds, makes it by no means improbable that an acid of this form may of itself, or under the influence of reagents, undergo transformation into the tautomeric form:



(b) (c)
Trimetaphosphimic acid.

An acid of the form (*a*) may be expected to give two sodium salts in which, respectively, 3 and 6 atoms of hydrogen are replaced. A salt with 6 atoms of sodium can not be produced, however, by any method which I have tried. The only salt besides the ordinary one with 3 atoms of sodium is one with 4 atoms, and this is formed in the presence of a large excess of caustic soda; it is very unstable and is reconverted into the 3-atom salt by repeated precipitation from aqueous solution by alcohol. It is not obvious why an acid of the form (*a*) should give such a salt. If we assume that (*b*) represents the correct formula, and that the acid is the symmetrical inner anhydrid or lactam of an open chain acid, we may regard this salt as being formed by addition, thus:



the latter being a salt of amido-diimidotriphosphoric acid.[1] Unfortunately I have been unable to prove this with certainty. A silver salt of the composition $P_3N_3O_7H_4Ag_4$ would render it extremely probable, as all silver salts of phosphorus nitrogen acids hitherto observed are free from crystal water. A salt with 4 atoms of silver can be obtained from the above 4-atom sodium salt, but it is very unstable, and its composition does not agree with sufficient sharpness with that of the cyclic or open chain form to establish either formula definitely.

I am therefore inclined to give preference to formula (*b*). It seems likely, however, that salts of triphosphonitrilic acid may also exist. The hexa-silver salt has been observed in two well-defined forms, as well as a third, possibly intermediate one. One of these is white, amorphous, and soluble in ammonium nitrate. It is easily converted into the other of identical composition, which is red, crystalline, and insoluble in the same reagent. The colorless salt probably contains silver united to oxygen only, while in the other one-half is united to nitrogen.

Decomposition products of trimetaphosphimic acid.—An aqueous solution of trimetaphosphimic acid, or of one of its salts acidified with one of the stronger mineral acids, decomposes slowly in the cold, rapidly on heating, the ultimate products being orthophosphoric acid and ammonia. If, however, the action be limited, there results a mixture of intermediate acids. The analysis of this mixture, which involved many experimental difficulties, proved the presence of the following:

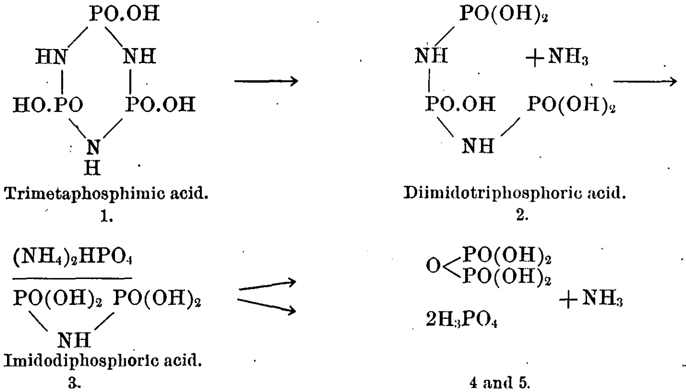
1. Unchanged trimetaphosphimic acid, $P_3N_3O_6H_6$.
2. Diimidotriphosphoric acid, $P_3N_2O_8H_7$.
3. Imidodiphosphoric acid,[2] $P_2NO_6H_5$.
4. Pyrophosphoric acid, $P_2O_7H_4$.
5. Orthophosphoric acid, PO_4H_3.

---

[1] The acids $PO(OH)_2.O.PO(OH)_2$ and $PO(OH)_2.O.PO(OH).O.PO(OH)_2$ being frequently designated as di- and triphosphoric acid, I call those in which the linking oxygen is replaced by imide, NH, imido-di- and diimidotriphosphoric acid.

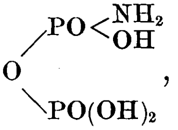
[2] This acid has the same composition and is probably identical with Gladstone's azophosphoric or pyrophosphamic acid. Jour. Chem. Soc. London [2], Vol. VI, p. 66, etc.

Assuming formula (*b*) for trimetaphosphimic acid, its decomposition would be thus represented:



The second acid is important as a connecting link, proving that trimetaphosphimic acid actually has the triple formula $(PNO_2H_2)_3$. Most remarkable is the formation of pyrophosphoric acid, which occurs directly from imidodiphosphoric acid. The facts are these: If sodium imidodiphosphate be weakly acidified with acetic acid and boiled from five to ten minutes, not more than 15 per cent is converted into pyrophosphoric acid and the remainder into orthophosphoric acid. Control experiments with sodium pyrophosphate showed that under the same conditions but a small portion is converted into orthophosphoric acid, 90 per cent of the pyrophosphate being recovered. The pyrophosphoric acid is therefore not an intermediate product, but the imidodiphosphate is converted for the greater part directly into orthophosphoric acid, and in a much less degree into pyrophosphoric acid.

The above formula of imidodiphosphoric acid containing the group P—NH—P, follows directly from that of trimetaphosphimic acid. In view of the ease with which the condensed phosphoric acids split up in aqueous solution into orthophosphoric acid, while the reverse never occurs, it is difficult to see how the action of water or acids on a body of the assumed formula could give pyrophosphoric acid. If we adopt Gladstone's formula[1]



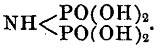
$$O\begin{cases} PO\begin{cases} NH_2 \\ OH \end{cases} \\ PO(OH)_2 \end{cases}$$

, we can explain the formation of pyrophosphoric acid, but must at the same time assume that somewhere in the series the group P—N—P has been converted into P—O—P, for in the chloronitride, $P_3N_3Cl_6$, phosphorus can be united only by nitrogen. If the acid were really the amide of pyrophosphoric acid, boiling with acetic acid would first convert it into pyrophosphoric acid which, as above shown, is fairly stable under the observed

---

[1] Jour. Chem. Soc. London, [2], Vol. VI, p. 70.

conditions, and should be found present to the extent of at least 90 per cent instead of only 15 per cent. On this ground, it seems to me, we must reject the amidopyrophosphoric formula, and regard the body as imidodiphosphoric acid,



$$NH{<}\begin{matrix}PO(OH)_2\\PO(OH)_2\end{matrix}.$$

This formula does not account for the pyrophosphoric acid. We may, perhaps, conceive that owing to the greater affinity of phosphorus for oxygen than for nitrogen, a group, $PO.(OH)_2$, is able to change places with a hydroxylic hydrogen atom:

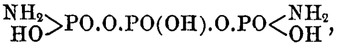
$$\begin{matrix}HO.PO.O{-}H\\|\\HN{-}PO(OH)_2\end{matrix} = \begin{matrix}HO.PO.O{-}PO(OH)_2\\|\\HN{-}H\end{matrix}$$

the latter, in common with other amido phosphoric acids, being unstable, and passing easily into pyrophosphoric acid. It may be noted that this transformation seems to be promoted by heat, apparently more pyrophosphoric acid being formed by decomposing trimetaphosphimic acid in hot than in cold solution.

The second acid of the series, diimidotriphosphoric acid, seems really to have the constitution,

$$PO(OH)_2.NH.PO(OH).NH.PO(OH)_2,$$

implied by the name. It forms an acid salt with 3, and a neutral salt with 5 atoms of silver, both of which are colorless. If it were a diamide of triphosphoric acid,



$$\begin{matrix}NH_2\\HO\end{matrix}{>}PO.O.PO(OH).O.PO{<}\begin{matrix}NH_2\\OH\end{matrix},$$

the penta-silver salt would have 2 atoms united to nitrogen, and such a salt, to judge from all phosphorus-nitrogen salts, where this is known to be the case, would be distinctly colored.

Still another intermediate acid is possible, preceding imidodiphosphoric acid, viz, amidoimidodiphosphoric acid,

$$\begin{matrix}NH_2\\HO\end{matrix}{>}PO.NH.PO(OH)_2.$$

I have been unable to detect this acid thus far, but the too high percentage of nitrogen invariably found in imperfectly purified imidodiphosphoric acid, may be due to the presence of small amounts of this body.

In giving formulas to these bodies, I wish to be understood as using them with full appreciation of their uncertainty. A much more exhaustive study is necessary before they can be regarded as established as firmly as those of many organic compounds. There are several directions in which such a study might be of value. Besides the question of tautomerism, the stereochemistry of nitrogen might be attacked with profit from this side. The analogy of nitrogen and phosphorus suggests the possibility of steric phenomena being shown by the latter also. The formula (*b*) suggested for trimetaphosphimic acid, for example, may imply a cis- and cis-trans-form depending on the position of the hydroxyls as well as of the imide hydrogen atoms; in short, quite a number of stereo-isomers may be conceived. I have thus far sought in vain for indications of the existence of such forms.

EXPERIMENTAL PART.

Analytical methods.—Salts of trimetaphosphimic acid and derived bodies are easily decomposed by fusion with sodium carbonate. As the process involves oxidation it is essential to keep the mass in a state of fusion for some time with access of air. Salts of silver of other easily reducible metals and those in which it is desired to determine alkali or nitrogen must be decomposed by strong sulphuric acid. The substance, contained in a platinum crucible, is first moistened with dilute, and then covered with 4 or 5 cubic centimeters strong sulphuric acid, and the covered crucible heated to fuming for an hour in a radiator, care being taken that the fumes do not escape. In determining alkali metal, the resulting phosphoric acid may be conveniently removed by the ferric chloride-acetate method. As the water of crystallization can not be completely expelled by heat without partial decomposition, it is best determined, together with the hydrogen of the salt proper, by combustion. This is conveniently carried out in a short combustion tube with a 10-centimeter spiral of oxidized copper gauze, the substance, contained in a boat, being covered with fused potassium bichromate. As nitrous fumes are formed in abundance, the usual precautions must be taken. In the following, where more than one determination is given, the numbers always refer to different preparations.

Preparation of trimetaphosphimic acid.—The sodium salt affords the starting material for all preparations of trimetaphosphimic acid. It may be obtained by saponifying triphosphonitrilic chloride by alcoholic soda, but with much loss, owing to the formation of ethers and other substances of unknown nature. The chloride, as observed by Liebig and by Gladstone, is practically unacted on either by water or anhydrous ether, but, as I have already pointed out elsewhere, its decomposition may readily be effected by shaking its ethereal solution protractedly with water, whereby intimate contact is secured. Decomposition by ether and water alone, however, results in much loss, as the liberated hydrochloric acid rapidly decomposes trimetaphosphimic acid. The following method is perfectly satisfactory and gives practically the theoretical yield.

Thirty grams of the chloride are dissolved in 150 cubic centimeters ether free from alcohol, and the solution gently agitated with a solution of 110 grams crystallized sodium acetate in 200 cubic centimeters water, the agitation being conveniently effected by slowly rotating with a small turbine. After about fifteen hours, well-formed crystals of sodium salt begin to appear, and about seventy or eighty hours are required for complete decomposition. This point is best observed by evaporating a few drops of the ether and taking up the residue with water, any undecomposed chloride remaining undissolved. It is best to continue the agitation for a short time longer in order to decompose the chlorhydrines, which are always formed as intermediate products. At the end of the operation nearly all the sodium salt has crystallized out, being almost insoluble in the strong salt solution; a further small amount can be recovered by mixing the solution with alcohol. After washing with 50 per cent alcohol, the salt is pure enough for most purposes, but may be redissolved in water and precipitated by gradual addition of alcohol.

The same salt also results by decomposing triphosphonitrilic tetrachlorhydrine with soda. It exists in two forms, apparently differing only in the amount of crystal water, the α-salt being formed at ordinary temperatures, the β-salt only above 80°.

α-Sodium trimetaphosphimate, $P_3N_3O_6H_3Na_3 + 4H_2O$.—The air-dried salt, prepared as above, gave the following figures:

	Calculated for $P_3N_3O_6H_3Na_3 + 4H_2O$.	Found.	
		1.	2.
P	24.79	24.74	24.82
N	11.22	11.26	....
Na	18.41	18.45	18.43
H	2.94	3.05	2.97

1. P:N:Na:H = 3:3.02:3.01:11.47.
2. P:Na:H = 3:2.97:11.

It loses weight slowly in vacuo, and 3 molecules of water are given off on long heating at 100°. After five hours at 100° the loss was:

	Calculated for $3H_2O$.	Found.
Loss	14.38	14.05

This is one of the most characteristic salts of trimetaphosphimic acid. It forms brittle orthorhombic prisms, usually about 1–2 millimeters across, of which fig. 1 represents the most common form.

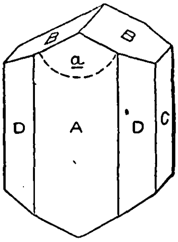


Fig. 1.

$A = \infty P \bar{\infty}$.
$B = P \breve{\infty}$.

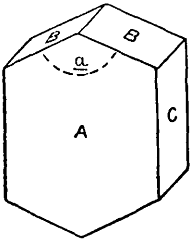


Fig. 2.

$C = \infty P \breve{\infty}$.
$D = \infty P$.

The angle *a*, measured roughly under the microscope, is about 130°. No other faces are ever observed, and D is frequently lacking, giving the form shown in fig. 2, which is often seen to be elongated in the direction of any one of the axes. They are especially well developed when slowly thrown down by acetic acid and alcohol from alkaline solution. When formed by rapid addition of alcohol in large excess they tend to elongation in the direction of the principal axis, being often acicular, often long, flat prisms with imperfectly developed ends.

At 20°, 100 parts water dissolve 18.3 parts; in hot water it is much more soluble, and from its hot solution it crystallizes but slowly; the larger crystals dissolve in hot water with a crepitating sound. The reaction toward litmus is neutral. On rapidly heating the dry salt it gives off water and later ammonia, and fuses to a clear glass. It is but slowly decomposed by boiling with water; after three hours heating traces of phosphoric and imidodiphosphoric acid were shown by magnesia mixture. Alkalies do not cause the evolution of any appreciable quantity of ammonia, even when hot; apparently, however, their very long-continued action is attended with decomposition.

β-Sodium trimetaphosphimate, $P_3N_3O_6H_3Na_3+H_2O$.—This form is deposited when the solution has a temperature of 80° or higher. It was obtained—

(1) By boiling the solid α-salt under a strong solution of sodium nitrite (analysis 1).

(2) By slowly adding boiling alcohol to a boiling solution of the α-salt (analysis 2).

(3) By pouring a boiling solution of the α-salt into a boiling 25 per cent solution of sodium acetate.

Doubtless other sodium salts would serve equally well, provided their hot solutions are sufficiently strong to throw it out.

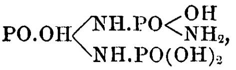
The salt lost nothing at 100° and gave:

	Calculated for $P_3N_3O_6H_3Na_3+H_2O$.	Found.	
		1.	2.
P	28.97	28.31	28.97
N	13.11	....	13.08
Na	21.51	21.86	21.19

1. P : Na = 3 : 3.12.
2. P : N : Na = 3 : 2.99 : 2.90.

This modification of the sodium salt forms needles, which, under the microscope, are seen to consist of flat prisms terminating in points; the terminal angles are of two kinds, one rather more, the other rather less than 90°; frequently both of these may be observed at opposite ends of the same crystal. Often, too, the crystals are cut off obliquely, owing to the development of but one terminal plane, in which case the terminal angles are respectively rather more and rather less than 45°. In general properties it resembles the α-salt, which it gives when reprecipitated from cold solution; whether the difference consists merely in the amount of crystal water, or whether it is a chemically distinct body can not be decided at present.

Tetra-sodium salt (*sodium amido-diimidotriphosphate*), $P_3N_3O_7H_4Na_4 + H_2O$.—As pointed out in the introduction, this is best regarded as the neutral salt of an open chain acid,



$$PO.OH\left\langle\begin{array}{l}NH.PO\left\langle\begin{array}{l}OH\\NH_2,\end{array}\right.\\NH.PO(OH)_2\end{array}\right.$$

of which trimetaphosphimic acid is the inner anhydride. As positive proof of this can not be adduced at present, I have preferred to place it among the trimetaphosphimates.

On dissolving sodium trimetaphosphimate in an excess of caustic soda, concentrating and allowing to cool, the salt crystallizes in long brittle needles (analysis 1). On adding alcohol to a caustic soda solution of sodium trimetaphosphimate (which need not have been heated), it is thrown out as a sirup which crystallizes, slowly if left to itself, at once on adding a fragment of previously prepared salt, to a mass of delicate colorless needles (analysis 2). These must be washed with alcohol containing a little caustic soda in solution, strongly pressed out and dried out of contact with carbon dioxide. It contains a large amount of crystal water, which it loses, with the exception of the last molecule, on drying in vacuo; the exact amount could not be determined. The substance dried in vacuo lost nothing at 100° and gave:

	Calculated for $P_3N_3O_7H_4Na_4 + H_2O$.	Found.	
		1.	2.
P	25.76	25.34	25.60
N	11.66	....	11.96
Na	25.51	25.60	25.76

1. P : Na = 3 : 4.08.
2. P : N : Na = 3 : 1.09 : 4.06.

This salt is very unstable, being decomposed even in the solid state by carbon dioxide. From its cold aqueous solution alcohol precipitates a mixture of unchanged salt and α-sodium trimetaphosphimate, a few reprecipitations converting it completely into the latter and free alkali. Its behavior toward silver nitrate is described under the silver trimetaphosphimates.

Salts with less than 3 or more than 4 atoms of sodium could not be obtained.

Potassium trimetaphosphimate, $P_3N_3O_6H_3K_3$.—A solution of this salt was obtained by decomposing the barium salt with potassium sulphate; on evaporation a transparent, glassy mass resulted. Alcohol precipitated it as a sirup, which on repeated treatment with absolute alcohol was converted into indistinct crystals. It was not further examined.

Ammonium trimetaphosphimate, $P_3N_3O_6H_3(NH_4)_3 + H_2O$.—A solution of this salt was obtained by double decomposition from the barium and silver salts and by neutralizing the free acid with ammonia. It loses ammonia on evaporation and leaves a transparent amorphous residue. Its solution, treated with alcohol, gives a deposit of large and beautiful pearly scales, which are characteristic. As these form even in the presence of a large excess of ammonia it appears that a body analogous to the tetra-sodium salt can not be thus formed.

The air-dried substance gave:

	Calculated for $P_3N_3O_6H_3(NH_4)_3 + H_2O$.	Found.
P	30.38	30.19
N	27.50	27.03

Magnesium trimetaphosphimate, $(P_3N_3O_6H_3)_2Mg_3$(?).—Strong solutions of sodium trimetaphosphimate and magnesium chloride give no precipitate, even on boiling. A solution of the magnesium salt may be obtained by double decomposition. From this alcohol throws down an amorphous flocculent precipitate and it leaves a soluble transparent residue on evaporating. On boiling the solution is slowly decomposed.

A mixture of a not too dilute solution of sodium salt with an excess of a strong solution of magnesium acetate remains clear, but is precipitated by acetic acid; on adding a little water this precipitate redissolves, reappears on heating, and redissolves on cooling. The nature of these precipitates has not been investigated. With more water the solution remains clear on short boiling, but on continued heating a crystalline precipitate forms which examination shows to consist of magnesium pyrophosphate and imidodiphosphate, orthophosphoric acid remaining in solution.

The fact that trimetaphosphimic acid is not precipitated in the cold by ammoniacal magnesia mixture affords a valuable means of separating it from some of its decomposition products.

Barium trimetaphosphimates.—Much time was spent in studying these salts, until it was found that they are devoid of characteristic properties, and that they are of exceedingly varying composition. Both neutral and basic salts exist, and there is a strong tendency to form double salts. The tendency to form complex salts is so strong that when barium nitrate, chloride, or acetate is used as the precipitant, the product is invariably contaminated by these. It has proved impossible to obtain a single satisfactory analysis, but the following data may be mentioned:

A salt obtained by decomposing an ethereal solution of phosphorus chloronitride with excess of baryta water consisted of a pulverulent, indistinctly crystalline substance for which the ratio P : Ba = 6 : 4.48 was found, while the calculated ratio for neutral salt is 6 : 3.

The potassium salt, precipitated by ammoniacal barium chloride, gave a preparation in which P : Ba = 6 : 3.68.

Triphosphonitrilic tetrachlorhydrine gave a clear solution with ammonia and barium chloride; on boiling a granular precipitate resulted (analysis 1).

