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J. W. POWELL, DIRECTOR

REPORT OF WORK DONE

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FRANK WIGGLESWORTH CLARKE

CHIEF CHEMIST

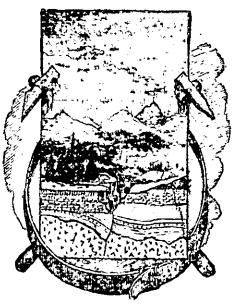

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ILLUSTRATION.

LETTER OF TRANSMITTAL

DEPARTMENT OF THE INTERIOR,
UNITED STATES GEOLOGICAL SURVEY,
DIVISION OF CHEMISTRY,
Washington, D. C., October 7, 1893.

SIR: The accompanying bulletin, like its predecessors, Bulletins 9, 27, 42, 55, 60, 64, 78, and 90, contains an account of the miscellaneous investigations carried out in the Division of Chemistry during the stated time. Hitherto these bulletins have been annual, but the present one, for various reasons, represents two years of work. A year ago, when the usual bulletin fell due, a great reduction was made in the resources of the division, the force was largely cut down, and the laboratory was removed to its present quarters in the building occupied by the main offices of the Survey. At the end of the fiscal year 1891–'92 several of the investigations intended for its bulletins were not quite complete, and as the year following was evidently to be one of much smaller output, it seemed best to finish the work on hand and to consolidate both years in one report.

In one other respect the present report differs from its predecessors. Hitherto, under the heading "Miscellaneous analyses," a large volume of routine work has been recorded. This work, however, finds its proper publication in the memoirs of the geologists and petrographers of the Survey, and it is now omitted from the report of this division. Only those miscellaneous analyses which directly pertain to the work of the chemical division appear in its published record. The physical investigations carried out by Dr. Barus also appear in separate form in several independent bulletins.

Very respectfully,

F. W. CLARKE,
Chief Chemist.

Hon. J. W. POWELL,
Director U. S. Geological Survey.

WORK DONE IN THE DIVISION OF CHEMISTRY IN 1891–'92 AND 1892–'93.

TSCHERMAK'S THEORY OF THE CHLORITE GROUP AND ITS ALTERNATIVE.

By F. W. Clarke.

In the micas, vermiculites, the clintonite group, and the chlorites, we meet a large number of minerals having similar properties. All are probably monoclinic, all are commonly foliated in structure, and within certain limits they shade into each other in composition. Their external resemblances are very close, and it is therefore a fair presumption that they are also alike in constitution. A satisfactory explanation of their chemical structure ought to emphasize their obvious relationships and be sufficiently general to include all the individual species in a single definite theory. The problem is easily stated, but its solution can be effected only by slow degrees. Like other similar problems, it must be solved by a series of approximations; and every step towards order is a gain, even though it be not absolutely final.

Among the men who have advanced our knowledge of these minerals, no one is entitled to higher credit than Professor Tschermak. His successive papers upon the mica, clintonite, and chlorite groups have all been long strides forward; and whether his interpretations are ultimately confirmed or abandoned, they have none the less been of real service in the development of knowledge.

In his latest paper,[1] Professor Tschermak seeks to explain the chemical structure of the chlorites, and masses the available evidence most admirably. This group of minerals he divides into two subgroups, called orthochlorites and leptochlorites, respectively, and for each division a special explanation is offered. The orthochlorites, which include pennine, clinochlore, leuchtenbergite, prochlorite and corundophilite, are simply represented as mixtures of two end products, serpentine and amesite; and so far as the mere ultimate composition of the minerals is concerned, the interpretation is quite satisfactory. On theoretical grounds it leaves something to be desired, as will appear later. The leptochlorites, however, or chlorites outside of the main series, are less easily handled; and for these, in addition to the serpentine

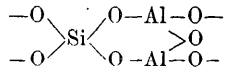
[1] Die Chloritgruppe. II Theil. Sitzungsb. Akad. d. Wiss. in Wien, 19 Feb. 1891.