Ethereal chloronitride and barium acetate solution gave a preparation from which the figures under analysis 2 were obtained.

A precipitate from the potassium salt and neutral barium chloride gave the results recorded under analysis 3.

	Calculated for $(P_3N_3O_6H_3)_2Ba_3 + 4H_2O$.	Calculated for $(P_3N_3O_6H_3)_2Ba_3 + 6H_2O$.	Found.		
			1.	2.	3.
P	19.89	19.16	19.91	20.86	20.46
Ba	43.96	42.35	41.75	41.91	43.79

1. P : Ba = 6 : 2.85. Dried at 100°.
2. P : Ba = 6 : 2.73. Dried in vacuo.
3. P : Ba = 6 : 2.91. Dried at 100°.

The neutral salt is slightly soluble in water and easily in a solution of ammonium chloride; on boiling the latter it is partially reprecipitated. It also dissolves readily in a strong solution of sodium chloride, and, on warming, the barium sodium salt is precipitated.

Barium sodium trimetaphosphimate, $P_3N_3O_6H_3NaBa + 1\frac{1}{2}(?)H_2O$.—This salt is almost insoluble in water, and forms a heavy, crystalline powder, which is seen under the microscope to consist of spherical aggregates with many rhombic facets, or occasionally of single minute crystals, apparently rhombohedra. The ordinary amorphous barium salt is invariably formed by precipitating any soluble trimetaphosphimate with a barium salt in the cold, but if the chloride or other salts of sodium be present in sufficient quantity, this passes into the crystalline barium sodium salt, at once on heating, or in the cold after a period varying from a few minutes to several hours. The latter also forms at once on precipitating in hot solutions. It was also obtained by decomposing an ethereal solution of chloronitride (1 molecular weight) with a solution of barium acetate (1 molecular weight) and sodium acetate (9 molecular weights). As is so common with salts of barium, this tends to "carry down" a considerable amount of the precipitant. A preparation made by the last method mentioned contained 0.49 per cent chlorine, corresponding to a contamination of 1.44 per cent barium chloride. After making correction for this the figures under analysis 3 were obtained, which approximate closely to the theoretical.[1] The excess of barium in analyses 1 and 2 is accounted for in the same manner. Possibly the difficulty is due to the presence of half dissociated barium ions (e. g.—BaCl) in the solution.

The substance lost but little at 100° and gave:

	Calculated for $P_3N_3O_6H_3NaBa+1\frac{1}{2}H_2O$.	Found.		
		1.	2.	3.
P	22.09	21.50	21.86	21.99
N	9.99	9.91	....	....
Na	5.47	....	5.56	5.53
Ba	32.56	35.67	34.22	32.86
H	1.43	....	....	1.32

1. P : N : Ba = 3 : 3.05 : 1.12.
2. P : Na : Ba = 3 : 1.03 : 1.06.
3. P : Na : Ba : H = 3 : 1.02 : 1.01 : 5.58.

Similar salts containing potassium or ammonium could not be obtained. A barium silver salt consisting of microscopic spherules was obtained by adding silver nitrate to a solution of the neutral barium salt in ammonium nitrate; a qualitative examination showed the presence of barium and silver.

Tri-silver trimetaphosphimate, $P_3N_3O_6Ag_3$.—This is the most important salt obtained, on account of its highly characteristic crystalline form, and because it is anhydrous and easily prepared pure, thereby establishing the empirical composition of trimetaphosphimic acid. As those salts which contain crystal water do not lose it completely at a temperature short of decompositon, we should otherwise be unable to decide between the formulas $P_3N_3O_6H_6$ and $P_3N_3O_7H_8$. For comparison the theoretical figures for a silver salt of both of these are given.

The salt may be prepared by precipitating a cold dilute solution (1–50) of the sodium salt by silver nitrate, when it is thrown down at once in the form of colorless elongated microscopic plates, terminated by an angle of 78° (analyses 1–4). Much better crystals are obtained if the solution of the sodium salt be acidified with several equivalents of nitric acid and the silver nitrate added slowly, finally in large excess. In this way the crystallization is made to extend over a considerable time, but the precipitation is never complete (analysis 5). Thus formed the crystals are usually very well developed, though seldom over 2 millimeters long, and consist of thick, monoclinic plates of the forms represented in figs. 3 and 4, the latter resulting when the crystallization extends

---

[1] Richards has pointed out the necessity of making a similar correction in determining sulphuric acid as barium sulphate. Zeitschr. anorg. Chem., Vol. VIII, p. 413.

over several hours. No other faces are ever observed, and the angle *a* (between the edges) measured under the microscope is very nearly 78°.

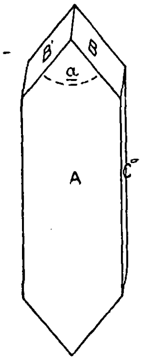


Fig. 3.

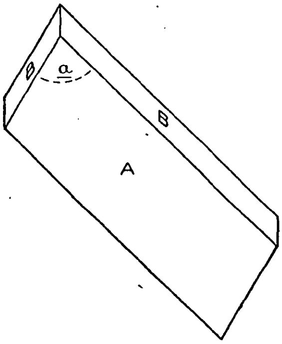


Fig. 4.

$A = \infty P \bar{\infty}$. $B = P \grave{\infty}$. $C = \infty P \grave{\infty}$.

The air-dried salt lost nothing at 100° and gave:

	Calculated for $P_3N_3O_6H_3Ag_3$.	Calculated for $P_3N_3O_7H_5Ag_3$.	Found.					
			1.	2.	3.	4.	5.	6.
P	16.68	16.16	16.50	16.70	16.74	16.64	....	15.71
N	7.55	7.31	....	7.53	7.67	....	7.72	....
Ag	58.04	56.20	57.75	57.90	57.77	57.93	57.80	60.08
H	0.54	0.87	....	0.62	....	....	....	....

1. P : Ag = 3 : 3.02.
2. P : N : Ag : H = 3 : 2.99 : 2.99 : 3.47.
3. P : N : Ag = 3 : 2.98 : 3.04.
4. P : Ag = 3 : 3.
5. N : Ag = 3 : 3.
6. P : Ag = 3 : 3.3

The salt is insoluble in water, easily soluble in ammonia, and somewhat difficultly in dilute nitric acid. It is not affected by light, but on boiling under water it becomes somewhat yellow, owing to the formation of a superficial coating of the 6-atom salt and the liberation of free acid, the decomposition products of which can be detected in the liquid. If free from silver nitrate, caustic soda does not discolor it, even on boiling. On heating it swells up, gives off ammonia, and fuses to a mass which contains metallic silver. In order to ascertain if it is actually precipitated in the anhydrous form, or if it contains water which is given off on standing, a freshly precipitated sample was washed with alcohol and ether, pressed out, and at once weighed; it lost nothing at 100°, indicating that even at the moment of formation it is anhydrous. Precipitation from boiling solution seems to have no influence on its composition; if, however, the solution of the sodium salt be added to a large excess of a solution of silver nitrate, the resulting precipitate, though white, is amorphous and contains much too high a percentage of silver (analysis 6), probably indicating an admixture of a more basic salt.

If tri-silver trimetaphosphimate be heated in a current of dry air at a temperature rising gradually from 200° to 260°, very nearly one-third of the nitrogen is given off as ammonia:

	Calculated for NH_3.	Found.
Loss	3.05	2.86

The product is no longer completely soluble in dilute acid. Alternate treatment with sodium chloride and ammonia extracts the silver and an acid which gives an amorphous precipitate with magnesium nitrate mixture. A considerable white residue remains in the form of pseudomorphs of the original substance, which is insoluble in ammonia, and soluble in hydrochloric acid only on boiling.

Salt with 4 atoms of silver, $P_3N_3O_6H_2Ag_4$ or $P_3N_3O_7H_4Ag_4$.—If silver nitrate be added slowly to a solution of the 4-atom sodium salt (sodium amidodiimidotriphosphate), each drop produces a white precipitate, which, on stirring, turns yellowish, in presence of an excess of sodium salt; when the latter is used up and an excess of silver nitrate has been added, it again becomes white. If, on the contrary, the sodium salt be added to the silver nitrate, each drop gives a yellow precipitate, turning white on stirring, and remaining so as long as an excess of silver is present. This white amorphous salt is decomposed by washing with pure water, turning yellow, while trimetaphosphimic acid goes into solution. The change may be represented thus:

$$3P_3N_3O_7H_4Ag_4 = 2P_3N_3O_7H_2Ag_6 + P_3N_3O_6H_6 + H_2O.$$

Silver nitrate prevents this change; the precipitate must therefore be washed with 1 per cent aqueous solution of silver nitrate, then with 1 per cent alcoholic solution of the same, and finally with ether. On pressing and drying, it then remains colorless. Preparations made in this manner gave the following results after drying at 100°, at which temperature the salt remains white:

	Calculated for $P_3N_3O_6H_2Ag_4$.	Calculated for $P_3N_3O_7H_4Ag_4$.	Found.		
			1.	2.	3.
P	14.01	13.63	13.32	13.70	13.29
Ag	64.92	63.22	65.79	64.71	65.89

1. P:Ag=3:4.26.
2. P:Ag=3:4.07.
3. P:Ag=3:4.28.

Unfortunately, the figures do not admit of a positive decision as to the formula, but the extreme instability of the salt, as compared with the others, may indicate an acid of different nature from trimetaphosphimic acid.

If this salt be allowed to stand for a day or two under pure water, it is converted into a mixture of tertiary silver trimetaphosphimate and a yellow crystalline salt with 6 atoms silver.

$$3P_3N_3O_7H_4Ag_4 = P_3N_3O_7H_2Ag_6 + 2P_3N_3O_6H_3Ag_3 + 2H_2O.$$

The same change occurs rapidly on boiling. Whatever may be the nature of the salt, this change is doubtless due to the tendency of the silver to wander to the nitrogen; silver nitrate, by opposing dissociation, prevents alteration.

Salts with 6 atoms of silver, $P_3N_3O_6Ag_6$ and perhaps $P_3N_3O_7H_2Ag_6$ also.—Equally unsatisfactory analytical results are given by the salts with 6 atoms of silver. The figures indicate the tendency to formation of salts with the ratio P:Ag=3:6, but the actual ratio only approximates to this, and it is impossible on the basis of the analyses alone to decide which of the formulas $P_3N_3O_6Ag_6$ and $P_3N_3O_7H_2Ag_6$ should be adopted in most cases. After many experiments I have been compelled to abandon for the present the attempt to obtain these substances in entirely satisfactory condition, and give the figures as actually obtained.[1]

If sodium trimetaphosphimate be added to an excess of an ammoniacal solution of silver nitrate,[2] or of a solution of silver oxide in ammonium nitrate,[3] a portion of the trimetaphosphimic acid is precipitated as a pure white voluminous and amorphous body, which, as analysis shows, contains approximately 6 atoms of silver. The precipitation is very incomplete, especially when ammoniacal silver nitrate is used, but in this case the substance contains very nearly 6 atoms of silver, while if the silver oxide solution be employed the percentage of silver is considerably too low.[4] Heated under the mother liquor it becomes yellowish, and becomes white again on cooling. After washing out (whereby it becomes yellowish) it dissolves quite readily in strong ammonium nitrate solution, but if boiled with less of the same, or less rapidly if heated with water alone, it is quickly converted into a heavy pulverulent substance. This, if highly magnified, is seen to consist of spherules or indistinct prisms, and has a color varying from orange to deep orange-red, usually the latter. This salt likewise contains 6 atoms of silver. The transformation is prevented by any silver nitrate in the solution, unless the effect of this is neutralized by a large quantity of ammonium nitrate.

---

[1] See p. 146 of this bulletin for an explanation of these difficulties.

[2] Prepared by adding ammonia to silver nitrate solution till the brown precipitate just redissolves.

[3] Three grams silver oxide, 10 grams ammonium nitrate, and 50 cubic centimeters water.

[4] The filtrate, on evaporation over sulphuric acid, deposits an imperfectly crystalline substance, at first white, then yellow, which is probably identical with the yellow salt referred to below.

If a solution of sodium trimetaphosphimate, to which exactly 3 molecular weights caustic soda, or an excess of ammonia, have been added, be dropped into an excess of dilute silver nitrate, a light sulphur-yellow, voluminous, and amorphous precipitate is formed, which may be washed with cold water without change, and does not change color on drying. This likewise contains 6 atoms of silver, and is insoluble in ammonium nitrate. If boiled with a trace of silver nitrate it remains unchanged; but if boiled with pure water it changes slowly, or if sodium trimetaphosphimate or ammonium nitrate be present, in a few moments, into the same orange-red, crystalline powder above mentioned.[1] On one occasion a deep red crystalline powder was obtained, but the conditions for its formation could not be determined. The following figures resulted from the analyses of these salts, in every case dried at 100°:

	Calculated for $P_3N_3O_7H_2Ag_6$.	Calculated for $P_3N_3O_6Ag_6$.
P	10.39	10.59
Ag	72.21	73.69

WHITE SALT (AMORPHOUS).

	Found.			Remarks.
	Lowest.	Highest.	Mean.	
P	10.54	11.28	10.92	4 preparations.
Ag	71.04	71.93	71.58	Mean ratio P : Ag = 3 : 5.66.

YELLOW SALT (AMORPHOUS AND CRYSTALLINE).

P	10.23	10.65	10.44	7 preparations.
Ag	71.55	73.13	72.53	Mean ratio P : Ag = 3 : 5.99.

ORANGE-RED SALT (CRYSTALLINE).

P	10.69	10.91	10.81	5 preparations.
Ag	72.38	72.91	72.61	Mean ratio P : Ag = 3 : 5.79.

RED SALT (CRYSTALLINE).

P	....	....	10.65	1 preparation.
Ag	....	....	73.18	Ratio P : Ag = 3 : 5.93.

---

[1] This is seen to crystallize from the liquid, so that temporary solution must take place.

Unsatisfactory as these figures are, they appear to indicate the existence of:

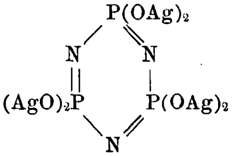
(1) A yellow salt, usually amorphous, occasionally crystalline, approximating in composition to $P_3N_3O_7H_2Ag_6$. As this is only formed in the cold from a trimetaphosphimate to which alkali has been added, it may be a salt of the supposed open-chain acid.

(2) A red crystalline salt of the formula $P_3N_3O_6Ag_6$.

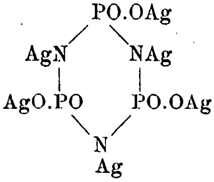
(3) A white amorphous salt of nearly the same composition.

The orange-red salt, invariably containing too little silver, and varying in depth of color, may be a mixture or an intermediate form.

As the white salt is formed only in the presence of silver ammonia compounds, and is quite soluble in ammonium nitrate, it is clearly different in nature from the others. Probably it contains silver united to oxygen only, while in the red salt one-half the metal is associated with nitrogen. We may regard them as salts of the two forms of trimetaphosphimic acid:



Hexa-silver triphosphonitrilate.



Hexa-silver trimetaphosphimate.

The action of silver nitrate in preventing the transformation may be ascribed to its opposing dissociation. No deep decomposition occurs during the transformation, as the ammoniacal solution is not precipitated by magnesia mixture, and sodium trimetaphosphimate is regenerated by treatment with sodium chloride and acetic acid.

Ferric trimetaphosphimates.—Gladstone[1] states that when pyrophosphodiamic acid is added to ferric sulphate, acidified with sulphuric acid, a clear solution results, which, on boiling, deposits white ferric pyrophosphamate, which is insoluble in acids but soluble in ammonia. The ferric trimetaphosphimates seem to vary considerably in composition and properties and present no characteristic features. The following points were noted: On adding ferric chloride to a moderately strong solution of sodium trimetaphosphimate an amorphous white precipitate forms which redissolves in an excess of the sodium salt, probably with formation of a ferric-sodium salt, but which becomes permanent on adding more ferric chloride. This is scarcely soluble in dilute hydrochloric acid, but readily soluble in ammonia with faint red color. Sodium hydroxide regenerates sodium salt. If, however, the solution of the sodium salt be dilute, no precipitate forms in the cold, even with an excess of ferric chloride, but on boiling, after acidifying,

---

[1] Quart Jour. Chem. Soc. London, Vol. III, p. 135; Jour. Chem. Soc., London, [2], Vol. II, p. 229; [2], Vol. IV, p. 290; [2], Vol. VI, p. 67.

a white amorphous precipitate is produced, which, like the above, is nearly insoluble in dilute acid and easily soluble in ammonia and consists of trimetaphosphimate mixed with decomposition products.

The solubility of these salts in ammonia, which they show in common with other ferric amidophosphates and pyrophosphates, may be ascribed to the formation of complex ions containing iron; in other words, of ferri-trimetaphosphimic acids, analogous to ferri-oxalic acid[1] and similar bodies.

Free trimetaphosphimic acid.—Silver trimetaphosphimate, decomposed under cold water by hydrogen sulphide, gives a solution from which, when fresh, the characteristic salts may be prepared, and from which much alcohol gradually throws out an amorphous sticky mass. The solution, on evaporation in vacuo, leaves a transparent, gummy residue from which alkalies evolve much ammonia, and which, after redissolving, gives a precipitate with magnesium mixture, indicating partial decomposition. The acid seems therefore to be incapable of crystallization.

In marked distinction from metaphosphoric acid, trimetaphosphimic acid does not coagulate albumen.

DECOMPOSITION PRODUCTS OF TRIMETAPHOSPHIMIC ACID.

Orthophosphoric acid and ammonia are the ultimate products of the action of acids on trimetaphosphimic acid, as well as of the decomposition of the free acid alone in aqueous solution when heated or kept for a long time. I have, however, been able to isolate three well-marked intermediate bodies, viz:

Diimidotriphosphoric acid, $P_3N_2O_8H_7$;
Imidodiphosphoric acid, $P_2NO_6H_5$;
Pyrophosphoric acid, $P_2O_7H_4$.

If sodium trimetaphosphimate solution (1–15) be boiled with 2–3 molecular weights nitric acid, the transformation into ammonia and orthophosphoric acid is complete in about ten minutes, but on interrupting the boiling after three to four minutes and cooling, the presence of these products can be detected; the same change occurs slowly in the cold, many days being required for complete decomposition. From this solution silver nitrate throws down first the silver salt of unchanged trimetaphosphimic acid, then the others in the order named, and finally silver phosphate, which is most easily soluble in nitric acid.

Although these products were first detected in this way, many experiments have convinced me that it is not a practical method of separation. The separation by fractional precipitation is not sharp; the properties of trimetaphosphimic and diimidotriphosphoric acids are so similar and the stability of the latter so slight that the results are very unsatisfactory. In the absence of trimetaphosphimic acid, however, diimidotriphosphoric acid is readily separated from the later decomposition

---

[1] See Rosenheim, Zeitschr. anorg, Chem., Vol, XI, p. 214, etc.

products. If, therefore, we have ascertained the time required for all the trimetaphosphimic acid to be decomposed under given conditions, while diimidotriphosphoric acid still remains, we can isolate the latter in a condition of purity. Since the latter is merely a transition product, the amount present at any time is small, and the actual yield is only about 10 per cent of the theoretical.

The following method leads to the desired result: 1 molecular weight α-sodium trimetaphosphimate is dissolved in 15 parts cold water, 3 molecular weights nitric acid (strength about 15 per cent) added, and the solution allowed to stand for seven days at the ordinary temperature. Enough ammonia is then added to give a faint odor and an excess of magnesium nitrate mixture[1] added, which throws down imidodiphosphoric, pyrophosphoric, and orthophosphoric acids, while diimidotriphosphoric acid remains wholly in solution. The liquid is removed as far as possible from the semigelatinous precipitate by suction and pressing out in the filter,[2] without washing. The filtrate is approximately neutralized with nitric acid and precipitated by silver nitrate, a considerable excess of which should be used, as penta-silver diimidotriphosphate is much less soluble in dilute silver nitrate than in water. The slightly washed silver salt still contains some imidodiphosphate, as the magnesium salt of this acid is not wholly insoluble. To remove this it is dissolved in the smallest possible volume and amount of ammonia and a little magnesium nitrate mixture added, which throws out the remaining imidodiphosphoric acid. The liquid is again filtered by suction, with but little washing, and the silver salt again precipitated by neutralizing with nitric acid, with addition of a little silver nitrate. The moist silver salt is treated with an excess of moderately strong solution of sodium chloride, acidified with acetic acid, the silver chloride filtered off with but little washing and an equal volume of alcohol added to the filtrate, which precipitates tri-sodium diimidotriphosphate. This is purified by dissolving in a little water and reprecipitating by alcohol.

The magnesium precipitate, containing imidodiphosphoric, orthophosphoric, and a little pyrophosphoric acids, is pressed out strongly under a screw press, pulverized, and dissolved in the least possible amount of dilute nitric acid.[3] Ammonia is added drop by drop till a slight permanent precipitate forms, and after filtering, silver nitrate added as long as the precipitate is white. Nearly all the orthophosphoric acid remains in solution, even after adding much silver nitrate; but, if too much be added, or if the amount of orthophosphoric acid be relatively great, the latter portions of the precipitate are yellow. Exact quantitative data can not be given, but in general it is necessary to use an amount of silver nitrate at least ten times the weight of the mixed magnesium salts. Silver pyrophosphate is partly precipitated toward the end, and partly

---

[1] Made by dissolving 100 grams crystallized magnesium nitrate and 35 grams ammonium nitrate in water, adding enough ammonia to give a faint odor and diluting to 1 liter.

[2] Schleicher and Schüll's hardened filters, No. 575, have proved indispensable in this operation.

[3] This is best done by rubbing up with water in a glass mortar, adding the acid gradually.

remains in solution. To get rid of it entirely, as well as of traces of orthophosphoric acid and of a substance of relatively high percentage of nitrogen, the tri-silver imidodiphosphate must be dissolved in ammonia, reprecipitated as magnesium salt, pressed out, and reconverted into the silver salt in the same manner. The mother liquor of the second silver precipitation, if neutralized with ammonia, gives a mixture of silver imidodiphosphate and pyrophosphate. This, after conversion into the sodium salt by sodium chloride, addition of a little caustic soda, and precipitating by alcohol, gives a sirup which is converted by vigorous rubbing into a pasty mass. This, by repeated solution and reprecipitation by alcohol, gives the characteristic flat prisms of sodium pyrophosphate. After conversion into the silver salt this proved to be free from nitrogen and an analysis gave:

	Calculated for $Ag_4P_2O_7$.	Found.
Ag	71.27	70.23

Tedious as the above method is, many experiments have failed to lead to the discovery of a better one, and have convinced me that it can not be abbreviated in the least without injuriously affecting the quality of the products.

DIIMIDOTRIPHOSPHORIC ACID, $P_3N_2O_8H_7$.

This acid forms two series of salts in which 3 and 5 atoms of hydrogen are replaced. The alkali salts with 3 atoms of metal are of neutral; those with 5 atoms of alkaline reaction. It seems impossible to replace the 2 remaining atoms, as is pointed out under the silver salts.

Tri-sodium diimidotriphosphate, $P_3N_2O_8H_4Na_3$.—The preparation of this salt is described above. It is easily soluble in water, this solution leaving on evaporation a mass of indistinct prisms. Precipitated from its aqueous solution by alcohol, it usually forms granules without evidence of crystalline form; but when very slowly precipitated it may be obtained as flat, very obtusely pointed prisms or rhombic plates, visible only when magnified 400 diameters. It contains no crystal water. The substance dried at 100° gave:

	Calculated for $P_3N_2O_8H_4Na_3$.	Found.
P	28.89	28.73
N	8.72	8.77
Na	21.45	20.69

$P : N : Na = 3 : 2.02 : 2.92$.

A penta-sodium salt probably exists, being obtained by decomposing the penta-silver salt with sodium chloride. It has alkaline reaction and is precipitated by alcohol as an uncrystallizable sirup.

The tri-sodium salt is not precipitated even in strong solution by magnesium chloride or magnesia mixture unless the latter contains much ammonia; in this case the resulting precipitate is easily soluble in ammonium salts, and hence is probably merely magnesium hydroxide. Barium chloride precipitates from a not too dilute solution microscopic spherules, which dissolve readily in a cold, strong solution of sodium chloride. On boiling this solution a crystalline precipitate is at once formed, consisting of microscopic rhombohedra (?) resembling sodium barium trimetaphosphimate and probably a double salt.

Silver salts.—Two of these were obtained, one having the formula $P_3N_2O_8H_4Ag_3$, and the other $P_3O_2O_8H_2Ag_5$. The tendency to formation of the latter is so strong that a solution of the tertiary sodium salt gives, with silver nitrate, a white amorphous precipitate, which, however, is mixed with some crystals of the former.

Tri-silver diimidotriphosphate, $P_3N_2O_8H_4Ag_3$.—This salt is very characteristic. It can be obtained pure only by precipitating an acidified solution of the tertiary sodium salt by an excess of silver nitrate. To a solution of the sodium salt in 30 parts water, 1 to 2 molecular weights nitric acid are added, and then silver nitrate gradually; as soon as a milkiness, due to the formation of the penta-salt, is observed, more acid is added, and then more silver nitrate, acid being added as often as necessary; the crystallization soon starts, but several times the theoretical amount of nitrate is required, and under no circumstances is the precipitation complete. Generally spherules with many rhombic facets are obtained, but with slow crystallization (from more dilute solutions) the forms shown in figs. 5 and 6 result.

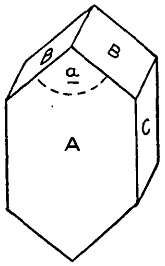


Fig. 5.

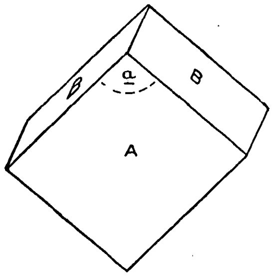


Fig. 6.

$A = \infty\ P\ \bar{\infty}$. $B = P\ \grave{\infty}$. $C = \infty\ P\ \grave{\infty}$.

The colorless crystals are monoclinic, and suggest those of tertiary silver trimetaphosphimate, but are shorter and thicker, and approach more nearly to the orthorhombic form. No other faces are ever seen. The angle *a* (between the edges), measured under the microscope, is very nearly 98°; the acute angle between the edges of B is, roughly speaking, 80°, so that when the form fig. 6 occurs, and this face is uppermost, it is apt to be mistaken under superficial observation for trimetaphosphimate (angle *a*, 78°).

The salt is practicably insoluble in water, easily in ammonia, and rather difficultly in dilute nitric acid. When pure it is not discolored by light or by caustic soda. It contains no crystal water. Analysis gave:

	Calculated for $P_3N_2O_8H_4Ag_3$.	Found.	
		1.	2.
P	16.14	16.39	16.29
N	4.87	4.76	....
Ag	56.10	55.94	56.36

1. P : N : Ag = 3 : 2.01 : 2.94. Direct from decomposed solution of trimetaphosphimic acid.
2. P : Ag = 3 : 2.99. From sodium salt.

Penta-silver diimidotriphosphate, $P_2N_2O_8H_2Ag_5$. — One molecular weight tertiary sodium salt is dissolved with addition of not less than 1½ nor more than 4 molecular weights ammonia, and added to an excess of a solution of silver nitrate; the pure white amorphous voluminous precipitate is washed, sucked out, and dried in vacuo. When fresh it is colorless, but on drying it assumes a yellowish tint, and after standing for some time it is partially converted into crystals, the nature of which was not determined. On boiling with water it also becomes yellowish, and in each case the change of color is accompanied by decomposition, as its ammoniacal solution is partially precipitated in amorphous form by magnesia mixture, an effect which is not observed in the perfectly fresh white salt. Warming with ammonium nitrate destroys the yellow color, which is consequently not due to silver phosphate. The fact that it remains white on boiling with ammonium nitrate serves to distinguish it from the trimetaphosphimates, the more basic silver salts of which, as pointed out, become orange-red under these conditions. The salt is very difficultly, yet perceptibly, soluble in water, and is reprecipitated by adding considerable silver nitrate; it is easily soluble in ammonia, and nitric acid converts it partly into the tertiary salt before dissolving it.

Dried at 100° it gave:

	Calculated for $P_3N_2O_8H_2A_5$.	Found.		
		1	2	3
P	11.77	12.05	11.96	11.75
N	3.55	3.66	3.65	....
Ag	68.23	68.96	68.92	69.24

1. P : N : Ag = 3 : 2.02 : 4.94.
2. P : N : Ag = 3 : 2.02 : 4.97.
3. P : Ag = 3 : 5.08.

Attempts to replace one or both of the remaining hydrogen atoms by silver proved unsuccessful. If the tertiary sodium salt be dissolved with 1–2 molecular weights caustic soda, or even with 5–6 molecular weights ammonia, and added to silver nitrate, the resulting precipitate is discolored by free silver oxide. On standing several days it becomes yellow, but its ammoniacal solution is now precipitated by magnesia mixture, indicating decomposition. The magnesia precipitate gave a silver salt resembling tertiary imidodiphosphate, but the exact nature of the decomposition was not investigated.

IMIDODIPHOSPHORIC ACID, $P_2NO_6H_5$.

This is probably the substance described by Gladstone under the name pyrophosphamic acid. It is moderately stable in cold, not too acid, solution, and hence occurs in large amount among the decomposition products of trimetaphosphimic acid.

Tri-sodium imidodiphosphate, obtained by decomposing the tertiary silver salt by sodium chloride, has alkaline reaction. Its solution, as well as that of the tetra sodium salt, is precipitated by alcohol as a sirup which can not be made to crystallize, and the aqueous solution of which dries to a transparent gummy mass. It is more soluble in dilute alcohol than sodium pyrophosphate.

The magnesium salt above described is amorphous, voluminous, and nearly, but not quite, insoluble in water, and somewhat more soluble in solutions of ammonium salts.

Tri-silver imidodiphosphate, $P_2NO_6H_2Ag_3$.—This is obtained as an amorphous, white precipitate, when the free acid, or a solution of a tertiary salt is precipitated by silver nitrate. Thus formed, it tends to collect in small lumps, a property which distinguishes it from any of the other silver salts referred to in this paper. When precipitated by acid from its ammoniacal solution it forms a powder that settles slowly. When slowly separating, or when precipitated from hot solutions, it forms semicrystalline granules, often united to crusts or dendritic forms. When formed in a moderately acid solution it usually shows a slight deficiency of silver (analyses 1–2), probably due to a trace of a more acid salt; but such a salt can not be obtained in pure form. Pure tertiary salt can be obtained by decomposing the crude salt with somewhat less than the required amount of sodium chloride, and reprecipitating. It is insoluble in water and is not affected by light.

Dried at 100° it gave:

	Calculated for $P_2NO_6H_2Ag_3$.	Found.				
		1.	2.	3.	4.	5.
P	12.47	13.19	12.75	12.34	12.60	12.19
N	2.82	3.13	3.14	2.86	2.96	2.92
Ag ...	65.03	63.70	63.87	65.21	65.06	66.46

1. P : N : Ag = 2 : 1.05 : 2.78.
2. P : N : Ag = 2 : 1.09 : 2.78.
3. P : N : Ag = 2 : 1.02 : 3.04.
4. P : N : Ag = 2 : 1.04 : 2.97.
5. P : N : Ag = 2 : 1.06 : 3.14.

Tetra-silver imidodiphosphate, $P_2NO_6HAg_4$.—This salt exists in a white and in a yellow form. The former is obtained by precipitating a solution of silver oxide in ammonium nitrate by the sodium salt. It forms a voluminous, flocculent precipitate, which remains white only in presence of its mother liquor; on washing out it undergoes partial transformation into the yellow form, the same change occurring temporarily on boiling under the mother liquor. It shows a slight deficiency of silver (analysis 4).

The yellow form is obtained as an amorphous, flocculent precipitate by adding an ammoniacal solution of an imidodiphosphate to an excess of silver nitrate (analyses 1–2), or as an imperfectly crystalline powder, by evaporating such an ammoniacal solution, containing an excess of silver, over sulphuric acid (analysis 3). From this it appears that the remaining hydrogen atom is not replaceable by metal. The difference between the white and yellow forms is perhaps due to tautomerism.

Dried at 100°, it gave:

	Calculated for $P_2NO_6HAg_4$.	Found.			
		1.	2.	3.	4.
P	10.27	10.17	10.07	....	10.80
N	2.32	2.28	2.45	....	....
Ag	71.39	72.19	72.35	71.01	69.72

1. P : N : Ag = 2 : 0.99 : 4.01.
2. P : N : Ag = 2 : 1.07 : 4.13.
3. P : Ag = 2 : 3.71.

Imidodiphosphoric acid is easily distinguished from diimidotriphosphoric acid by the insolubility of its magnesium salt, by the peculiar granular or lumpy appearance of its tertiary silver salt, by its sirupy tertiary sodium salt, and by its ammoniacal solution giving a yellow salt with silver nitrate, while the silver salt of the latter, found under the same conditions, is either white, or, when too much ammonia has been used, discolored by silver oxide.

Ferric imidodiphosphate.—No analysis of this was made. It is thrown down on boiling an acidified solution with a ferric salt as a white, amorphous precipitate, difficultly soluble in acids and easily soluble in ammonia.

Cupric imidodiphosphates.—Several of these appear to exist. The amorphous, light-blue precipitate formed by cupric sulphate in a solution of the sodium salt redissolves in an excess of the latter, is again reprecipitated by an excess of cupric salt, but under no circumstances completely. It dissolves in caustic potash to a violet solution. The soluble sodium double salt is partially precipitated on heating its aqueous solution, the precipitate redissolving on cooling. The precipitate with excess of cupric sulphate dissolves readily in cold acetic or sulphurous acid, and is temporarily reprecipitated on heating the solution, unless too dilute and too strongly acid, in which case some pyrophosphate crystallizes out on long heating. The same temporary precipitation occurs in a less degree on heating its solution in very dilute nitric acid.

The property of being precipitated from an acid solution on boiling is one which cupric imidodiphosphate shares with the pyrophosphate, and the same is observed with the magnesium salts, but with the difference that the pyrophosphates do not redissolve on cooling, while the imidodiphosphates redissolve either at once or in a short time. It is not possible to effect a complete separation of the two acids in this way, however, for if pyrophosphoric acid be present, more or less imidodiphosphate remains in the permanent precipitate, apparently because of the formation of complex salts containing both acids. The only method for separating the two acids when mixed in approximately equal proportions is to convert them into the sodium salts, and to precipitate repeatedly by alcohol, finally recrystallizing the pyrophosphate from water.

Decomposition of imidodiphosphoric acid.—When a soluble imidodiphosphate is boiled with acetic acid, it is converted for the most part into orthophosphoric acid, and to a much less extent into pyrophosphoric acid. The signficance of this fact is pointed out in the introduction to section 2 of this paper. A solution of the sodium salt (which analysis has proved to be free from pyrophosphate) in 30–50 parts water is weakly acidified with acetic acid, boiled seven to eight minutes, and cooled. If this solution be made alkaline with caustic soda, and alcohol added, an abundant crystallization of tertiary sodium phosphate is formed, which may be recognized by its crystalline form and by the usual reactions. In this the microscope shows a few crystals of sodium pyrophosphate. The latter acid may be isolated by making use of the fact that a solution of freshly precipitated magnesium pyrophosphate in excess of cold acetic acid is quantitatively precipitated on boiling, in a permanently insoluble form, while magnesium orthophosphate remains dissolved. The above weak acetic solution is mixed with magnesium acetate in excess, the precipitate dissolved by adding about one-fifth volume of strong acetic acid, and boiled a few minutes. The precipitated granular magnesium pyrophosphate is dissolved in nitric acid, in the manner described for the separation of the decomposition products of trimetaphosphimic acid, converted into silver salt and then into sodium salt. This, after several precipitations by alcohol, is recrystallized from water. A careful determination of the yield of pyrophosphoric acid in two experiments gave 13.5 and 16 per cent of the theoretical. For analysis the sodium salt was converted into silver pyrophosphate, which gave:

	Calculated for $Ag_4P_2O_7$.	Found.
P	10.24	10.35
Ag	71.27	70.74

DECOMPOSITION OF SODIUM TRIMETAPHOSPHIMATE BY ACETIC ACID.

As before pointed out, this salt is not decomposed by acetic acid in the cold, or on short heating. If, however, its solution is heated for two or three hours with 30 per cent acetic acid and magnesium acetate, under the conditions mentioned under the magnesium salt, a granular precipitate is obtained, consisting of a mixture or double salt of magnesium pyrophosphate and imidodiphosphate, which does not perceptibly redissolve on cooling, while the liquid contains much orthophosphoric acid. The sodium pyrophosphate, separated from this by the above method, showed the characteristic form. For analysis it was converted into the silver salt, and gave:

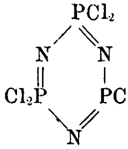
	Calculated for $Ag_4P_2O_7$.	Found.
P	10.24	10.43
Ag	71.27	70.33

3. ON TETRAMETAPHOSPHIMIC ACID.

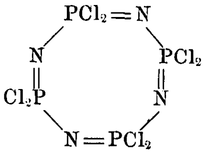
Trimetaphosphimic acid and its decomposition products have been described in the preceding pages. Some account will now be given of the next higher member of the series, *tetrametaphosphimic acid*, $P_4N_4O_8H_8$, which results from the decomposition by water of tetraphosphonitrilic chloride, $P_4N_4Cl_8$. The molecular weight of the chloride having been established with certainty, that of the acid follows directly. Although the free acid crystallizes with 2 molecules of water, the silver salts and the acid potassium and ammonium salts are anhydrous and conform to the above formula.

Notwithstanding the proximity of these two acids in the series, and the general similarity of the chloronitrides from which they are derived, they differ exceedingly, trimetaphosphimic acid being extremely soluble, uncrystallizable, undergoing rapid spontaneous decomposition, and yielding but two series of salts; while tetrametaphosphimic acid is very difficultly soluble, highly crystalline, permanent when dry, offers marked resistance to the action of acids, and forms three series of salts, $P_4N_4O_8H_6M'_2$, $P_4N_4O_8H_4M'_4$, and $P_4N_4O_8M'_8$. Those metals which form insoluble salts are precipitated from solutions of their chlorides or nitrates even by the free acid, but a very slight excess of either being required to make the precipitation complete. As is the case with trimetaphosphimic acid, the 8-atom silver salt exists in a white and a yellow modification, the former, however, being very unstable; these may be regarded as corresponding to the tautomeric forms $(PN(OH)_2)_4$ and $(PO.NH.OH)_4$. Under the action of stronger acids it is ultimately converted into orthophosphoric acid and ammonia, but its great stability, and the instability of the intermediate products, have rendered the isolation of the latter impossible.

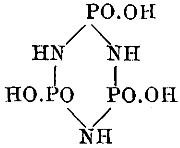
Experimental data for a discussion of the constitution of the acid are therefore almost wholly wanting. Presumably the phosphorus atoms in the nucleus P_4N_4 are united by nitrogen atoms, but whether they constitute a ring of 8 atoms can not be decided definitely in the absence of intermediate decomposition products. It is quite likely that the reason of the greater stability of the acid may be found in steric considerations, and in this connection it is interesting to observe that while $P_4N_4O_8H_8$ is much more stable than $P_3N_3O_6H_6$, the reverse is true of the chloronitrides, for while $P_4N_4Cl_8$ also resists the action of boiling water and can be distilled with steam, it is perceptibly easier to saponify than $P_3N_3Cl_6$. If we assume the formulas



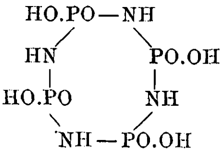
and



for the chloronitrides, and



and



for the acids, it is obvious that the nitrile configuration is more stable in a ring of 6 than in one of 8 atoms, while for the group —NH—PO(OH)—NH— the reverse is true.

EXPERIMENTAL PART.

Preparation of tetrametaphosphimic acid.—Tetraphosphonitrilic chloride can be saponified by alcoholic alkalies, but the yield of tetrametaphosphimic acid is poor, owing to the formation of ethers, which, however, can be decomposed by prolonged treatment. Satisfactory results are obtained by using an ethereal solution, which is agitated, in the manner described under trimetaphosphimic acid, with either water, ammonia, or a solution of ammonium acetate.