and amesite molecules, four other fundamental compounds are assumed, namely, two derivatives of amesite, strigovite, and chloritoid. Six types of molecule are, in all, adopted, which, by mixtures in various proportions, account for all the species. Written semiempirically, these molecules are as follows:

Serpentine,	Sp.	$MgSi_2O_7 . H_2 . (MgOH)_2$
Amesite,	At.	$Al_2SiO_7 . H_2 . (MgOH)_2$
" 1st deriv.,	At'.	$Al_2SiO_7 . H_3 . MgOH$
" 2d "	At''.	$Al_2SiO_7 . H_4$
Strigovite,	St. SiO_2.	$Al_2SiO_7 . H_2 . (MgOH)_2$
Chloritoid,	Ct.	$Al_2SiO_7 . H . Mg$

Of these compounds, four are represented by known minerals, although the amesite and strigovite formulæ rest each upon a single analysis. Two, the molecules At' and At'', are hypothetical. Empirically, all the chlorites of well-established character correspond in composition to mixtures of these six molecules; but a few of the allied minerals, such as epichlorite and stilpnomelane, are unaccounted for. The latter are yet to be brought into line.

At a first glance the six molecules, as just written, appear to be remarkably alike in form. But when they are written structurally, as Tschermak himself writes them, they become somewhat dissimilar. Serpentine is then represented as a salt of the acid $H_6Si_2O_7$. Amesite, with its two derivatives and chloritoid, appear as basic orthosilicates. Strigovite is given as a salt of the acid $H_4Si_2O_6$. That is, three different silicic acids are involved in Tschermak's theory, and the first apparent simplicity of the scheme disappears. All of the six molecules, however, with the single exception of the nonaluminous serpentine, are supposed to contain the structural nucleus



to which the remarkable similarities of the chlorites may be due. Through chloritoid the chlorites become affiliated with the clintonite group; but with the micas, at least as the latter have been interpreted by Tschermak hitherto, no special analogies of structure appear.

Now, admitting that Tschermak's theory accounts for the known facts as fully as he believes, the question arises whether his mode of interpretation is the only one possible. If it is, then the problem of the chlorite group is solved, and controversy is out of court. But if other schemes can be devised, representing the facts equally well, further investigation becomes necessary. Pending the acquirement of new experimental evidence, we may discuss rival systems upon philosophic grounds; and that which is simplest, most general, and best supported by analogies, should have preference. Ultimately, of course, the problem must be attacked by means of experiment, through which alone the questions at issue can be finally settled.

In several previous papers, some of them written in joint authorship with others,[1] I have sought to establish the hypothesis that the more complex silicates are merely substitution derivatives of normal salts. For instance, many minerals are easily and naturally represented as so derived from the normal aluminum compound $Al_4(SiO_4)_3$; successive aluminum atoms being equivalently replaced by other atoms or groups. Among these minerals, the micas seem to form a conspicuous family, and with them are found the clintonite group and some vermiculites. To this family I shall recur later.

In two quite recent papers, Schneider and I have tried, by experimental methods, to obtain some positive evidence as to the nature of the chlorites. That our results are not final, and that Tschermak's criticism of them is perfectly legitimate, I cheerfully concede, and yet we have found clues which are not without meaning. The reaction between dry hydrochloric acid and the hydromagnesian silicates we are still investigating, and its actual character and significance we hope to determine in due time. So far, however, in every case of a true chlorite examined by us, and in the case of serpentine also, we have found that the chemical constitution *may* be represented by a mixture of molecules of the general form $Mg_2(SiO_4)_2\,R'_4$, in which R′ may be either AlH_2O_2, MgOH, or H, with of course the usual equivalent replacements of aluminum and magnesium by ferric and ferrous iron. These molecules are evidently substitution derivatives of the normal compound olivine, when the ordinary formula of the latter is doubled and made $Mg_4(SiO_4)_2$. Since we do not know the true molecular weight of any metallic silicate, this doubling of the simplest possible formula is perfectly allowable, and a reason for it will appear later. Here, then, for a few chlorites at least, is a scheme of interpretation quite unlike Tschermak's; and we have to determine whether it is equally exact and equally general.

Taking Tschermak's paper as a basis for comparison, and discussing at first only the analyses discussed by him, I find that all of his orthochlorite series, except corundophilite and amesite, reduce sharply to the above given type of formula. Omitting amesite, which will be separately considered further on, every orthochlorite may be written $R''_2(SiO_4)_2R'_4$, with various relations between the several components collectively represented by R'_4. In fact, Tschermak's formulæ and mine, although quite dissimilar, are curiously parallel, as the following scheme, based upon his classification of the orthochlorites, plainly shows. His arrangement of the subgroup is this:

Pennine	Sp_3At_2 to SpAt
Clinochlore	SpAt to Sp_2At_3
Prochlorite	Sp_2At_3 to Sp_3At_7
Corundophilite	Sp_3At_7 to $SpAt_4$

[1] Bull. U. S. Geological Survey, Nos. 27, 42, 60, 64, and 78.

Transforming these expressions, and, for brevity, writing $AlH_2O_2=A$, and $MgOH=M$, we have:

$Sp_3At_2 = Mg_8(SiO_4)_8 \ . A_4M_5H_7 = nMg_2(SiO_4)_2R'_4$
$SpAt = Mg_3(SiO_4)_3 \ . A_2M_2H_2 = \ "$
$Sp_2At_3 = Mg_7(SiO_4)_7 \ . A_6M_5H_3 = \ "$
$Sp_3At_7 = Mg_{13}(SiO_4)_{13} \ . A_{14}M_{10}H_2 = \ "$
$SpAt_4$ = approximate agreement only.

In the last case, corundophilite, Tschermak's formula agrees better with the actual analyses than any formula derived from my system. The cause of divergence will be considered in connection with the structure of amesite, later. Although the difference is small it ought not to be ignored.

In general, then, the orthochlorites may be provisionally regarded as mixtures of the three typical or generic salts $Mg_2(SiO_4)_2A_4$, $Mg_2(SiO_4)_2M_4$, and $Mg_2(SiO_4)_2H_4$. Whether these compounds exist separately in the mineral kingdom is an open question, and one not easy to answer. To each of them there are approximations; ekmannite, for example, is near $Fe_2(SiO_4)_2H_4$ in composition; but it is more probable that the chlorites proper are mixtures of intermediate salts. Some pennines, for instance, fall near the compound $Mg_2(SiO_4)_2AMH_2$; and other like substances appear among the minerals which Tschermak places in the subgroup of leptochlorites. A consideration of the latter must precede further discussion of theory.

According to Tschermak, the leptochlorites form three subgroups, as follows:

I.	Daphnite	$At_5At'_5Sp$
	Chamosite	$At_5At'_3Sp$
II.	Metachlorite	$At_6St_2Sp_3$
	Klementite	At_4St_2Sp
	Cronstedtite	$AtSt$
	Thuringite	$AtSt$
	Euralite	At_3St_4
	Strigovite	St
III.	Diabantite	Ct_4Sp_7
	Aphrosiderite	$Ct_6At_6Sp_4$ to $Ct_3At_6Sp_4$
	Delessite	$Ct_2At_2Sp_5$ to $CtSp$
	Rumpfite	$Ct_4At''_4Sp$

Epichlorite, grengesite, melanolite, etc., he regards as chlorites, but as not yet definable. The delessite from Friedrichsroda he places provisionally in the first division of the leptochlorites, along with daphnite and chamosite. The formulæ given are deduced from specific analyses, but when several analyses exist for a species a considerable variability becomes manifest, which must influence all attempts to fix the molecular structure.