Decomposition by water.—As tetrametaphosphimic acid is not perceptibly attacked by cold hydrochloric acid, water may be used when it is desired to obtain the free acid directly. One part $P_4N_4Cl_8$ is dissolved in 15 volumes alcohol-free ether and gently agitated with 5 volumes water. Within half an hour needles of the free acid begin to separate from the aqueous portion, and after many hours the latter has become converted into a thick pasty mass of needles suspended in dilute hydrochloric acid. Chlorhydrines are formed as intermediate products, and these remain dissolved in the ether. It is not necessary to continue the agitation until they are completely decomposed; as soon as a few drops of the ether leave a residue wholly soluble in water, the ether is decanted and the aqueous portion filtered, the crystals being washed with 10 per cent hydrochloric acid or alcohol. The ethereal portion, containing the chlorhydrines, is evaporated cautiously. The chlorhydrines which remain as an oil from which crystals separate after complete removal of the ether, are dissolved in a little cold water and warmed, with addition of dilute hydrochloric acid, in which tetrametaphosphimic acid is much less soluble than in pure water. The separation of the acid is nearly complete after a few minutes. This portion is better crystallized than that obtained directly, but is otherwise the same. The acid may be recrystallized from hot water, but this is quite unnecessary. Yield, about theoretical.

Decomposition by ammonia.—The ethereal solution of the chloronitride is shaken for a short time with aqueous ammonia. This does not give chloramide as is the case with $P_3N_3Cl_6$, but produces at once neutral ammonium tetrametaphosphimate, $P_4N_4O_8H_4(NH_4)_4+4H_2O$, which is precipitated by adding alcohol and washed with dilute alcohol. The decomposition is complete in a few minutes.

Decomposition by ammonium acetate.—One part chloronitride, dissolved in 15 volumes ether, is agitated with a solution of 4 parts ammonium acetate in 8 parts water. After several hours crystals begin to separate. The final product is a mixture of acid ammonium salt with some neutral salt and some free acid, and is nearly insoluble in the strong salt solution. It is washed with alcohol, dissolved in dilute ammonia, and reprecipitated by alcohol. Yield, theoretical. Ammonium acetate is to be preferred to sodium acetate, as the sodium salt does not precipitate well with alcohol.

Chlorhydrines.—None of these were isolated. The oil left on distilling off the ether solidifies to plates as soon as the ether is completely removed. The crystalline substance is much more soluble in ether than the chloronitride, even momentary exposure to ether-vapor causing it to liquefy. It dissolves in cold water to a clear solution, from which, in a few minutes, or sooner on warming, tetrametaphosphimic acid is deposited. On one occasion the flask containing the chlorhydrines was placed in hot water and a current of dry air passed through. Some hydrochloric acid was given off, and on treatment with water incomplete solution occurred, a portion being converted into a sandy powder, which, under the microscope, was seen to consist of short, spindle-shaped crystals. This acid was insoluble in boiling water, and warm ammonia converted it without dissolving into an acicular ammonium salt, difficultly soluble in water and insoluble in an excess of ammonia; nitric acid dissolved this salt, which was precipitated by ammonia in a bulky amorphous form like precipitated alumina, which quickly changed to needles. This ammonium salt was very slowly attacked by hot concentrated sulphuric acid, and contained 27.96 per cent phosphorus and 13.28 per cent nitrogen (P : N=4 : 4.2). Lack of material prevented further study of this finely crystallized acid, of the nature of which I can form no conjecture.

Tetrametaphosphimic acid, $P_4N_4O_8H_8+2H_2O$.—The free acid may be prepared by the first method above described. It is not readily obtained pure by decomposing most of its soluble salts, as even in the presence of a large excess of acid more or less acid salt is deposited. Thus on dissolving neutral ammonium salt and adding a large excess of hot 5 per cent nitric acid, nearly pure acid salt was obtained. It may also be prepared by boiling the silver salt with much water, containing about the requisite amount of hydrochloric acid for its decomposition, and precipitating by further addition of the same acid to the filtrate.

The analytical methods are the same as those employed for trimetaphosphimates, but much longer heating with strong sulphuric acid is necessary because of its greater stability.

Analyses of four air-dried preparations gave:

	Calculated for $P_4N_4O_8H_8+2H_2O$.	Found.			
		1.	2.	3.	4.
P	35.23	35.01	35.27	35.38	35.20
N	15.94	15.93	....	15.99	15.92
H	3.41	....	....	3.55	3.59

1. P : N=4 : 4.02.
3. P : N : H=4 : 4.06 : 12.43. From chlorhydrine.
4. P : N : H=4 : 4 : 12.64. First method, from aqueous portion.

The crystal water is not given off in vacuo over sulphuric acid. At 100° it loses weight rapidly, then slowly, but the total loss never reaches the theoretical, a portion of the water being taken up in producing intramolecular changes.

Loss calculated for $2H_2O$	10.22
(1) Loss after twenty-four hours (weight constant)	9.37
(2) Loss after seventy-eight hours (weight constant)	8.91

If rapidly heated to 130–140° the loss is still less, and is soon replaced by a gain; after thirty hours at this temperature a net increase of 11.15 per cent, corresponding to somewhat more than 2 molecules H_2O, was observed, which must have come from the atmosphere. The product consisted of unchanged acid with ammonium phosphate and apparently pyrophosphate.

Tetrametaphosphimic acid forms colorless needles, either single or in radiating groups, and visible without a lens; they appear to consist of flat rectangularly terminated prisms. One hundred parts water at 20° dissolve 0.64 part crystallized acid; in boiling water it is somewhat more soluble, but is insoluble in alcohol. From its saturated aqueous solution it is partially precipitated by adding one of the stronger acids, and more rapidly if heated; 100 parts by weight of 10 per cent nitric acid at 20° dissolve only 0.26 part of the crystallized acid, but on decomposing its salts in the cold by an excess of acid it frequently dissolves completely and separates out later. Its saturated aqueous solution does not coagulate albumen. Boiling alkaline solutions cause no evolution of ammonia. Its stability toward acids is illustrated by the following: 0.1 gram, dissolved in 200 cubic centimeters water with 8 cubic centimeters strong nitric and some hydrochloric acid, was evaporated to dryness on the water bath, whereby a large part was recovered unchanged; ten minutes' heating would have sufficed for the total decomposition of the same quantity of trimetaphosphimic acid. Nitrous acid has no perceptible action.

Di-potassium tetrametaphosphimate, $P_4N_4O_8H_6K_2$.—The free acid dissolves easily in cold dilute caustic potash; on strongly acidifying with acetic acid the solution remains clear, but on warming the above salt is deposited as a heavy, sandy powder, consisting of microscopic thick rectangular (quadratic?) prisms with basal planes. It is very difficultly soluble even in boiling water.

The air-dried substance lost nothing at 100° and gave:

	Calculated for $P_4N_4O_8H_6K_2$.	Found.
P	31.61	31.26
K	19.93	20.05

P : K = 4 : 2.03.

The tetra-potassium salt formed large, flat, obliquely terminated plates, very soluble, and was not isolated.

Tetra-sodium tetrametaphosphimate, $P_4N_4O_8H_4Na_4 + 2\frac{1}{2}(?)\ H_2O$.—The acid is suspended in a little water and an excess of dilute caustic soda added, whereby complete solution occurs. The separation of the neutral salt soon begins in the form of obliquely terminated flat prisms, sometimes single, sometimes in twins or quadruplets; the filtrate deposits more on heating, but in imperfect forms, broader at one end than at the other. Sometimes nothing separates from the alkaline solution until it is heated. On the contrary, strong caustic soda converts the solid acid in the salt without dissolving it. The salt is rather difficultly soluble in cold, quite easily in hot, water, but much less soluble in the presence of an excess of alkali, and the latter throws it down from its saturated aqueous solution. Sodium carbonate gives the same salt.

The substance, pressed out without washing and dried in vacuo, lost nothing at 100° and gave:

	Calculated for $P_4N_4O_8H_4Na_4$ $+2\frac{1}{2}H_2O$.	Found.	
		1	2
P	27.62	27.61	27.71
Na	20.50	21.23	20.80

1. P : Na = 4 : 4.14.
2. P : Na = 4 : 4.05.

Alcohol precipitates this salt in a slimy form, which filters with difficulty.

A solution of the tetra-sodium salt, strongly acidified with acetic acid, gave a deposit of granules, probably the acid salt. A salt with more than 4 atoms of sodium[1] was not observed.

Tetra-ammonium tetrametaphosphimate, $P_4N_4O_8H_4(NH_4)_4+4H_2O$.—Strong ammonia converts tetrametaphosphimic acid into this salt without dissolving it; from its solution in weaker ammonia it is precipitated by alcohol. It usually forms well-developed, flat, monoclinic prisms with pinakoid and basal planes, the base being occasionally replaced by a set of many small planes. It is easily soluble in water, but difficultly in strong ammonia. Its solution undergoes partial decomposition into acid salt on evaporating. It loses nothing in vacuo, and analysis gave:

	Calculated for $P_4N_4O_8(NH_4)_4$ $+4H_4O$.	Found.		
		1	2	3
P	27.19	27.12	....	27.25
N	24.61	24.74	....	24.66
H	6.15	....	5.94	....

1. P : N = 4 : 8.12.
3. P : N = 4 : 8.

---

[1] Compare the behavior of trimetaphosphimic acid toward excess of alkali.

Di-ammonium tetrametaphosphimate, $P_4N_4O_8H_6(NH_4)_2$.—This salt forms whenever a solution of the neutral salt is strongly acidified, and was at first mistaken for the free acid, which it somewhat resembles. It forms 4- and 6-sided prisms with base (tetragonal?), closely resembling the acid potassium salt, and, like this, is very difficultly soluble even in boiling water. It separates on heating a solution of the neutral salt with acetic acid in excess (analyses 1 and 2), or with a stronger acid, in which case it may be slightly contaminated with free acid. The preparation under analysis 3 was crystallized from a large excess of hot 5 per cent nitric acid. It contains no crystal water. Analysis gave:

	Calculated for $P_4N_4O_8H_6(NH_4)_2$.	Found.		
		1.	2.	3.
P	35.42	34.41	35.10	35.20
N	24.04	24.32	24.33	23.17

1. $P:N=4:6.26$.
2. $P:N=4:6.15$.
3. $P:N=4:5.82$.

Barium tetrametaphosphimate, $P_4N_4O_8H_4Ba_2 + 2H_2O$.—A solution of the di- or tetra-ammonium salt in 500 parts cold or, better, boiling water, is precipitated by an excess of barium chloride. The salt forms a voluminous precipitate consisting of microscopic needles, branched or forked, insoluble in water, and undecomposed by acetic acid. These have approximately the composition of neutral salt, with a slight deficiency of barium.

The air-dried salt lost nothing at 100° and gave:

	Calculated for $P_4N_4O_8H_4Ba_2$ $+2H_2O$.	Found.	
		1.	2.
P	20.28	20.17	20.18
Ba	44.83	42.91	42.39

1. $P:Ba=4:1.93$. From acid ammonium salt.
2. $P:Ba=4:1.90$. From neutral ammonium salt.

Basic barium salts of indefinite properties seem to exist, but no indication of an acid salt could be obtained.

No satisfactory results were obtained with *magnesium* salts, a large variety of crystalline and amorphous precipitates being obtained under different conditions.

Manganese salts give with free tetrametaphosphimic acid a flocculent precipitate of neutral manganese tetrametaphosphimate; on adding a mineral acid this is decomposed, according to the proportion of the latter, into acid salt or free acid, or a mixture of both. The acid salt forms handsome pinkish rectangular plates, often superposed at various angles, and is one of the most characteristic salts obtained.

Ferric chloride gives no precipitate with a cold dilute solution of the neutral ammonium salt; on warming a white amorphous precipitate forms, which is soluble only on warming with much hydrochloric acid, from which solution, on cooling, the free acid separates.

Tetra-silver tetrametaphosphimate, $P_4N_4O_8H_4Ag_4$.—If to a cold solution of tetrametaphosphimic acid silver nitrate be added the resulting precipitate is white, curdy, and, under the microscope, granular or amorphous; formed in the presence of some alcohol it is even flocculent. These amorphous precipitates, after drying, slowly change to needles, and this occurs at once if they be boiled under water. The salt is obtained at once in crystalline form if a slight excess of silver nitrate be added to a hot solution of tetrametaphosphimic acid in 200–300 parts water. It requires but a slight excess of silver nitrate to bring about complete precipitation, the liberated nitric acid exercising a scarcely perceptible solvent action. Neutral ammonium salt may be used, but the addition of a little nitric acid is essential, otherwise the product is yellowish from contamination with the 8-atom silver salt.

When precipitated hot the salt sometimes consists of thick needles with tufts or brushes at each end, sometimes of long pointed plates, more rarely of rhombic plates, and in no case are they well formed or very characteristic. An acid salt could not be obtained, but the neutral salt always shows a slight deficiency of silver.

The air-dried substance lost nothing at 100° and gave:

	Calculated for $P_4N_4O_8H_4Ag_4$.	Found.					
		1.	2.	3.	4.	5.	6.
P	16.68	16.78	17.04	17.04	16.68	16.84	16.74
N	7.55	....	....	....	....	....	7.62
Ag ...	58.04	....	57.06	56.13	57.09	57.09	57.40

2. P : Ag = 4 : 3.85.
3. P : Ag = 4 : 3.79.
4. P : Ag = 4 : 3.94.
5. P : Ag = 4 : 3.90.
6. P : N : Ag = 4 : 4.02 : 3.95.

Octa-silver tetrametaphosphimate, $P_4N_4O_8Ag_8$.—If an ammoniacal solution of a tetrametaphosphimate be added to an excess of silver nitrate, a yellowish flocculent precipitate forms, which is insoluble in ammonium nitrate and which does not change on boiling under its mother-liquor or under pure water. On drying at 100° it became grayish olive colored, apparently because of the separation of some silver oxide. It gave the figures under 1, 2, and 3.

If a solution of a neutral tetrametaphosphimate be added to ammoniacal silver nitrate containing the least possible excess of ammonia, a nearly white flocculent precipitate forms in small amount, which is soluble in ammonium nitrate solution on gently warming; from this solution an orange-yellow semicrystalline body is thrown out on boiling for a moment. The latter is obtained in greater abundance by boiling the original filtrate from the silver-nitrate precipitate. It seems to be merely the crystalline modification of the above amorphous yellow salt. It gave the figures under analysis 4. The nearly white modification is obtained in greater amount by using a solution of silver oxide in ammonium nitrate solution. It shows a considerable deficiency of silver (P : Ag = 4 : 6.7) and seems to be less stable than the corresponding white hexa-silver trimetaphosphimate, as it can not be obtained entirely free from the yellow modification. The yellow form also shows a slight deficiency of silver, and unlike the trimetaphosphimate, it can not be converted into a red form.

The yellow salts, dried at 100°, gave:

	Calculated for $P_4N_4O_8Ag_8$.	Found.			
		1.	2.	3.	4.
P	10.59	10.47	10.88	10.80	10.89
Ag	73.69	71.86	71.60	71.96	72.21

1. P : Ag = 4 : 7.90. } Amorphous.
2. P : Ag = 4 : 7.57. } Amorphous.
3. P : Ag = 4 : 7.66. } Amorphous.
4. P : Ag = 4 : 7.63. Semicrystalline.

4. THE HIGHER CHLORONITRIDES.

In the first section of this paper I have shown that in addition to the phosphonitrilic chloride,[1] $P_3N_3Cl_6$, discovered by Liebig, there exists another, $P_4N_4Cl_8$, of similar properties, which is formed at the same time, but in smaller quantity. The opinion was expressed that these bodies belong to a series of polymers, $(PNCl_2)_n$, the existence of other members of which was indicated by the formation, in small amount, of a liquid of the same empirical composition. The yield of this secondary product, only 2 per cent of the theoretical or 1 per cent of the pentachloride used, was too small to allow of its preparation in quanti-

---

[1] I propose in future to use the term phosphorus chloronitride to denote any body composed of phosphorus, nitrogen, and chlorine, the name phosphonitrilic chloride being reserved for chloronitrides belonging to the series $(PNCl_2)_n$.

ties large enough to admit of the isolation of its supposed constituents, but a fractional distillation of the few grams at my disposal showed that it contained crystalline substances of higher boiling points than those of the two bodies thus far known.

The method of preparation then employed consisted in distilling phosphorus pentachloride with a large excess of ammonium chloride in a retort, at atmospheric pressure; it offered but little prospect of obtaining the higher members. The total yield of phosphonitrilic chloride was but 15 per cent of the theoretical, most of the pentachloride being converted into "phospham" by the excess of ammonium chloride, while only those members could be obtained which distill unchanged at atmospheric pressure. Decreasing the amount of ammonium chloride resulted only in a loss of pentachloride by volatilization, without increasing the yield of the bodies sought after.

The following method has been found to give entirely satisfactory results; several new bodies have been obtained, and the simpler phosphonitrilic chlorides, at least, are now easily accessible substances. If equal molecular weights of phosphorus pentachloride and ammonium chloride be heated in a sealed tube, there results a mixture of chloronitrides, which is partly crystalline and soluble in gasoline, but for the greater part liquid and insoluble in this solvent, and of a high degree of complexity. This may be distilled almost without residue, the distillate being a crystalline mass, impregnated with an oil, and composed almost wholly of a mixture of members of the series $(PNCl_2)_n$ in nearly theoretical amount, containing about 50 per cent $P_3N_3Cl_6$, and 25 per cent $P_4N_4Cl_8$, the remainder consisting of the higher homologues. From this distillate the new bodies, with one exception, have been isolated.

The series, as at present known, consists of the following:

	Melting point. (Corrected.)	Boiling point. (Corrected.)	
		13 mm.	760 mm.
	Degrees.	*Degrees.*	*Degrees.*
Triphosphonitrilic chloride, $(PNCl_2)_3$.	114	127	[a] 256.5
Tetraphosphonitrilic chloride, $(PNCl_2)_4$.	123.5	188	[b] 328.5
Pentaphosphonitrilic chloride, $(PNCl_2)_5$.	40.5-41	223-224.3	Polymerizes
Hexaphosphonitrilic chloride, $(PNCl_2)_6$.	91	261-263	Polymerizes
Heptaphosphonitrilic chloride, $(PNCl_2)_7$.	Below—18	289-294	Polymerizes
Polyphosphonitrilic chloride, $(PNCl_2)_x$.	Below red heat.	Depolymerizes on distillation.	

[a] 183.8° at 100 mm. [b] 242° at 100 mm.

There were obtained, further, a liquid residue of the same empirical composition, of a mean molecular weight corresponding nearly to

$(PNCl_2)_{11}$, and a small amount of a chloronitride, $P_6N_7Cl_9$, not belonging to the above series. The absence of the lower members, $PNCl_2$ and $(PNCl_2)_2$, is remarkable, and theoretically significant. Indications of a trace of a substance more volatile than the compound $(PNCl_2)_3$ and of similar but stronger odor, were observed, but there is no evidence that it consists of one of the missing bodies.

One of the most remarkable properties of the phosphonitrilic chlorides is that each member of the series is converted by heat into the rubber-like polyphosphonitrilic chloride, a body, or mixture of bodies, of very high molecular weight, which is highly elastic and insoluble in all neutral solvents, but which swells enormously in benzene, and which, on distilling at a higher temperature, breaks down into a mixture of all the lower members mentioned above, which can then be separated by appropriate means. In this way it is possible to convert any phosphonitrilic chloride quantitatively into any other by heat and distillation alone. In preparing any desired member, therefore, we are not limited to the quantity obtained from the first reaction product, but may work the residues over and over again until completely converted into the body sought after. With the exception of a few cases, in which the number of members is limited, as the aldehydes and cyanic acids, this series is therefore unique; I know of no other series of inorganic compounds in which this is possible. Polymerization takes place slowly, but perceptibly, at 250°, and is almost instantaneous at 350°, while depolymerization begins at about 350°, and is rapid at a temperature close to incipient red heat. Triphosphonitrilic chloride, $P_3N_3Cl_6$, is the only member which can be distilled in considerable amount at atmospheric pressure without considerable polymerization, and even this polymerizes almost completely on long boiling; at 760 millimeters pressure the tetra-compound, $P_4N_4Cl_8$, boils at 328.5°, a temperature at which polymerization occurs quite rapidly, but this, as well as the penta compound, $P_5N_5Cl_{10}$, and the hexa-compound, $P_6N_6Cl_{12}$, can readily be distilled at 13 millimeters; the hepta-compound, $P_7N_7Cl_{14}$, suffers marked polymerization on distilling even at this pressure, and its isolation is therefore attended with much loss. Owing to the rapid change at higher temperatures, I have been unable to isolate any of the higher members, which remain as a considerable oily residuum, and there seems to be but little probability of this being effected by any known method, unless by distilling in a nearly absolute vacuum.