Taking now the analyses as cited by Tschermak, a number of them reduce at once to the same type of substitution formula as that which I have assigned to the orthochlorites. Uniting like oxides, Fe_2O_3 with Al_2O_3, MgO with FeO, etc., we get at once the following expressions

from the analytical data. The name of the analyst follows the name of the species:

Daphnite, Zeynek ..... $Fe''_{39}(SiO_4)_{40} . H_{15}A_{44}M_{22}$
Chamosite, Boricky ..... $Fe''_{42}(SiO_4)_{43} . H_{20}A_{37}M_{23}$
Delessite, Pufahl ..... $Mg_{49}(SiO_4)_{50} . H_{38}A_{40}M_{22}$
Thuringite, Gintl ..... $Fe''_{41}(SiO_4)_{39} . H_{11}A_{49}M_{15}$
" Keyser ..... $Fe''_{44}(SiO_4)_{40} . H_{12}A_{50}M_{11}$

An approximation to close agreement with theory is evident at a glance; but a better conception of the agreement may be obtained by calculation, using the following formulæ:

Daphnite ..... $Fe_2(SiO_4)_2A_2(FeOH)_1H_1$
Chamosite ..... " " "
Delessite (Friedrichsroda) ..... $\begin{cases} 1\ Fe_2(SiO_4)_2A_2(FeOH)_1H_1 \\ 3\ Mg_2(SiO_4)_2A_2M_1H_1 \\ 1\ Fe_2(SiO_4)_2H_4 \end{cases}$
Thuringite ..... $\begin{cases} 3\ Fe_2(SiO_4)_2A_2(FeOH)_1H_1 \\ 1\ Fe_2(SiO_4)_2A_4 \end{cases}$

To this list we may add the thuringite from Lake Superior, analyzed by Penfield and Sperry, which becomes 5 $Fe_2(SiO_4)_2(FeOH)_4 + 9\ Fe_2(SiO_4)_2A_4$. The analyses, reduced to typical form and to 100 per cent, as is usual, are as follows:

	Daphnite. Zeynek.	Chamosite. Boricky.	Delessite. Pufahl.	Thuringite. Gintl.	Thuringite. Keyser.	Thuringite. P. & S.
SiO_2	23·44	25·17	29·75	23·58	24·15	21·35
Al_2O_3	22·08	18·41	20·58	25·11	25·44	24·02
FeO	43·41	45·37	19·42	40·08	39·39	43·88
MgO	.....	.....	17·53	.....	.....	.....
H_2O	11·07	11·05	12·72	11·23	11·02	10·75
	100·00	100·00	100·00	100·00	100·00	100·00

Calculated from the formulæ just given they become:

	Daph. & Cham.	Deless.	Thuring. G. & K.	Thuringite, P. & S.
SiO_2	24·39	30·30	23·81	21·54
Al_2O_3	20·73	20·60	25·30	23·54
FeO	43·90	18·18	39·29	44.31
MgO	.....	18·18	.....	.....
H_2O	10·98	12·74	11·60	10·61
	100·00	100·00	100·00	100·00

In short, these chlorites are apparently compounds of precisely the same type as the orthochlorites. Daphnite and chamosite vary from theory by small amounts in opposite directions, the one having a trifling excess of an FeOH salt, the other an excess of an AlH_2O_2 compound. Closer agreements could not be reasonably expected.

In order to properly interpret the remaining leptochlorites, we must return to the fundamental idea of the substitution hypothesis. Start-

ing with the normal orthosalt, we get at once the following probable series of derivatives:

Olivine	$Mg_4(SiO_4)_2$
Orthochlorites	$Mg_3(SiO_4)_2R'_2$
	$Mg_2(SiO_4)_2R'_4$
	$Mg(SiO_4)_2R'_6$

In the first of these derivatives, the compound intermediate between the orthochlorite type and olivine, we find the key to most of the leptochlorites. Again, discussing the analyses mainly considered by Tschermak, omitting strigovite and rumpfite for separate inspection, we get the subjoined semiempirical expressions:

Metachlorite,	Zeynek	$Fe''_{45}(SiO_4)_{40} \cdot H_{12}A_{41}M_{20}$
Euralite,	Wiik	$Mg_{65}(SiO_4)_{56} \cdot H_{59}A_{32}M_4$
Diabantite,	Hawes	$Mg_{69}(SiO_4)_{56} \cdot H_{53}A_{25}M_9$
Klementite,	Klement	$Mg_{61}(SiO_4)_{48} \cdot H_7A_{56}M_7$
Delessite,	Heddle[1]	$Mg_{75}(SiO_4)_{57} \cdot H_{39}A_{38}M_1 + 34$ aq.
Cronstedtite,	Ludwig	$Fe_{49}(SiO_4)_{35} \cdot A_{44}$, nearly.
Aphrosiderite,	Rammelsberg	$Fe_{54}(SiO_4)_{41} \cdot H_3M_8A_{44}$

Metachlorite, at one end of this series, corresponds nearly to the orthochlorites; while aphrosiderite, at the other end, approaches the composition $Fe_3(SiO_4)_2A_4$. All the other minerals in the series fall between these extremes. Reduced to general form, the expressions become:

Metachlorite	$4R''_2(SiO_4)_2R'_4$	+	$1R''_3(SiO_4)_2A_2$	
Euralite	7	"	+ 3	"
Diabantite	4	"	+ 3	"
Klementite	1	"	+ 1	"
Delessite	1	"	+ 2	"
Cronstedtite	1	"	+ 4	"
Aphrosiderite	0	"	+ 1	"

These ratios, of course, are not rigidly exact, but they vary no more from the analyses considered than the analyses of the different occurrences in any one species vary among themselves. In the last case, the actual analyses show small admixtures of the orthochlorite type; but the approximation is nevertheless quite close to theory. It will be seen that the value of R'_2 in the second term of each expression is constant; that is, that we have either AlH_2O_2 or the corresponding ferric radicle; but the values of the first term are somewhat different. In metachlorite, as in daphnite and chamosite, $R'_4 = A_2MH$; in cronstedtite it is A_4, and in delessite it is H_4. In klementite we have $R'_4 = A_3M$; in diabantite, $3R'_4 = M_4H_8$; and in euralite, $7R'_4 = A_{22}H_6$. Such ratios, however, are difficult to fix sharply, because of the uncertainties in the water determinations. In Heddle's analyses, however, the water given off at 100° is distinguished from that retained at

[1]The delessite from Bowling Quarry. The samples from Dumbuck and Long Craig agree well with this.

higher temperatures, and the results are correspondingly favorable to theory. In his delessite, for instance, the water becomes partly water of crystallization; and the mineral from Bowling quarry agrees well with the formula $2Mg_3(SiO_4)_2A_4$, $2aq + Mg_2(SiO_4)_2H_4$; with about two-sevenths of the magnesium replaced by ferrous iron. Calculating the composition of each mineral from the formulæ given below, and comparing the results with the *reduced* analyses from which the expressions were derived, we can judge of the closeness with which the facts and the theory agree.

Metachlorite .....$4Fe_2(SiO_4)_2A_2(FeOH)H + Fe_3(SiO_4)_2A_2$
Euralite.....$7Mg_2(SiO_4)_2R'_4 + 3Mg_3(SiO_4)_2A_2$
Diabantite .....$4Mg_2(SiO_4)_2R'_4 + 3Fe_2(SiO_4)_2A_2$
Klementite..... $Mg_2(SiO_4)_2A_3M + Mg_3(SiO_4)_2A_2$
Delessite ..... $Mg_2(SiO_4)_2H_4 + 2Mg_3(SiO_4)_2A_2$, 2aq.
Cronstedtite..... $Fe_2(SiO_4)_2(Fe'''H_2O_2)_4 + 4Fe_3(SiO_4)_2(Fe'''H_2O_2)_2$
Aphrosiderite..... $Fe_3(SiO_4)_2A_2$

	Metachlorite.		Euralite.		Diabantite.	
	Found.	Calculated.	Found.	Calculated.	Found.	Calculated.
SiO_2	23·82	24·57	37·74	38·15	34·05	34·34
Al_2O_3	20·42	20·88	18·48	19·45	12·80	12·51
Fe_2O_3	.....	.....	.....	.....	.....	.....
FeO	45·76	44·23	.....	.....	26·32	26·49
MgO	.....	.....	30·91	29·24	16·70	16·35
H_2O	10·00	10·32	12·87	13·16	10·13	10·31
	100·00	100·00	100·00	100·00	100·00	100·00

	Klementite.		Cronstedtite.		Aphrosiderite.	
	Found.	Calculated.	Found.	Calculated.	Found.	Calculated.
SiO_2	28·85	28·78	21·18	21·56	24·54	25·31
Al_2O_3	30·36	30·57	.....	.....	22·59	21·52
Fe_2O_3	.....	.....	35·74	34·48	.....	.....
FeO	.....	.....	35·19	36·20	43·87	45·57
MgO	28·73	28·78	.....	.....	.....	.....
H_2O	12·06	11·87	7·89	7·76	9·00	7·60
	100·00	100·00	100·00	100·00	100·00	100·00

	Delessite.	
	Found.	Calculated.
SiO_2	34·00	33·83
Al_2O_3	19·34	19·17
MgO	30·24	30·08
H_2O	10·36	10·15
Aq	6·06	6.77
	100·00	100·00

In reducing the data, and in calculating the formulæ, I have commonly assumed R″ to be all magnesium or all iron according as one or the other predominated. Only in diabantite the relation between the Fe and Mg was so simple that it seemed desirable to keep both in view. I have also used relatively simple ratios between component molecules, rather than the more complex terms which might give a closer agreement between analyses and theory—that is, when $Mg_2(SiO_4)_2R'_4$, and $Mg_3(SiO_4)_2A_2$ stood actually in the relation of 11 to 10, I have computed on the basis of 1:1. Most of the divergences between "found" and "calculated" are due to this cause; but in the case of cronstedtite, which is least concordant of all, there is probably a small admixture of some more basic compound, of the character, possibly, of amesite.

There now remain to be considered, of all of Tschermak's typical chlorites, only strigovite, rumpfite, amesite, and in part corundophilite. Of these, the first three depend each upon a single analysis, and the available evidence is therefore not conclusive. To strigovite, the general formula $H_4Fe''_2Al_2Si_2O_{11}$ seems to apply; which, in the constitutional expression given to it by Tschermak has already been cited. This may also be written $Fe_2(SiO_4)_2.H(AlH_2O_2)(AlOH)$, which is of the orthochlorite type with the bivalent group AlOH in place of R'_2. In rumpfite, which has the empirical formula $H_{28}Mg_7Al_{16}Si_{10}O_{65}$, the same group AlOH appears, and also a molecule of the form of the last derivative of olivine, $Mg(SiO_4)_2R'_6$. In detail, rumpfite agrees very nearly with the composition

$$Mg_2(SiO_4)_2A_2H_2+2Mg(SiO_4)_2A_2(AlOH)_2;$$

which gives with the analysis by Firtsch reduced as usual, the following comparison:

	Rumpfite.	
	Found.	Calculated.
SiO_2	31·01	30·20
Al_2O_3	42·02	42·79
MgO	13·73	13·42
H_2O	13·24	13·59
	100·00	100·00

It must be remembered that in order to account for rumpfite, Tschermak assumed the existence of the constituent molecule At″, which appears in none of his other chlorites. Both in his scheme and in mine the mineral is exceptional, and undoubtedly it needs further study.