The greatest difficulty in the separation of the members is caused by polymerization. It requires but a small amount of polyphosphonitrilic chloride to cause the liquid to thicken or gelatinize, and therefore to be incapable of further distillation, and some of this body is always formed in the course of a prolonged fractioning of the higher members. It was found, however, that this polymer is much more easily attacked by water than the lower members; when signs of polymerization are observed, it is only necessary to interrupt the distillation, and heat the residue for some time with water, when the resulting oil is again in a condition to continue fractioning. The loss in this operation is small, but the tediousness of a fractional distillation is thereby extraordinarily increased.

It is noteworthy that no regular progression exists in the melting points of the phosphonitrilic chlorides, and the same is true of their solubility in the ordinary neutral solvents, but the solubility varies in the same sense as the fusibility. Of the members of known molecular weight, the second, tetraphosphonitrilic chloride, is the least soluble and has the highest melting point, while the corresponding tetrametaphosphimic acid is the least soluble and most stable of the derived acids. With respect to their stability toward water, the new members (polyphosphonitrilic chloride excepted) resemble those already described, being scarcely attacked by prolonged boiling. In ethereal solution, however, there is a perceptible decrease of stability toward water as we rise in the series, a fact already noted with regard to the first two members.

Notwithstanding the high molecular weight of the bodies isolated, no indication of isomers has been observed, although the fractioning was carried out very thoroughly up to 300° at 13 millimeters.

EXPERIMENTAL PART.

A mixture (which need not be very intimate) of 4 parts perfectly dry phosphorus pentachloride and 1 part ammonium chloride, as required by the equation

$$PCl_5 + NH_4Cl = PNCl_2 + 4HCl,$$

is introduced into an ordinary "bomb" tube, which has previously been drawn out to a neck. It is practicable to fill the tube entirely to the neck, so that the charge for a tube of ordinary dimensions is about 125 grams, yielding 50–55 grams of chloronitrides. After sealing, the length of the neck, exclusive of the rather long capillary, should be about 10 centimeters. As the mixture liberates 55 per cent hydrochloric acid, it is necessary to regulate the heating with great care and to open the tube repeatedly. The temperature of the furnace is allowed to rise to 150°, at which the reaction begins, when the gas is at once shut off, and the tube opened at about 100° (in the furnace!). This operation is repeated several times, the temperature being allowed to rise 1°–2° higher each time. When the evolution of hydrochloric acid has slackened and the contents of the tube are mainly liquid while hot, the temperature may be carried to 200° or higher, until little or no gas is given off. The operation requires care and judgment, but with careful working it is possible to avoid explosions, and to obtain with a four-tube furnace about 200 grams of mixed chloronitrides in sixteen hours.

The contents of the tube, after cooling, generally consists of a buttery mass or of a thick, yellow liquid filled with fine prisms and plates; if heated much above 200°, the liquid frequently separates into two layers. The crystals are soluble in gasoline, but the bulk of the product remains as an immiscible oil.

The neck of the tube is now bent down, the tube placed in an inclined combustion furnace, and by cautious heating, finally to incipient redness, the contents are distilled out. There remains in the tube a very voluminous, spongy, black residue of inconsiderable weight, due to unavoidable impurities and to the impossibility of causing complete reaction in the sense of the above equation. The distillate consists of a crystalline mass impregnated with a yellow oil, and contains about 95 per cent of the theoretical amount of phosphonitrilic chlorides, with some phosphorus pentachloride, the chloronitride $P_6N_7Cl_9$, and other substances of unknown nature. Before proceeding further, it is necessary to remove the pentachloride, and for this purpose the distillate is melted, poured into cold water, and the flask heated in the water-bath for about two hours, the liquids being mixed by blowing air through them. The chloronitrides are then allowed to clear under the hot water, and forced out by means of a wash-bottle arrangement; a separatory funnel can not be used, as the substance solidifies in the neck, and if allowed to solidify under the wash water it absorbs so much of this as to cause annoyance in the subsequent distillation. Special drying before distilling is unnecessary.

The product is then distilled up to 200° at 13–15 millimeters, using an Anschütz flask, as the distillate solidifies instantly on cooling. The residue, containing the members $P_5N_5Cl_{10}$ up, is set aside for later systematic fractional distillation.[1] The distillate, about 70 per cent, consists essentially of $P_3N_3Cl_6$ and $P_4N_4Cl_8$, which, if desired, may be easily separated by fractional distillation in vacuo, followed by crystallization from benzene. This is more convenient than the method of separating by steam. If it is desired to convert it into the higher members, it is placed in a combustion tube bent down at about 20 centimeters from the open end, and which it should not fill more than one-half after melting. This is laid in an inclined combustion furnace and heated to gentle boiling of the contents. It is well to heat the tube somewhat strongly at a short distance above the liquid, as superheating the vapor pro-

---

[1] This residue contains the small amount of $P_6N_7Cl_9$ formed as a secondary product of the original reagents, and as this is apt to cause inconvenience at a later stage by accumulating with the $P_6N_6Cl_{12}$, it is perhaps well to remove as much as possible at this point. For this purpose the residue is allowed to stand for a day or two at the room temperature, and the crystals removed by sucking out under a good vacuum, best in a large Gooch crucible. The filtrate is cooled for a day or two in a refrigerator, and the new crop of crystals separated in the same way, the filtering flask being allowed to stand in the icebox. The oily filtrate is set aside, and the united crystalline products distilled up to 240° at 13 millimeters, whereby most of the $P_5N_5Cl_{10}$ passes over. The residue, consisting of $P_6N_6Cl_{12}$, the small amount of $P_6N_7Cl_9$, and the adhering oil, is allowed to crystallize in the refrigerator, and the viscous mass is extracted several times with small amounts of gasoline (boiling at 50°-80°). The residue is boiled with benzene, which extracts the $P_6N_7Cl_9$, which crystallizes on concentrating and cooling. The portion dissolved by the gasoline is worked up with the other residues.

This is the method actually employed, but I am not entirely convinced of its necessity, as it is not possible to remove all the $P_6N_7Cl_9$ in this way.

motes polymerization. The time required for polymerization varies greatly; pure triphosphonitrilic chloride may require two hours or more. With the above mixture the time is less, and is shorter the higher the boiling point; it is shortened by adding already gelatinized substance, which causes the liquid to thicken, and may then be but a few minutes; it is also shortened by heating under pressure. Sooner or later the liquid begins to thicken, and finally it is converted into a stiff, transparent mass, with little or no liquid, and generally discolored by traces of organic matter. The tube is then connected with a long-necked receiver, exhausted, and the depolymerization and distillation effected by heating, from the front backward, to incipient redness. This part of the operation proceeds rapidly, as it is only necessary to guard against frothing over, and to insure complete condensation, the latter being easily effected by having the limb of the tube at least 20 centimeters long. One hundred grams can be worked up at one time and the tube can be used repeatedly. The residue does not weigh more than a few milligrams. The distillation may also be made at atmospheric pressure, but the yield of higher products is thereby diminished. The distillate, which entirely resembles that first obtained, excepting in containing no phosphorus pentachloride and no $P_6N_7Cl_9$, is distilled as before, the washing being omitted. In this way the whole quantity of material can finally be converted into a mixture of members higher than $P_4N_4Cl_8$.

The united residues boiling above 200° are now submitted to systematic fractional distillation at 13–15 millimeters, using an Anschütz flask, provided with a "trap," to prevent flowing back. During the first distillation polymerization generally begins when the temperature of the bath has reached 270°, but with later distillations at a higher temperature, and the higher the purer the fractions are. When polymerization begins, which is indicated by frothing and thickening, the operation is interrupted and the residue heated in the flask with water in the water bath until it has completely liquefied, which is assisted by agitation, the oil separated,[1] and the distillation continued. It has not been found practicable to continue the distillation at a higher temperature than that obtained by heating the bath to 370°, for the liquid begins to polymerize in a few moments, and but an inconsiderable distillate can be obtained. Moreover, at this temperature the polymer shows signs of breaking down into simpler bodies, and the distillate does not consist only of high-boiling members. The total amount of final residue is not very great, and, as shown below, consists likewise of phosphonitrilic chlorides of still higher molecular weight. In later distillations from 200° upward, polymerization usually stops the process at 260°–270°, but after appropriate washing the residue may be

---

[1] In this case a separatory funnel may be used, as the mixture of higher chloronitrides is liquid below 80°.

distilled to a much higher temperature. After eight to ten distillations three main fractions are obtained, which are then worked up separately. As $P_5N_5Cl_{10}$, though crystalline, is extremely soluble, it is necessary to carry out the distillations with the first main fraction until a practically sharp boiling point is obtained, in which connection it may be noted that at 17–20 millimeters a change of 1 millimeter pressure causes a change of about 1° in the boiling point, and at 13 millimeters a change of about 2°. $P_7N_7Cl_{14}$, being liquid, must also be isolated by distillation only, but at its boiling point polymerization is so rapid that great loss ensues during a series of distillations.

$P_6N_6Cl_{12}$ can not be separated by distillation from the $P_6N_7Cl_9$ which accompanies it in small amount, the latter having nearly the same boiling point, nor is repeated recrystallization effective. The separation is best effected by adding a crystal of pure $P_6N_6Cl_{12}$ to the supersaturated benzene solution, and filtering before the $P_6N_7Cl_9$ begins to deposit. The latter thus concentrated is recrystalized from benzene.

Owing to many modifications introduced in developing the above method, no accurate statement of the yield can be given; the final product was about 225 grams $P_5N_5Cl_{10}$, 110 grams $P_6N_6Cl_{12}$, 10 grams $P_7N_7Cl_{14}$, and 5 grams $P_6N_7Cl_9$.

Analytical methods.—With the exception of polyphosphonitrilic chloride, the chloronitrides were analyzed by decomposing in the following manner:

For phosphorus, by warming with alcohol and a little ammonia in a platinum crucible until completely dissolved, evaporating to dryness and heating to fuming for an hour with strong sulphuric acid, the crucible being kept covered.

For nitrogen, by treating as above, omitting the ammonia.

For chlorine, by heating with alcohol and ammonia. It is necessary to precipitate with silver nitrate in the presence of a large volume of 10 per cent nitric acid and to filter hot, in order to avoid the formation of silver metaphosphimates, which are difficultly soluble in dilute nitric acid.

In decomposing polyphosphonitrilic chloride, which is attacked by water alone, the alcohol was omitted. The method of Carius was used for determining chlorine, as it was found that otherwise compounds insoluble in dilute nitric acid were formed. For the other chloronitrides this method offers no advantage.

Molecular weight determinations were made by the boiling-point method with the apparatus of Hite,[1] using as solvent carefully purified and dried benzene.

---

[1] Am. Chem. Jour., Vol. XVII, p. 512. The molecular weight of $P_3N_3Cl_6$ has been determined by the vapor-density method, Jour. Chem. Soc. London [2], Vol. II, p. 225. A series of determinations by the boiling-point method gave 346, 350, 353. Calculated 347.9.

Pentaphosphonitrilic chloride, $P_5N_5Cl_{10}$.—This body, carefully purified by fractional distillation, as described above, gave on analysis:

	Calculated for $P_5N_5Cl_{10}$.	Found.
P	26.75	26.87
N	12.11	12.05
Cl	61.14	61.42

P : N : Cl = 1 : 0.99 : 2.00.

Molecular weight. (Solvent, benzene.)

Grams solvent.	Grams substance.	Elevation (degrees).	Molecular weight found.	Percentage variation from theoretical.
46.49	1.4688	0.137	619	+6.2
46.49	2.9439	.287	589	+1.6
46.49	4.4337	.437	583	+ .5

Calculated for $P_5N_5Cl_{10}$, 579.8.

Pentaphosphonitrilic chloride fuses at 40.5°–41°, and boils at 223°–224.3° (corrected) at 13 millimeters. Its vapor is without the pronounced and characteristic aromatic odor possessed by that of triphosphonitrilic chloride. At its melting point it is miscible in all proportions with benzene, gasoline, ether, and carbon disulphide, and can not be recrystallized from any of these solvents; in fact, small fragments liquefy instantly in their concentrated vapors. Glacial acetic acid also dissolves it quite readily, and from this solution water throws it out as an oil, solidifying at once on touching. It shows a decided tendency to superfusion, especially when not absolutely pure; when left by evaporating its ether or benzene solution, it may remain liquid for days, but solidifies at once on touching with a glass rod, usually to a decidedly crystalline mass, at other times to a transparent glass. The pure substance, when fused, slowly solidifies, long, flat crystals shooting out through the liquid, which are limited only by the size of the vessel, crystals of 10 centimeters in length being readily obtained. It contracts greatly on solidifying. When pure the solidified mass is naturally dry, but the least contamination with other members of the series causes a portion to remain liquid, which is easily detected by crushing on a piece of filter paper; this is a very good test of its purity. This tendency to superfusion must be borne in mind in separating it by fractional distillation; a nearly pure sample will remain liquid much longer than the higher or lower fractions. In ether solution it is perceptibly more easily attacked by water than the preceding chloronitride, but hot water alone is almost without action.

Hexaphosphonitrilic chloride, $P_6N_6Cl_{12}$.—After repeated crystallization from benzene,[1] this gave:

	Calculated for $P_6N_6Cl_{12}$.	Found.
P	26.75	26.98
N	12.11	12.37
Cl	61.14	60.98

P : N : Cl = 1 : 1.01 : 1.98.

Molecular weight. (*Solvent, benzene.*)

Grams solvent.	Grams substances.	Elevation (degrees).	Molecular weight.	Percentage variation from theoretical.
47.12	1.8058	0.152	673	—3.2
47.12	3.6190	.293	700	+0.6
45.72	1.0101	.083	711	+2.1
45.72	4.4898	.365	718	+3.2
45.72	8.0070	.664	704	+1.2

Calculated for $P_6N_6Cl_{12}$, 695 8.

Hexaphosphonitrilic chloride fuses at 90° (corrected), and boils at 261°-263° (corrected) at 13 millimeters, and at 281°-282° (corrected) at 26 millimeters. It may be recrystallized from benzene, in which, however, it is more soluble than triphosphonitrilic chloride; ether, gasoline, and carbon disulphide also dissolve it readily; in alcohol it dissolves somewhat slowly, with decomposition. It shows no tendency to superfusion. It crystallizes well, in rather large crystals, which were examined by Mr. Wirt Tassin, to whom I am indebted for the following statement:

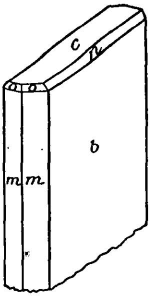


Fig. 7.

"$P_6N_6Cl_{12}$ crystallizes in the orthorhombic system in long, prismatic crystals, showing the following forms: *c* (001), *b* (010), *m* (110), *o* (111), *n* (011). Of these *c* is the dominant form; *b* large and well developed; *m* fair, though usually narrow, and *o* and *n* small and usually in similar development. *c, b, m, o* is the combination occurring most frequently; less often *c, b, m, n, o;* and rarely *c, b, m.* Angles *m*: *m* 57° 28′, *b*: *m* 61° 16′, *b*: *n* 40° 23′, *n*: *c* 49° 37′. Axial ratio $a : b : c = 0.54824 : 1 : 1.17568$. The crystals are optically positive. Plane of the optic axes (100);

---

[1] A contamination with $P_6N_7Cl_9$ may be detected by treatment with gasoline, when the much smaller crystals of the latter are seen to dissolve much more slowly.

colorless to white; transparent, and have a perfect basal cleavage." (See fig. 7.)

It is scarcely attacked by boiling water, but if kept in moist air it very slowly evolves hydrochloric acid. Its ether solution, shaken with water, slowly gives a metaphosphimic acid; sirupy chlorhydrines are formed as intermediate products.

Heptaphosphonitrilic chloride, $P_7N_7Cl_{14}$.—After many distillations, this gave:

	Calculated for $P_7N_7Cl_{14}$.	Found.
P	26.75	26.57
N	12.11	12.12
Cl	61.14	61.28

P : N : Cl = 1 : 1.01 : 2.02.

Molecular weight. (*Solvent, benzene.*)

Grams solvent.	Grams substance.	Elevation (degrees).	Molecular weight.	Percentage variation from theoretical.
47.09	3.5621	0.250	808	—0.5
47.09	7.3979	.523	802	—1.2

Calculated for $P_7N_7Cl_{14}$, 811.7.

Heptaphosphonitrilic chloride is a nearly colorless, rather viscous liquid, which does not solidify at —18°, and which boils at 289°–294° (corrected) at 13 millimeters, undergoing some polymerization. It is readily miscible with benzene, gasoline, and ether, and toward water shows the stability manifested by the preceding chloronitrides.

Residual oily phosphonitrilic chlorides.[1]—The residue, which did not distill at 13 millimeters when the temperature of the bath was 370°, was boiled with water to remove the solid polyphosphonitrilic chloride, filtered, and carefully dried in vacuo over sulphuric acid. It is a thick liquid which gave on analysis:

	Calculated for $(PNCl_2)_x$.	Found.
P	26.75	26.79
N	12.11	12.39
Cl	61.14	62.00

P : N : Cl = 1 : 1.02 : 2.02.

---

[1] It is unlikely that these consist entirely of the original depolymerization products; a portion is doubtless formed by polymerization during distillation.

Although the oil is doubtless a mixture, the above figures show that the constituents are members of the series $(PNCl_2)_n$. A determination of the mean molecular weight was made, with the following results:

Grams solvent.	Grams substance.	Elevation (degrees).	Molecular weight.
46.72	4.130	0.178	1,326
46.72	7.853	348	1,290

Mean 1,308. This does not lie far from that required by the formula $P_{11}N_{11}Cl_{22}$ (calculated, 1,276). This result is interesting in as far as it shows that a phosphonitrilic chloride of this molecular weight may exist; that it is stable and miscible with benzene, gasoline, and ether, and that the molecular weight of the solid polymer described below, which is insoluble, is probably very much higher. The oil has a reddish-brown color, due to dissolved impurities, which are destroyed by heating with strong nitric acid. It can not be distilled even at 13 millimeters, as it polymerizes almost instantly. In its behavior toward water it resembles the preceding members of the series.

Polyphosphonitrilic chloride $(PNCl_2)_x$.—This remarkable body, frequently alluded to above, is formed when any of the lower members are heated, slowly at 250°, and very rapidly at 350°. As the change is reversible, complete transformation can not be effected, but reaches perhaps 90 per cent, the remainder consisting not only of the original phosphonitrilic chloride, but of others. These can be extracted by anhydrous benzene. The sample, the analysis of which is given, was prepared by heating pure triphosphonitrilic chloride in a sealed tube at 350°–460°. The transparent elastic product was repeatedly extracted with benzene dried over sodium and the absorbed benzene removed in a vacuum with constant exhaustion over paraffin, and finally by heating in vacuo at 110°. Analysis gave:

	Calculated for $(PNCl_2)_x$	Found.
P	26.75	26.78
N	12.11	12.27
Cl	61.14	60.45

P:N:Cl = 1:1.01:1.98.

Polyphosphonitrilic chloride, when perfectly pure, is colorless and transparent, but is generally somewhat discolored by traces of organic matter. Its most striking property is its elasticity. It may be drawn out like rubber, and shows even a greater tendency to rebound from hard surfaces. It is readily cut with the shears. It is insoluble in all neutral solvents, but absorbs benzene, swelling to many times its original volume and forming a jelly of but little coherence; on evaporating the benzene it returns to its original condition. Ether is absorbed, but less readily, and other chloronitrides are taken up in a similar manner. Hot water slowly dissolves it with decomposition; in warm dilute ammonia it swells, gelatinizes, and finally dissolves; hot caustic soda does not dissolve it readily, apparently insoluble sodium salts being formed. It begins to depolymerize toward 350°, and this change is rapid just below red heat, and is accompanied by partial fusion, the products being, as described above, a mixture of lower phosphonitrilic chlorides. These transformations are not modified by heating in an atmosphere of hydrochloric acid. When perfectly pure, it leaves no residue whatever on distilling. No difference could be detected in the product formed from different phosphonitrilic chlorides.

Nitrilo-hexaphosphonitrilic chloride, $P_6N_7Cl_9$.—The separation of this chloronitride, which does not belong to the phosphonitrilic chloride series, is described above. After four crystallizations from benzene, it gave:

	Calculated for $P_6N_7Cl_9$.	Found.
P	30.84	30.74
N	16.29	16.29
Cl	52.87	53.01

A molecular weight determination, kindly made for me by Dr. H. C. Jones, of the Johns Hopkins University, with a limited quantity of material, in benzene solution, gave 667; calculated for $P_6N_7Cl_9$, 603.5. This, with the analysis, suffices to establish the above molecular formula.

Nitrilo-hexaphosphonitrilic chloride strikingly resembles the phosphonitrilic chlorides. It fuses at 237.5° (corrected) and boils at 251°–261° (corrected) at 13 millimeters without change. The boiling point coincides closely with that of hexaphosphonitrilic chloride (261°–263°, corrected at 13 millimeters), hence it is found associated with the latter. Heated in small quantities on foil, it volatilizes without residue, but at a higher temperature in a sealed tube it undergoes a change the exact nature of which has not been determined, but which involves the formation of a substance resembling polyphosphonitrilic chloride, which yields lower phosphonitrilic chlorides on distilling. It crystallizes in transparent prisms of not more than 1 millimeter in length, apparently rhombic, which are often united to acicular forms. When pulverized it becomes electrified. It dissolves in about 20 parts cold and 5 parts boiling benzene,[1] is more soluble in carbon disulphide, but less soluble

---

[1] Approximate only.

in gasoline and in ether. Toward water it is nearly as stable as hexaphosphonitrilic chloride, but is slowly attacked when exposed to atmospheric moisture. Hot dilute ammonia dissolves it very slowly, but more rapidly when alcohol is added.

This body is obviously a secondary product of the reaction of phosphorus pentachloride and ammonium chloride, as it is never found when a pure phosphonitrilic chloride is polymerized and depolymerized. It is noteworthy that no indication of other bodies of a similar nature has been observed, although no reason appears why they should not be formed at the same time. Whether it is in reality hexaphosphonitrilic chloride in which 3 chlorine atoms are replaced by one of nitrogen or not can not be decided at present.

5. THE HIGHER METAPHOSPHIMIC ACIDS.

In the preceding sections on the metaphosphimic acids it was shown that the two lower phosphonitrilic chlorides, $P_3N_3Cl_6$ and $P_4N_4Cl_8$, give on saponification two well-defined acids, trimetaphosphimic acid, $P_3N_3O_6H_6$ and tetrametaphosphic acid, $P_4N_4O_8H_8$. In a later section the existence of the higher phosphonitrilic chlorides $P_5N_5Cl_{10}$, $P_6N_6Cl_{12}$, and $P_7N_7Cl_{14}$ was shown, and it was further demonstrated that the series does not end here, but is continued through a number of members, which are incapable of separation by existing methods, and terminates with a rubber-like polymer of high molecular weight.

The work outlined in the present section was begun with the expectation of finding that each of the new phosphonitrilic chlorides would give on saponification the corresponding metaphosphimic acid of the general formula $(PNO_2H_2)_n$. The result, however, has not justified this anticipation. It has been found that penta- and hexaphosphonitrilic chlorides give true penta- and hexametaphosphimic acids, $(PNO_2H_2)_5$ and $(PNO_2H_2)_6$, but that heptaphosphonitrilic chloride gives, not $(PNO_2H_2)_7$, but an acid $(PNO_2H_2)_7 + H_2O$. The metaphosphimic series, therefore, appears to be limited by the acid $(PNO_2H_2)_6$.

The metaphosphimic acids are the lactams of the imidophosphoric amides,[1] and it is therefore not surprising that there should be a certain similarity of behavior between these and certain organic oxy- and amido-acids. The γ and δ oxy- and amido-acids, while existing as salts in alkaline solution, pass more or less readily in the free state into the inner anhydrides, the lactones and lactams, a behavior which is not observed when the hydroxyl or amido-group is still further removed from the carboxyl. Joh. Wislicenus has shown[2] that the geometric configuration of the lactone-giving acids is such as to bring the reacting groups into

---

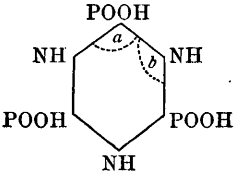
[1] The imidophosphoric acids consist of chains of alternate NH and PO groups, the first being imidodiphosphoric acid, $PO(OH)_2.NH.PO(OH)_2$. This and diimidotriphosphoric acid are described in the section on trimetaphosphimic acid, and triimidotetraphosphoric acid in the present section. The amides, of which the metaphosphimic acids are the lactams, may be regarded as imidophosphoric acids having one terminal hydroxyl replaced by an amido group.

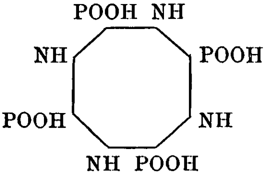
[2] Räumliche Anordnung der Atome, p. 67.

close proximity, thus admitting of inner anhydride formation, while in other cases this is not possible, owing to their remoteness. Von Baeyer,[1] in his well-known "tension theory," has shown that the series of methylene-ring hydrocarbons, $(CH_2)_n$, may be expected to possess a maximum of stability in the pentamethylene ring, a ring in which there is the least "strain," because the attraction of the carbon atoms for each other acts very nearly in the direction which the valences naturally assume, a deduction which has been confirmed by recent work on the reduction of aromatic hydrocarbons, showing the tendency of these to form pentamethylene rings when reduced.[2]

The speculations of Wislicenus and von Baeyer admit of application to the series of acids derived from the phosphonitrilic chlorides, and as far as the subject has been worked out the analogy is a complete one. The acids in the open form are amides of imidophosphoric acids; those with from 3 to 6 phosphorus atoms have the open form in alkaline solution, from which they are thrown out by silver nitrate as salts of the general formula $(PNO_2Ag_2)_n + H_2O$, but in acid solution they spontaneously form the inner anhydrides; i. e., the metaphosphimic acids, which can be precipitated as silver salts of the general formula $(PNO_2HAg)_n$. The acid with 7 phosphorus atoms, on the contrary, does not form the anhydride under any conditions. Not only does the series possess an extremely marked maximum of stability in tetrametaphosphimic acid, but the higher acids, on being subjected to energetic attack, break up, yielding this body.

In previous chapters I have assumed that tri- and tetrametaphosphimic acids contain phosphorus-nitrogen rings:





We know nothing of the steric relations of phosphorus and but little of those of nitrogen, and have therefore no definite theoretical grounds for assuming the magnitude of the angle *a* formed by the lines joining a POOH group with two NH groups, nor of the angle *b* formed by lines connecting a NH group with two POOH groups, in the case when these are free to assume a relation of greatest stability or least tension, as in an open chain. Neither can we assert that in a 6-sided ring, P_3N_3, with alternate phosphorus and nitrogen, the angles *a* and *b* must each be 120°. We are, however, justified in assuming that the *mean* of *a* and *b* is 120°. Similarly in an 8-sided ring, P_4N_4, the *mean* angle is 135°, even though *a* may be 180° and *b* 90°.

---

[1] Ber. Deutsch. chem. Gesell., Berlin, Vol. XVIII, p. 2277.

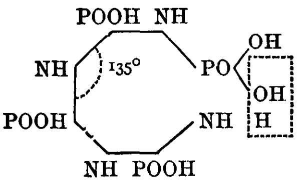
[2] Zelinsky, Ber. Deutsch. chem. Gesell., Berlin, Vol. XXX, pp. 387, 1539.

Experiment having shown that tetrametaphosphimic acid, $P_4N_4O_8H_8$, is vastly more stable than any other acid of the series, we may regard the angle $\frac{a+b}{2}$ of the octagonal nucleus P_4N_4, which is 135°, as that which most nearly coincides with the angle of least tension in the sense of von Baeyer's theory, and as approximating to that which would be assumed in an open chain, and we may expect that the stability of each ring will be less the more the angle $\frac{a+b}{2}$ differs from 135°. In the following table the mean angle and its difference from 135° are shown:

Ring.	Number of sides.	Mean angle.	Difference from 135°.
		Degrees.	*Degrees.*
PN	2	0	—135
P_2N_2	4	90	— 45
P_3N_3	6	120	— 15
P_4N_4	8	135	0
P_5N_5	10	144	+ 9
P_6N_6	12	150	+ 15
P_7N_7	14	154.3	+ 19.3
P_8N_8	16	157.5	+ 22.5

It is therefore to be expected that as we ascend in the series there will be a very rapid increase of stability to a maximum, followed by a gradual decrease. This coincides with what we find. $P_3N_3O_6H_6$ is vastly less stable than $P_4N_4O_8H_8$; the latter may be heated for hours with acids without complete decomposition, while the former is destroyed under the same conditions in a few minutes. $P_5N_5O_{10}H_{10}$ is much less stable than $P_4N_4O_8H_8$, but markedly more stable than $P_3N_3O_6H_6$, corresponding to the difference of only 9° from 135° in one case against 15° in the other. $P_6N_6O_{12}H_{12}$ is perceptibly less stable than $P_5N_5O_{10}H_{10}$, and finally the ring P_7N_7 of heptametaphosphimic acid is incapable of existence under the usual conditions, and as a result we get, instead of the ring acid $P_7N_7O_{14}H_{14}$, the open chain $P_7N_7O_{15}H_{16}$.

When any of the acids above tetrametaphosphimic acid is broken up, the latter is formed in considerable amount. This may be explained in two ways: either the P_4N_4 nucleus exists as such in the higher acid, or it is formed from the decomposition products. The former is highly improbable, for, considering its great stability, it should persist and be found in nearly theoretical amount, which is by no means the case. ($P_5N_5O_{10}H_{10}$ gave 12 per cent and $P_6N_6O_{12}H_{12}$ 30 per cent of the theoretical.) Its formation from the decomposition products is easily explained on the tension hypothesis. If a ring of POOH and NH groups be broken up by the action of a stronger acid, the molecules resulting from its decomposition will tend to assume a configuration determined by the mean angle of least tension, 135°, and this configuration in the case of the molecule of amido-triimidotetraphosphoric acid will be either a zigzag line or the form represented by



a configuration which admits of the formation of the anhydride or lactam, which is nothing else than tetrametaphosphimic acid. A theoretical yield of this can not be expected, for when a chain, P_5N_5, for example, is further broken up, the disruption may occur at any one of nine points, but only when one of the resulting products contains P_4N_4 can tetrametaphosphimic acid be formed. A simple calculation shows that at most only 27 per cent of that required by the equation

$$P_5N_5O_{10}H_{10} + 2H_2O = P_4N_4O_8H_8 + NH_4H_2PO_4$$

can be expected. A chain P_6N_6, however, offers more chances for the formation of fragments containing P_4N_4, and hence, as actually found, the yield of tetrametaphosphimic acid is greater, instead of less, as would be the case if the nucleus of this acid existed as such in hexametaphosphimic acid.

The first two chloronitrides, $PNCl_2$ and $P_2N_2Cl_4$, have not been obtained, and of the corresponding mono- and dimetaphosphimic acids the former is unknown and the existence of the latter questionable. Mente[1] has described salts of an acid to which he gives the formula of dimetaphosphimic acid, $P_2N_2O_4H_4$, but no proof is given that it is not some other polymer of PNO_2H_2, and the method by which he obtained it is one which is not likely to give a body of this molecular weight. The dimetaphosphimic ring would have a mean angle of 90°, which differs from that of tetrametaphosphimic acid by 45°. Such a ring should be much less stable than even that of heptametaphosphimic acid, and it is therefore quite possible that it is incapable of existence as such, and can exist only as the hydrate $P_2N_2O_5H_6$. This is perhaps the acid described by Gladstone[2] as pyrophosphodiamic acid.

The chloronitride series presents a maximum of stability in triphosphonitrilic chloride, but this is by no means as marked as that existing in the acid series. That such a maximum should occur in one case in a ring of 6 sides, and in the other in an 8-sided ring, and that the series should be limited in one case and unlimited in the other, involves no contradiction. Triphosphonitrilic chloride is stable only in the sense that it is formed in the largest amount and that its chlorine

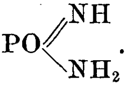
---

[1] Ann. Chem. (Liebig), Vol. CCXLVIII, p. 244.

[2] Quart. Jour. Chem. Soc. London, Vol. III, pp. 135, 354; Ann. Chem. (Liebig), Vol. LXXVI, p. 79; Vol. LXXVII, p. 315; Jour. Chem. Soc. London [2], Vol. II, p. 231.

is most tenaciously held, while the term is applied to the acids as indicating the difficulty with which the ring is broken open. In the one case, the series consists of polymers of $—PCl_2=N—$ and in the other of $—POOH—NH—$, and the two series can not therefore be considered analogous in a stereochemical sense.

Only tri- and tetrametaphosphimic acids give characteristic salts. The salts of the acids with 5, 6, and 7 atoms of phosphorus are totally devoid of crystallizing power, the alkaline salts being precipitated from aqueous solution by alcohol as sirups, which can easily be converted into the solid form by dehydration with absolute alcohol, but which are still wholly amorphous. The tendency to diminished acidity of unneutralized hydroxyls, well known in the case of orthophosphoric acid, is here apparent, and to an increasing extent as we rise in the series. Trimetaphosphimic acid forms a salt with 3 atoms of sodium which has neutral reaction and is not decomposed by strong acetic acid; tetrametaphosphimic acid readily gives salts with 2 and 4 atoms of sodium. The 5-atom sodium salt of pentametaphosphimic acid is strongly alkaline and shows a tendency to hydrolytic dissociation, and the same tendency is still more marked in the higher acids. Owing to this and to their amorphous nature it is impossible to obtain salts of definite composition from any but the first two acids unless certain conditions are rigidly adhered to. Qualitative differences between the analogous salts of the higher acids are almost wanting, and only a quantitative study and a knowledge of their derivation serve to distinguish them. As with other phosphorus-nitrogen acids, no ammonia is evolved on boiling with alkalies.

Amides of the metaphosphimic acids.—Gerhardt[1] has described, under the name "phosphamide," a body of the empirical composition PN_2OH_3, which he obtained by action of ammonia and water on phosphorus pentachloride and to which he gave the formula  $PO\begin{cases}NH\\NH_2\end{cases}$. This corresponds to the amide of a metaphosphimic acid, but its properties indicate that it is probably a substance of high molecular weight. I have attempted to obtain amides of the first three metaphosphimic acids by acting on the corresponding chloronitrides with gaseous or strong aqueous ammonia. The efforts were but partially successful. The P:N ratio is sometimes rather higher, sometimes rather lower, than is required by the formula $(PN_2OH_3)_n$. They have none of the properties of Gerhardt's phosphamide, but are extremely soluble in water, uncrystallizable, and unstable, and have weakly acid properties, forming alkali and silver salts, which, however, are of very variable composition and of ill-defined properties. Like the metaphosphimic acids, they give off no ammonia on boiling with alkali, but are easily decomposed on treatment with acids.

---

[1] Ann. Chim. Phys. [3], Vol. XVIII, p. 188.

GENERAL SUMMARY.

The principal results of the preceding investigations may be summed up as follows:

1. There exists a series of bodies of the general formula $(PNCl_2)_n$, beginning with Liebig's chloronitride of phosphorus, and extending indefinitely upward.

2. Each of these bodies yields, on saponification, an acid with the same number of phosphorus and nitrogen atoms.

3. The first four of these acids exist in two forms—the lactam form, $(PNO_2H_2)_n$ (metaphosphimic acids), where n is either 3, 4, 5, or 6, which is formed only in neutral or acid solution, and the open-chain form $(PNO_2H_2)+H_2O$, formed under the influence of alkalies.

4. The acid derived from the fifth chloronitride, $P_7N_7Cl_{14}$, and possibly those from the higher members, do not form lactams, but persist in the open form under all circumstances.

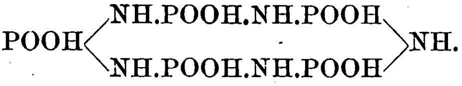
5. The properties of these acids with respect to stability, power of forming lactams, and nature of decomposition products may be explained by stereochemical considerations, analogous to those of von Baeyer on the methylene hydrocarbons and of Joh. Wislicenus on the lactones.

EXPERIMENTAL PART.

Saponification of the phosphonitrilic chlorides.—As pointed out in the preceding papers, triphosphonitrilic chloride is conveniently saponified by shaking its ethereal solution with an aqueous solution of sodium acetate, and tetraphosphonitrilic chloride in a similar manner with water, the trifling quantities of secondary decomposition products being easily removed. These methods can not be applied to the higher chlorides, for the secondary products formed by the liberated acetic or hydrochloric acid can not be separated from the main product owing to the uncrystallizable nature of the latter. A smooth saponification without secondary products may be effected by using sodium hydroxide in sufficient amount to keep the solution always strongly alkaline.

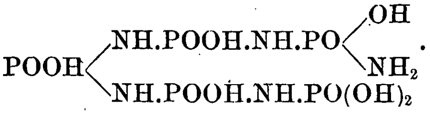
Four parts chloride are dissolved in about 20 parts alcohol-free ether and shaken with a solution of 5 parts pure sodium hydroxide in 20 parts water. A bottle with a carefully paraffined glass stopper must be used, corks being inadmissible, as they give rise to colored products which can not be removed. The shaking is conveniently effected by a rotator, moved by a small electric motor, and about fifty hours are sufficient for complete saponification. As soon as the ether is found to be practically free from chloronitrides, the alkaline solution is drawn off and precipitated by 2 or 3 volumes of alcohol. This throws down the sodium salt as a thick sirup, which is repeatedly washed by stirring with 60 per cent alcohol, dissolved in water, reprecipitated by alcohol, and again washed in the same way until it is free from sodium chloride. It is then dehydrated by stirring, kneading, and finally pulverizing under renewed portions of absolute alcohol. After standing several hours under absolute alcohol it is filtered off and dried in vacuo over sulphuric acid. The yield in each case is about 90 per cent of the theoretical, the remainder being lost in the alcoholic solution.

PENTAMETAPHOSPHIMIC ACID.



$$\mathrm{POOH}\left\langle\begin{array}{l}\mathrm{NH.POOH.NH.POOH}\\ \mathrm{NH.POOH.NH.POOH}\end{array}\right\rangle\mathrm{NH.}$$

This is the lactam of *amidotetrimidopentaphosphoric acid*,



$$\mathrm{POOH}\left\langle\begin{array}{l}\mathrm{NH.POOH.NH.PO}\left\langle\begin{array}{l}\mathrm{OH}\\ \mathrm{NH_2}\end{array}\right.\\ \mathrm{NH.POOH.NH.PO(OH)_2}\end{array}\right. .$$

It exists in the lactam form in the 5-atom silver salt and apparently in the solution of its acid and normal salts; in alkaline solutions, however, it has probably the open form, as the silver salt prepared from such a solution has a composition corresponding to this.

The free acid may be obtained, somewhat contaminated with decomposition products, by decomposing the silver salt under water by hydrogen sulphide, care being taken to keep the liquid cool. The solution has an acid, somewhat astringent, taste, and is imperfectly precipitated by alcohol in a gelatinous form, resembling precipitated alumina. This shows the reaction of the salts, but is impure, as caustic alkali causes the evolution of little ammonia.

Sodium salts.—As all the sodium salts are amorphous and precipitated by alcohol, in a sirupy or viscous form, it is not easy to obtain any of them pure. The salt prepared in the above manner contains about 5.4 atoms of sodium (analyses 1 and 2) and forms a white, sandy, amorphous powder, which is not hygroscopic, but which slowly absorbs carbon dioxide. Under water it first becomes pasty and then slowly dissolves, with considerable evolution of heat. Salts with 4 or more atoms of sodium invariably contain 2 molecules of water which are retained at 100°.

The penta-sodium salt, $P_5N_5O_{10}H_5Na_5+2H_2O$, may be obtained by adding to the solution of a salt containing a known excess of sodium nearly enough nitric acid to neutralize the excess and precipitating by alcohol, or by nearly neutralizing with acetic acid, with phenolphthalein as indicator, and precipitating by alcohol. In the latter case, however, there is a slight deficiency of sodium (analyses 3 and 4). The normal salt has a strongly alkaline reaction and loses some alkali by repeated precipitation by alcohol.

For analysis the salts were dried at 100°.

	Calculated for $P_5N_5O_{10}H_5Na_5+2H_2O$.	Found.			
		1.	2.	3.	4.
P	28.64	28.23	28.24	29.10	29.13
N	12.96	12.90	12.86	13.29	13.22
Na	21.27	22.74	22.64	21.54	20.77

1 and 2 were precipitated directly from alkaline solution.

1. P:N:Na=5:5.02:5.42.
2. P:N:Na=5:5.03:5.40.

3 and 4 were precipitated from a solution neutralized with acetic acid with phenolphthalein as indicator.

3. P: N: Na=5: 5.03: 4.75.
4. P: N: Na=5: 5.02: 4.80.

The tetra-sodium salt, $P_5N_5O_{10}H_5.Na_4H+2H_2O$, is obtained by dissolving the crude salt in water with its own weight of 80 per cent acetic acid and precipitating twice by alcohol. It resembles the normal salt, but has neutral reaction.

It gave after drying at 100°:

	Calculated for $P_5N_5O_{10}H_5.Na_4H+2H_2O$.	Found.
P	29.85	30.02
Na	17.74	17.71

P: Na=5: 3.97.

Salts with still less alkali can be obtained by precipitating the crude salt by alcohol from a nitric acid solution. This precipitate is viscous rather than sirupy, as with the salts with 4 and 5 atoms of sodium. Salts with 5 or more atoms of sodium can be kept indefinitely without alteration and do not evolve ammonia with alkalies, but those with less gradually decompose.

Barium salt.—A solution of the sodium salt gives, with barium chloride, a voluminous precipitate of unknown composition, insoluble in water and acetic acid.

Magnesium salts.—Pentametaphosphimic acid forms several salts with magnesium alone, as well as double salts with magnesium and other metals.

A solution of the sodium salt, strongly acidified with acetic acid, gives, with magnesium salts, a voluminous, amorphous precipitate, nearly insoluble in water and but slightly more soluble in strong acetic acid. The composition of this, after drying at 100°, approximates to $P_5N_5O_{10}H_5.Mg_2H+5H_2O$.

	Calculated for $P_5N_5O_{10}H_5.Mg_2H+5H_2O$.	Found.	
		1.	2.
P	29.26	28.82	29.05
Mg	9.16	9.52	10.10

1. P : Mg = 5 : 2.11.
2. P : Mg = 5 : 2.22.

A considerable portion of the acid remains in solution, however, even in the presence of a large excess of the precipitant, in combination with less than 2 atoms of magnesium, and can be precipitated by alcohol as a salt soluble in water. If this insoluble magnesium salt be dissolved in dilute nitric acid and ammonia added to incipient precipitation, the solution, after filtering, contains essentially the primary salt $(P_5N_5O_{10}H_9)_2Mg$; from this solution silver nitrate throws down an amorphous magnesium silver salt with a varying amount of silver. The primary salt is easily soluble in water and is remarkably stable, giving no precipitate with ammonia, sodium hydroxide or carbonate, even on boiling. The magnesium can be removed only by adding to its solution ammonia and an alkaline phosphate. On boiling in neutral or acetic acid solution, however, a precipitate of the 2-atom salt at once forms. Even the latter dissolves in boiling sodium carbonate solution.

Indications of an intermediate salt were observed, but it could not be isolated in pure condition.

Silver salts.—The silver salts of the phosphorus-nitrogen acids are invariably free from water, and it is upon these, therefore, that the formulas of the acids themselves are based. There is no difficulty in obtaining normal silver tri- and tetrametaphosphimates of theoretical composition, and their crystalline nature affords a guaranty of their homogeneity. The same difficulty is encountered with the silver pentametaphosphimates, however, as with the sodium salts; they are amorphous flocculent precipitates, the composition of which corresponds to a definite formula only when they are formed under special conditions. In this case, as in others in this paper, the actual percentage composition expresses very little, if compared with the calculated composition of a definite salt. It is therefore better to express the results of the analysis in a molecular formula based on the atomic ratios of phosphorus, nitrogen, and silver, as actually determined; a comparison of the percentage composition found, with that calculated for salts of the lactam and open chain acids containing phosphorus and silver in the same ratio, then shows at once to which of these acids the salt is to be referred.

The composition of the precipitates depends altogether on the relative amounts of the reacting bodies, and even the free acid can be almost completely precipitated, provided a sufficient excess of silver nitrate be used. The preparations analyzed were made by precipitating a solution of 1 gram sodium salt in 50 cubic centimeters water with 55 cubic centimeters one-fifth normal silver nitrate solution. To the sodium salt was added enough nitric acid to produce a salt of known composition. Under these conditions it was found that a salt with 4 atoms of sodium gives very nearly the normal salt, $P_5N_5O_{10}H_5Ag_5$ (analyses 3, 4, 6), the number of equivalents of silver in the precipitate always exceeding the number of equivalents of sodium. Up to 5 atoms of silver the precipitates are white; with more silver they become more and more yellow in proportion to the amount of silver they contain. An excess of 0.3 atom over the normal imparts a perceptible yellow tint. The salts are unaffected by light or by heating at 100°, and are decomposed by cold caustic alkalies[1] with separation of silver oxide.

In the following table the molecular formulas given are based on the ratio of phosphorus to silver actually determined and referred to the acids $P_5N_5O_{10}H_{10}$ and $P_5H_5O_{11}H_{12}$. A comparison shows that the salts are derivatives of the former, a true metaphosphimic acid. The salts were dried at 100°.

	Ratio P :N : Ag.		P.	N.	Ag.
1	5 :5.02 :5.18	$P_5N_5O_{11}H_{6.82}Ag_{5.18}$	16.03	7.26	57.80
		$P_5N_5O_{10}H_{4.82}Ag_{5.18}$	16.34	7.39	58.88
		Found	16.31	7.41	58.76
2	5 :5.06 :5.32	$P_5N_5O_{11}H_{6.68}Ag_{5.32}$	15.79	7.15	58.45
		$P_5N_5O_{10}H_{4.68}Ag_{5.32}$	16.09	7.28	59.55
		Found	16.04	7.35	59.37
3	5 :5.04 :4.95	$P_5N_5O_{11}H_{7.05}Ag_{4.95}$	16.45	7.45	56.66
		$P_5N_5O_{10}H_{5.05}Ag_{4.95}$	16.77	7.59	57.77
		Found	16.75	7.64	57.69
4	5 :4.96 :4.96	$P_5N_5O_{11}H_{7.04}Ag_{4.96}$	16.45	7.45	56.66
		$P_5N_5O_{10}H_{5.04}Ag_{4.96}$	16.77	7.59	57.77
		Found	16.77	7.53	57.82
5	5 :5.04 :5.15	$P_5N_6O_{11}H_{6.85}Ag_{5.15}$	16.09	7.28	57.65
		$P_5N_5O_{10}H_{4.85}Ag_{5.15}$	16.40	7.42	58.75
		Found	16.32	7.45	58.46
6	5 :5.05 :4.97	$P_5N_5O_{11}H_{7.03}Ag_{4.97}$	16.42	7.43	56.78
		$P_5N_5O_{10}H_{5.03}Ag_{4.97}$	16.74	7.57	57.89
		Found.	16.62	7.59	57.51

Tri- and tetrametaphosphimic acids, when precipitated from ammoniacal solution by excess of silver nitrate, gave amorphous yellow salts

---

[1] $P_3N_3O_6H_3Ag_3$ is scarcely affected by boiling with strong caustic potash and $P_4N_4O_8H_4Ag_4$ is scarcely affected in the cold, but is at once decomposed on boiling.

of the composition $P_3N_3O_7H_2Ag_6$ and $P_4N_4O_9H_2Ag_8$ respectively.[1] These are salts of the open-chain acids. A similar salt is obtained by precipitating an ammoniacal solution of pentametaphosphimic acid by silver nitrate, but in accordance with its less acid properties the quantity of silver does not reach 10 atoms, being in the specimen analyzed only 8.76 atoms, but the figures correspond closely to a derivative of amidotetrimidopentaphosphoric acid, $P_5N_5O_{11}H_{12}$, rather than pentametaphosphimic acid. Dried at 100° it gave:

Ratio P : Ag.		P.	Ag.
5 : 8.76	$P_5N_5O_{11}H_{3.24}Ag_{8.76}$	11.49	70.04
	$P_5N_5O_{10}H_{1.24}Ag_{8.76}$	11.64	70.98
	Found	11.48	70.03

It appears, therefore, that in alkaline solution the metaphosphimic acids become open-chain acids, just as lactones and lactams give γ- and δ-oxy- and amido-acids. On drying at 100°, the yellow silver salts become gray without loss of weight, probably owing to separation of silver oxide. This is perhaps due to a tendency to revert to the lactam form, with separation of silver oxide, rather than water.

DECOMPOSITION OF PENTAMETAPHOSPHIMIC ACID.

Pentametaphosphimic acid is markedly more stable in acid solution than trimetaphosphimic acid. In the section on the latter I described in detail its decomposition products when acted on by nitric acid. Under identical conditions the rate of decomposition of pentametaphosphimic acid was found to be very much slower. On account of this greater stability the action of hot acetic acid gives more satisfactory results. No attempt was made to isolate all the products, as these are numerous and the analytical difficulties considerable. The following were identified:

Tetrametaphosphimic acid, $P_4N_4O_8H_8$.
Triimidotetraphosphoric acid, $P_4N_3O_{10}H_9$.
Diimidotriphosphoric acid, $P_3N_2O_8H_7$.
Orthophosphoric acid, H_3PO_4.

Five parts sodium pentametaphosphimate are dissolved in 15 parts water, 5 parts strong acetic acid added, and the solution heated in the water bath. The separation of a crystalline precipitate of acid sodium tetrametaphosphimate begins in about fifteen minutes and continues for perhaps eight hours, at the end of which time the solution gives no precipitate with magnesium chloride, indicating the absence of pentametaphosphimate. The sodium tetrametaphosphimate, being insoluble in a solution of sodium salts, is completely precipitated. It is filtered off and washed a little with saturated sodium acetate solution. The

---

[1] In the third section of this paper the formula $P_4N_4O_8Ag_8$ was ascribed to the per-silver salt of tetrametaphosphimic acid; a recalculation of the analyses in the above manner, however, shows that they correspond much more closely to the open form $P_4N_4O_9H_2Ag_8$, with a slight deficiency of silver.

filtrate is concentrated to about one-half with addition of about 5 parts solid sodium acetate, whereby sodium triimidotetraphosphate separates, in the form of flat prisms or plates, which are washed with a little saturated sodium acetate solution and purified by dissolving in water and precipitating by alcohol, or by adding solid sodium acetate to their hot solution. On further concentrating the filtrate, large plates are often obtained, which give, with silver nitrate and nitric acid, a crystalline precipitate of the characteristic silver diimidotriphosphate, $P_3N_2O_8H_4Ag_3$. No satisfactory and certain method can be given for the separation of these two acids.

The *sodium tetrametaphosphimate* thus obtained usually has the form of spindles, but, when well developed, consists of brilliant double pyramids. It had not been observed at the time of writing the paper on tetrametaphosphimic acid. It is obviously an acid sodium salt, as it is formed only in the presence of acetic acid or a limited amount of a stronger acid. It was also obtained directly from the original sample of the acid, but was not analyzed, as it is difficult to obtain a sufficient quantity uncontaminated by the free acid. It is moderately soluble in water, but almost insoluble in solutions of sodium salts and is highly characteristic of this acid. The crude salt was dissolved in ammonia, with the addition of some ammonium nitrate, and precipitated by nitric acid as $P_4N_4O_8H_6(NH_4)_2$. The precipitation is almost quantitative. This pure salt was dissolved in ammonia, largely diluted, and, after acidifying with nitric acid, precipitated by an excess of silver nitrate in the form of the characteristic $P_4N_4O_8H_4Ag_4$. This gave:

	Calculated for $P_4N_4O_8H_4Ag_4$.	Found.
P	16.68	16.88
N	7.55	7.56
Ag	58.03	57.51

The free acid was obtained by decomposing the silver salt with hydrochloric acid in the characteristic form of difficultly soluble needles. It gave:

	Calculated for $P_4N_4O_8H_8+2H_2O$.	Found.
P	35.22	35.08
N	15.94	15.75

A comparison of the acid potassium, sodium, and ammonium salts and neutral ammonium salt with those prepared from a sample of tetrametaphosphimic acid from tetraphosphonitrilic chloride showed them to be identical in form. The yield of tetrametaphosphimic acid appears to be nearly independent of proportions and concentration, and was about 12 per cent of that required by the equation

$$P_5N_5O_{10}H_{10} + 2H_2O = P_4N_4O_8H_8 + NH_4H_2PO_4.$$

Triimidotetraphosphoric acid, $PO(OH)_2.NH.POOH.NH.POOH.NH.PO(OH)_2$.—The sodium salt of this, the third member of the imidophosphoric acid series obtained, crystallizes well in small rhombic or six-sided plates. The several specimens obtained were not analyzed, but converted into the silver salt. By analogy with $P_3N_2O_8H_7$, there can be little doubt that it is the acid salt, $P_4N_3O_{10}H_5Na_4$. It is easily soluble in water, but almost insoluble in saturated sodium acetate solution or dilute alcohol. It gives a precipitate with magnesium nitrate only on adding ammonia and ammonium chloride, when a voluminous precipitate is obtained, which, on standing, slowly changes to minute crystalline spherules.

Silver triimidotetraphosphate, $P_4N_3O_{10}H_5Ag_4$, is obtained as a voluminous amorphous white precipitate by adding silver nitrate to a solution of the sodium salt faintly acidified with nitric acid. On long standing under its mother-liquor it becomes crystalline and this change occurs in a few moments on washing the precipitate, shrinking to a heavy, sandy, crystalline powder, a very characteristic behavior. The same change can be observed under the microscope in the partially washed salt, the amorphous portion changing to minute particles showing active Brownian movement, which aggregate to prisms which are long and pointed and often tufted at the ends, and which can not be distinguished in appearance from silver tetrametaphosphimate. From a decidedly acid solution the salt is deposited slowly and without the intermediate amorphous form.

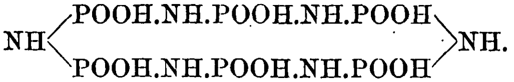
The salt gave after drying at 100°:

	Calculated for $P_4N_3O_{10}H_5Ag_4$.	Found.	
		1.	2.
P	16.26	16.43	16.48
N	5.52	5.62	5.55
Ag	56.58	56.61	57.18

1. P:N:Ag=4:3.03:3.96.
2. P:N:Ag=4:2.98:3.99.

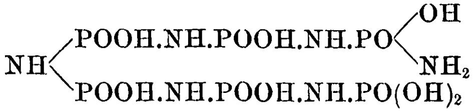
Triimidotetraphosphoric acid could not be obtained from tetrametaphosphimic acid, being much less stable than the latter. It is therefore probably derived from the breaking down of the chain of phosphorus and nitrogen atoms formed by the hydrolysis of the pentametaphosphimic ring.

HEXAMETAPHOSPHIMIC ACID.



$$\mathrm{NH}\left\langle\begin{array}{l}\mathrm{POOH.NH.POOH.NH.POOH}\\ \mathrm{POOH.NH.POOH.NH.POOH}\end{array}\right\rangle\mathrm{NH.}$$

This is the lactam of *amidopentimidohexaphosphoric acid*,



$$\mathrm{NH}\left\langle\begin{array}{l}\mathrm{POOH.NH.POOH.NH.PO}\left\langle\begin{array}{l}\mathrm{OH}\\ \mathrm{NH_2}\end{array}\right.\\ \mathrm{POOH.NH.POOH.NH.PO(OH)_2}\end{array}\right.$$

It is obtained as sodium salt by saponifying hexaphosphonitrilic chloride in ethereal solution by sodium hydroxide in the manner above described. In neutral or acid solution it has the lactam form, as shown by the composition of the silver salt, but in alkaline solution it has presumably the open form. The free acid, obtained in solution by decomposing the silver salt under water by hydrogen sulphide, has an astringent rather than acid taste, and can not be obtained pure in the solid form, as it is not precipitated by alcohol, and the solution, on evaporating, undergoes much decomposition, leaving a gummy residue.

Sodium hexametaphosphimate, $P_6N_6O_{12}H_6Na_6 + 2H_2O$.—The properties of this salt are essentially the same as those of the corresponding pentametaphosphimate. When containing an excess of alkali it is stable, but with a deficiency it decomposes more or less rapidly. A salt of approximately normal composition can be obtained by adding to the solution of a preparation with more than 6 atoms of sodium enough nitric acid to neutralize the excess and precipitating by alcohol (analyses 3 and 4). In the following table the results are expressed in formulas based on the determined ratio P : Na. The samples were dried at 100°.

	Ratio P : N : Na.		P.	N.	Na.
1	6 : 6.02 : 6.35	$P_6N_6O_{12}H_{5.65}Na_{6.35}+2H_2O$	28.62	12.95	22.50
		Found	28.55	12.96	22.45
2	6 : : 6.46	$P_6N_6O_{12}H_{5.54}Na_{6.46}+2H_2O$	28.51	....	22.80
		Found	28.31	....	22.63
3	6 : 6.04 : 5.93	$P_6N_6O_{12}H_{6.07}Na_{5.93}+2H_2O$	29.02	13.14	21.31
		Found	29.13	13.27	21.38
4	6 : 6.05 : 5.94	$P_6N_6O_{12}H_{6.06}Na_{5.94}+2H_2O$	29.02	13.14	21.31
		Found	29.16	13.29	21.43
5	6 : : 4.60	$P_6N_6O_{12}H_{7.40}Na_{4.60}+2H_2O$	31.05	....	17.70
		Found	30.89	....	17.60

1 and 2 precipitated from solution containing excess of alkali; 3 and 4, from solution in which excess over 5 Na had been neutralized; 5, from solution in large excess of acetic acid.

Magnesium salt.—A solution of the sodium salt precipitated by magnesium nitrate in the presence of acetic acid, under exactly the same conditions as were observed in preparing the corresponding pentametaphosphimate, gave a salt which closely resembles the latter, but which does not approximate to any definite formula (found P : Mg = 6 : 2.43). The precipitation is by no means complete, much remaining in solution as a salt which can be precipitated by alcohol, which is not decomposed by boiling with alkalies, and which, in general, resembles the primary salt of pentametaphosphimic acid.

Silver hexametaphosphimate, $P_6N_6O_{12}H_6Ag_6$.—The silver salt prepared from the sodium salt varies in composition with the relative amounts of the reacting bodies and with the amount of sodium. It was obtained of normal composition by dissolving 1 gram sodium salt in 50 cubic centimeters water, adding enough nitric acid to produce a salt with 5.75 atoms of sodium, and precipitating by 50 cubic centimeters one-fifth normal silver nitrate (analyses 3 and 4). It resembles the corresponding pentametaphosphimate, but is somewhat more gelatinous. Any excess of silver over 6 atoms tends to give it a yellow color. It is decomposed in the cold by caustic potash with separation of silver oxide. The analyses given in the following table of preparations dried at 100° show that it is derived from the true hexametaphosphimic acid, $P_6N_6O_{12}H_{12}$.

	Ratio P : N : Ag.		P.	N.	Ag.
1	6 : 6.08 : 5.65	$P_6N_6O_{13}H_{8.35}Ag_{5.65}$	16.97	7.68	55.60
		$P_6N_6O_{12}H_{6.35}Ag_{5.65}$	17.26	7.81	56.53
		Found	17.23	7.89	56.48
2	6 : : 6.21	$P_6N_6O_{13}H_{7.79}Ag_{6.21}$	16.09	....	57.97
		$P_6N_6O_{12}H_{5.79}Ag_{6.21}$	16.35	....	58.89
		Found	16.29	....	58.64
3	6 : 5.99 : 5.98	$P_6N_6O_{13}H_{8.02}Ag_{5.98}$	16.44	7.44	57.02
		$P_6N_6O_{12}H_{6.02}Ag_{5.98}$	16.71	7.56	57.95
		Found	16.70	7.54	57.90
4	6 : 6.04 : 6.02	$P_6N_6O_{13}H_{7.98}Ag_{6.02}$	16.38	7.41	57.18
		$P_6N_6O_{12}H_{5.98}Ag_{6.02}$	16.65	7.54	58.02
		Found	16.57	7.54	57.80

A yellow salt is obtained by precipitating the ammoniacal solution by silver nitrate.

Decomposition of hexametaphosphimic acid.—The sodium salt heated with acetic acid gives tetrametaphosphimic acid, which was isolated in the manner described above. The yield is 30 per cent of that required by

$$P_6N_6O_{12}H_{12} + 4H_2O = P_4N_4O_8H_8 + 2NH_4H_2PO_4.$$

After purifying, it was converted into the silver salt, which gave:

	Calculated for $P_4N_4O_8H_4Ag_4$.	Found.
P	16.68	16.63
N	7.55	7.50
Ag	58.03	57.58

P : N : Ag = 4 : 3.99 : 3.98.

Comparison of the crystals of free acid and of the acid and neutral ammonium salts, acid potassium salt, neutral sodium salt, and silver salt with similar preparations made from tetraphosphonitrilic chloride showed that they were identical.

The decomposition products were not further studied.

AMIDOHEXIMIDOHEPTAPHOSPHORIC ACID, $P_7N_7O_{15}H_{16}$.

The saponification of heptaphosphonitrilic chloride is effected in the usual manner with sodium hydroxide. As before pointed out, this acid does not give the lactam, heptametaphosphimic acid, even in acid solution, the silver salt having the composition of a salt of the open-chain acid.

Sodium salt.—The properties of this salt are similar to those of sodium penta- and hexametaphosphimate. Dried in vacuo and at 100°, it gave:

	Calculated for $P_7N_7O_{15}H_{8 \cdot 57}Na_{7 \cdot 43} + 2H_2O$.	Found.
P	28.16	28.31
Na	22.19	22.31

P : Na = 7 : 7.43.

Silver salt, $P_7N_7O_{15}H_9Ag_7$.—To obtain a salt of normal composition, 1 gram sodium salt is dissolved in 50 cubic centimeters water, enough nitric acid is added to form a salt with 6.85 atoms of sodium, and precipitated by 50 cubic centimeters one-fifth normal silver nitrate. More sodium or silver nitrate gives a salt richer in silver. The salt forms a white semigelatinous precipitate, which dries in vacuo to translucent brittle lumps, which were pulverized, dried again in vacuo and then carefully to constant weight at 100°.

	Ratio P : N : Ag.		P.	N.	Ag.
1	7 : : 6.93	$P_7N_7O_{15}H_{9.07}Ag_{6.93}$	16.55	....	56.99
		$P_7N_7O_{14}H_{7.07}Ag_{6.93}$	16.77	....	57.77
		Found	16.44	....	56.61
2	7 : : 7.21	$P_7N_7O_{15}H_{8.79}Ag_{7.21}$	16.17	....	57.97
		$P_7N_7O_{14}H_{6.79}Ag_{7.21}$	16.40	....	58.76
		Found	16.21	....	58.09
3	7 : : 7.08	$P_7N_7O_{15}H_{8.92}Ag_{7.08}$	16.35	....	57.51
		$P_7N_7O_{14}H_{6.92}Ag_{7.08}$	16.57	....	58.30
		Found	16.27	....	57.27
4	7 : 7.04 : 7.03	$P_7N_7O_{15}H_{8.97}Ag_{7.03}$	16.41	7.43	57.35
		$P_7N_7O_{14}H_{6.97}Ag_{7.03}$	16.64	7.53	58.16
		Found	16.35	7.44	57.14

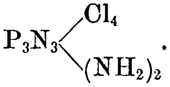
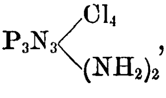
These figures show beyond question that the acid has the open form $P_7N_7O_{15}H_{16}$.

The decomposition of the sodium salt by acetic acid gives rise to a considerable amount of tetrametaphosphimic acid, characterized by its crystalline form and that of its salts.

HIGHER ACIDS.

Of the higher acids of the series but little can be said. The oil remaining over from preparation of chloronitrides, and which has a mean molecular weight nearly corresponding to $P_{11}N_{11}Cl_{22}$, on saponification gives a mixture of sodium salts which are precipitated by alcohol in a decidedly viscous form, and which are decomposed by acids, giving tetrametaphosphimic, diimidotriphosphoric, and triimidotetraphosphoric acids. They were not further investigated.

AMIDES OF METAPHOSPHIMIC ACIDS.

Amides of $P_3N_3O_6H_6$.—Strong ammonia gas acts slowly on a solution of $P_3N_3Cl_6$ in absolute ether, the product being at first ammonium chloride and the chloramide,  $P_3N_3\begin{cases}Cl_4\\(NH_2)_2\end{cases}$. This remains in solution and is gradually attacked further, but is the only product of the reaction which is soluble in ether; by further action of ammonia the chlorine is further substituted, but never completely, and the reaction product is thrown down, mixed with ammonium chloride. On washing this with alcohol, dissolving in water, and treating with enough silver nitrate to precipitate the chlorine, a solution is obtained which, by fractional precipitation with silver nitrate, gave the silver salt of an amide with the ratio P : N : Ag = 3 : 6.27 : 2.01. An ethereal solution of  $P_3N_3\begin{cases}Cl_4\\(NH_2)_2\end{cases}$, shaken with sodium hydroxide, gives the sodium salt of the diamide of trimetaphosphimic acid, from which the chlorine may be removed by neutralizing with nitric acid and adding the calculated amount of silver nitrate. From the filtrate an amorphous silver salt may be precipitated which gave the ratio P : N : Ag = 3 : 4.88 : 3.51. If $P_3N_3Cl_6$, $P_4N_4Cl_8$, or $P_5N_5Cl_{10}$ in ethereal solution is shaken with ammonia of sp. gr. 90, a strong reaction occurs at first, whereby a portion of the chlorine is replaced. On shaking two or three hours, the remainder is removed. The excess of ammonia was removed from the aqueous solution by blowing air through and the chlorine precipitated by the theoretical amount of silver nitrate. The ammonium salts of the amides thus obtained were thrown down by alcohol as sirups which can not be hardened under absolute alcohol. If these solutions are precipitated by silver nitrate, after adding a little ammonia, amorphous white precipitates of the amido silver salts are obtained, which do not show a constant composition. Analysis gave the following atomic ratios:

$$\text{Amide from } P_3N_3Cl - P : N : Ag = \begin{cases} 3 : 5.80 : 2.20 \\ 3 : 5.96 : 3.36 \\ 3 : 6.54 : 3.08 \end{cases}$$

$$\text{Amide from } P_4N_4Cl_8 - P : N : Ag = \begin{cases} 4 : 8.80 : 4.82 \\ 4 : 9.28 : 4.03 \end{cases}$$

$$\text{Amide from } P_5N_5Cl_{10} - P : N : Ag = 5 : 10.16 : 2.64$$

From these figures it appears that the amides are of very varying composition. As they are amorphous and very unstable, it is unlikely that any definite bodies can be obtained in this way. The silver salts are turned yellow by potassium hydroxide, a portion of the amide going into solution and a salt with a higher proportion of silver being formed.

ON A HYDROMICA FROM NEW JERSEY.

By F. W. CLARKE and N. H. DARTON.

While studying the Juratrias formation in New Jersey, one of us (Darton) found in an old "trap" quarry at Rocky Hill a hydromica, which occurred under such novel conditions that it appeared to be worthy of investigation. It is found in veins of calcite, mainly as a thin coating, and adjacent to the diabase of the vein walls. The latter consist of more or less decomposed rock, of which the principal product is a soft, dark-green chloritic material. In portions of the vein the mica extends down the cleavage planes into the masses of calcite. A considerable amount of the calcite was thrown out during the quarrying operations, but only a portion of it is covered with the mica. This portion presents the appearance of having been coated with bronze paint.

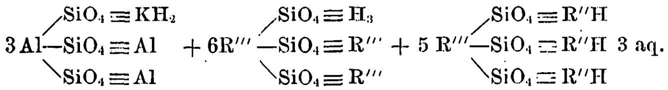
The mica occurs in minute flakes thinly matted together. Its color is golden bronze, although some portions are slightly greenish. The mineral is soft, and thinly foliated. Under the microscope it exhibits no definite crystalline form; and its optical properties, although not distinctive, suggest biotite. It appears to be biaxial, but with a very small axial angle, and it is pleochroic. When heated, it does not exfoliate. It fuses before the blowpipe, at a moderately high temperature, to a dark-colored bead. The specific gravity was not determined. It is readily decomposable by hydrochloric acid. The analysis, by Mr. George Steiger, of material not free from calcite is subjoined. In the second column of figures the reduced analysis is given, titanic oxide and calcite being thrown out, soda recalculated to terms of potash, and the whole adjusted to 100 per cent.

	Found.	Reduced.	Ratios.
SiO_2	32.72	40.24	.671
TiO_2	.24		
Al_2O_3	8.41	10.34	.101
Fe_2O_3	19.99	24.57	.154
FeO	4.24	5.21	.072
CaO	10.30		
MgO	5.51	6.78	.166
K_2O	.85	2.20	.024
Na_2O	.63		
CO_2	8.21		
H_2O at 100°	2.47	3.03	.168
H_2O above 100°	6.22	7.63	.424
	99.79	100.00	

This gives, as an orthosilicate, the formula

$$(KH)_{68}(MgFe)_{24}(AlFe)_{51}(SiO_4)_{67}.\quad 28H_2O.$$

It is evident, from these data, that the mica is one which has been largely, but not wholly, altered to a vermiculite; the latter term indicating a mica in which potassium has been replaced by hydrogen, and which has taken up water of crystallization. So far as the analysis goes, the condition of the water is uncertain; for it was determined in two fractions only, at and above 100°, whereas more fractions are needed for accurate diagnosis. Some crystalline water may be retained far above 100°, so that the loss above that temperature includes part of this fraction plus all the water of constitution. Apart from this uncertainty the ratios reduce easily in terms of the mica theory to the following molecular mixture:



$$3\,Al\begin{cases}SiO_4 \equiv KH_2\\ SiO_4 \equiv Al\\ SiO_4 \equiv Al\end{cases} + 6R'''\begin{cases}SiO_4 \equiv H_3\\ SiO_4 \equiv R'''\\ SiO_4 \equiv R'''\end{cases} + 5\,R'''\begin{cases}SiO_4 \equiv R''H\\ SiO_4 \equiv R''H\\ SiO_4 \equiv R''H\end{cases} 3\text{ aq.}$$

Calculating with the atomic ratios Al : Fe''' : : 2 : 3, and Fe'' : Mg : : 3 : 7, we have the following comparison between analysis and theory:

	Reduced.	Calculated.
SiO_2	40.24	40.55
Al_2O_3	10.34	10.51
Fe_2O_3	24.57	24.71
FeO	5.21	5.21
MgO	6.78	6.75
K_2O	2.20	2.27
H_2O, 100°	3.03	*a*4.34
H_2O, above 100°	7.63	*b*5.66
	100.00	100.00

a Crystalline. *b* Constitutional.

In short, the mica consists of muscovitic and phlogopitic molecules in the ratio of 9 : 5.

$$9\,R'''_3(SiO_4)_3R'_3,$$
$$5\,R'''(SiO_4)_3R''_3H_3,\ 3\text{ aq.}$$

The mineral is evidently an unusual mica, differing widely from any other hitherto described. Its very high proportion of ferric oxide is its chief characteristic, and suggests a ferric muscovite as one of the antecedent, unaltered molecules. Such a muscovite is theoretically conceivable, but is not actually known.

THE ALKALINE REACTION OF SOME NATURAL SILICATES.

By F. W. Clarke.

That pure water exerts a distinct solvent action upon many natural silicates has long been known. As far back as 1848 the Rogers brothers published a series of observations upon this subject,[1] and showed that some species of minerals would give an alkaline reaction to test paper. They did not, however, give details concerning the individual minerals thus investigated. The more recent researches of Daubrée and of Cossa are well known.

By the use of phenolphthalein as an indicator the alkalinity of many silicates can be demonstrated with the utmost ease, and the experiments described below serve to bring out very clearly the relative decomposability of certain minerals and rocks by pure water. The method adopted was as follows: A series of glass-stoppered bottles was placed against a white background. In each bottle half a gram of finely pulverized mineral was put, and then 50 cubic centimeters of distilled water, containing a very little alcoholic phenolphthalein, was added. As the indicator was mixed, once for all, with the total amount of water taken for the entire series, the 22 samples examined were treated exactly alike. Two of the bottles were filled with the water and indicator in blank, in order that possible action upon the glass itself might be detected if it occurred. The two blanks, however, remained colorless during the two weeks through which the experiments lasted. The results obtained were as follows:

Muscovite.—A doubtful trace of coloration, which soon disappeared.

Lepidolite.—Like muscovite.

Phlogopite.—The peculiar nonfluoriferous variety from Edwards, New York. Gave a very distinct, permanent pink coloration.

Orthoclase.—A trace of coloration which increased for a few days and then faded.

Oligoclase.—The transparent variety from Bakersville, North Carolina. Distinct and permanent, but pale coloration.

Albite.—From Amelia County, Virginia. Gave a good, permanent, alkaline reaction.

Leucite.—A slight reaction at first, which faded in a few days.

Nephelite.—The elæolite from Litchfield, Maine. Good coloration, but partly fading in time.

---

[1] Am. Jour. Sci., 2nd series, Vol. V, p. 401.

Cancrinite.—Litchfield, Maine. Gives a deep rose coloration, which is permanent.

Sodalite.—From Canada. A deep, permanent rose color.

Spodumene.—The transparent, yellow variety from Brazil. A good reaction, but gradually fading.

Scapolite.—The wernerite from St. Lawrence County, New York. Gave a faint, evanescent trace of coloration.

Laumontite.—A doubtful trace of coloration.

Stilbite.—Faint, evanescent coloration.

Chabazite.—Like stilbite.

Heulandite.—Slight reaction, but distinct.

Thomsonite.—Variety lintonite. A fairly strong reaction, fading in time.

Analcite.—Good alkaline reaction.

Natrolite.—From Bohemia. Strong coloration, permanent.

Pectolite.—From Bergen Hill. Gave a very deep rose-color.

Apophyllite.—From Bergen Hill. A very deep rose color.

In nearly every case the reaction was obtained at once, showing a more rapid action of water upon the silicate than had been anticipated. In some instances fading is noted. This is doubtless due, in general, to the action of light, but in certain cases the colored solution separated into two layers, the color being wholly in the lower. Here the color was really held as a coating upon the fine solid particles, and as they subsided the appearance of stratification was produced. Toward the end of the experiments the mineral aegirite was added to the series. This also gave a strong alkaline reaction and a fairly deep rose color.

A neat method of demonstrating the reactions described above is the following: Place a little of the mineral to be tested in a watch glass upon a sheet of white paper. Add a drop of alcoholic phenolphthalein solution, and then a few drops of pure water; in most cases the reaction is given instantaneously. Orthoclase gave no coloration, leucite a trace, and scapolite a trace; albite, nephelite, and phlogopite furnished distinct reactions. Under the same circumstances thomsonite, aegirite, natrolite, cancrinite, sodalite, pectolite, and apophyllite gave immediately a deep, rich, rose color. The strongest alkaline reactions seemed to be given by pectolite and apophyllite.

In general the order of intensity of the color produced was what might have been expected. Among the micas, muscovite and lepidolite showed little or no solubility, while phlogopite was distinctly attacked. In nature the magnesian micas are far more easily alterable than muscovite, a fact which is reiterated by these experiments. Again, orthoclase was slightly dissolved, albite much more so, and oligoclase gave a reaction between the two; that is, more than the one, less than the other. In other words, the plagioclase feldspars alter more easily than orthoclase, as is apparent in the study of the rocks themselves.

In order to bring out the latter point more clearly, a series of rocks which had been analyzed in the laboratory of the United States Geological Survey was placed in a row of bottles and treated, just as the mineral species had been, with water and phenolphthalein. A granite and an amphibole-gabbro gave no alkaline reaction. A rhyolite, trachyte, leucite-basalt, feldspar-basalt, and diorite gave faint traces of color. Granitite, gneiss, phonolite, diabase, and camptonite yielded distinct alkaline colorations.

In all of these instances the production of color is doubtless due to the solution from the mineral or rock of alkaline silicates. The noteworthy point is the quickness with which the reaction can be obtained. With minerals like cancrinite, sodalite, natrolite, pectolite, and apophyllite, the reaction is striking enough to be used as a lecture-table experiment.

THE SOLUBILITY IN WATER OF CERTAIN NATURAL SILICATES.

By George Steiger.

The results cited in the preceding paper are purely qualitative in character. The following experiments are analogous in kind, but are aimed at putting the subject on a quantitative basis. In both investigations the same samples of material were employed, so that the data are fairly comparable.

The work was carried out as follows: One-half gram of each of the finely ground minerals was weighed out, and placed in a 2-ounce bottle with 50 cubic centimeters of water. These bottles were set aside where the temperature remained about 70° F. for one month, and were skaken from time to time. At the end of the period all were filtered, and the solutions were titrated with a standard hydrochloric acid solution, methyl-orange being used for an indicator.

What has gone into solution by this treatment I can not say—sometimes soda, sometimes potash, possibly sometimes lime, but for the sake of comparison the results in the following table have been calculated in terms of Na_2O; although the percentage of sodium is very small in some of the specimens. I have given also in another column the percentage of the combined alkalies as shown by analysis of specimens from the same localities.

	Formula.	Per cent of combined alkalies by analysis.	Equivalent of Na_2O in solution.
Pectolite, Bergen Hill, N. J	$Ca_2(SiO_3)_3NaH$	9.11	0.57
Muscovite	$Al_3(SiO_4)_3KH_2$	10.00	.32
Natrolite, New Jersey	$Al_2(SiO_4)_3Na_2H_4$	15.79	.30
Lintonite, Lake Superior	$Al_6(SiO_4)_6(CaNa_2)_3.7H_2O$	5.92	.29
Phlogopite, Edwards, N. Y	$Al(SiO_4)_3Mg_3KH_2$	9.32	.22
Laumonite	$Al_2SiO_4Si_3O_8Ca.4H_2O$	1.00	.18
Lepidolite, Maine	$KHLiAl_3(SiO_4)_3$ $K_3Li_3(AlF_2)_3Al(Si_3O_8)_3$	13.00	.18
Elæolite, Litchfield, Me	$Al_3(SiO_4)_3Na_3$	21.17	.16
Heulandite, Nova Scotia	$Al_6(Si_3O_8)_6(CaNa_2)_3.16H_2O$	2.00	.13
Orthoclase	$KAlSi_3O_8$	16.00	.11

	Formula.	Per cent of combined alkalies by analysis.	Equivalent of Na_2O in solution.
Analcite	$NaAl(SiO_3)_2.H_2O$	14.00	.10
Oligoclase, Bakersville, N. C.	$AlNaSi_3O_8$ $Al_2CaSi_2O_8$	9.18	.09
Albite	$AlNaSi_3O_8$	12.10	.07
Wernerite, St. Lawrence County, N. Y.	$Ca_4Al_6Si_6O_{25}$ $Na_4Al_3Si_9O_{24}Cl$	11.09	.07
Leucite, Vesuvius, Italy	$KAl(SiO_3)_2$	21.39	.06
Stilbite, Nova Scotia	$Al_2(Si_3O_8)_2(CaNa_2).6H_2O$	1.00	.05
Chabazite, Nova Scotia	$Al_2SiO_4Si_3O_8(CaNa_2).6H_2O$	7.10	.05

It is worth noting in comparing the depth of color produced by phenolphthalein solution, as shown in Professor Clarke's paper, with the percentage of alkali in solution as shown in this work, that some of the minerals which give a deep coloration with the former, show in the above table a comparatively small amount of alkali in solution, and vice versa. Muscovite, for example, while giving only a faint coloration with phenolphthalein, contains in solution alkaline compounds equivalent to 0.49 per cent K_2O; pectolite, with 0.57 per cent Na_2O, being the only one of the series showing a larger amount. The cause of these discrepancies remains to be ascertained.

INDEX.