In amesite, which occurs with corundophilite, we find another chlorite of peculiar composition. It is the most basic member of the group, and contains more oxygen relatively to its silicon than any other chlorite known. Its formula, as written by Tschermak, is Al_2SiO_7, $H_2(MgOH)_2$, which is the equivalent of his serpentine molecule, with Al_2 in place of MgSi. As we have no experimental evidence from which

to reason, we may with equal propriety regard amesite as having the structure

$$O<\begin{matrix}Mg\\Mg\end{matrix}>SiO_4=(AlH_2O_2)_2;$$

when it becomes analogous in structure to the other chlorites, standing in a similar relation to them as that which the clintonite group bears toward the micas. On this supposition the micas and chlorites, as has already been shown elsewhere,[1] form two parallel series of compounds, as follows:

Normal orthosilicate,	$Al_4(SiO_4)_3$	$Mg_4(SiO_4)_2$
Whence derive—	*Micas*	*Chlorites*
Muscovite,	$Al_2(SiO_4)_3R_3$	Aphrosiderite, $Mg_3(SiO_4)_2R_2$
Normal biotite,	$Al_2(SiO_4)_3R_6$	Orthochlorites, $Mg_2(SiO_4)_2R_4$
" phlogopite,	$Al(SiO_4)_3R_9$	$Mg(SiO_4)_2R_6$
Clintonite,	$Al<\begin{matrix}O\\O\end{matrix}>R''$ $\backslash SiO_4$ R_3	Amesite, $O<\begin{matrix}Mg\\Mg\end{matrix}>SiO_4=R_2$

In certain respects, this general scheme is not incompatible with Tschermak's views. The orthochlorites, for example, he regards as mixtures of serpentine and amesite, representing the structure of those compounds in a special way. But if serpentine be written $Mg_2(SiO_4)_2$-$H_3(MgOH)$, and amesite as I have just suggested, the theory of substitution is satisfied, and the orthochlorites may be classified as intermediate between the two end terms. Then, however, the leptochlorites fall less easily into line, and the slight gain in apparent simplicity in the ortho series is offset by loss elsewhere. It is quite probable, however, that corundophilite is a mixture containing amesite molecules; and the formula which I give the latter mineral is sustained to some extent by the fact that both minerals occur intimately associated with diaspore. At Chester, the only locality for either corundophilite or amesite represented by analyses, the chlorites are commonly found in seams with diaspore on one side and emery on the other. Hence the group AlH_2O_2 is at least as likely to be found in amesite as the magnesian compound MgOH.

Still another analogy between the micas and the chlorites remains to be noted. In the phengitic muscovites, in some phlogopites and in the lithia micas, the ratio of silicon to oxygen is less than 1:4, and often approaches 1:3. This variability, as I have shown in my paper upon "A theory of the mica group,"[2] is easily explained by supposing an admixture of molecules containing the group Si_3O_8 in place of SiO_4. This equivalency is well recognized in the feldspar series; and among the micas it is forcibly emphasized by the existence of Lorenzen's polylithionite, in which the group Si_3O_8 replaces SiO_4 entirely. Does this group occur in chlorites also?

At the end of his discussion of the leptochlorites, Tschermak dismisses a number of minerals as doubtful in character, either because of unsatisfactory analyses, or uncertainty in the material described.

[1] Bull. U. S. Geological Survey, No. 90, p. 17.
[2] Bull. U. S. Geological Survey, No. 64.

In particular he names the species grengesite, hullite, melanolite, and stilpnomelane, to which he adds epichlorite. All of these minerals, together with epiphanite and possibly strigovite, may be reduced to typical form by assuming the presence of Si_3O_8. For grengesite and hullite the analyses are not satisfactory, and the formulæ deducible have therefore no weight. Strigovite has been already explained by assuming in it the group AlOH, but a reconsideration here is worth noting as offering an alternative formula to that previously given. The formulæ which I have obtained are as follows:

Stilpnomelane ..... $\left\{\begin{array}{l} 4Fe_2(Si_3O_8)_2(FeH_2O_2)_2H_2 \\ +3Fe_2(SiO_4)_2(FeH_2O_2)_2H^2 \end{array}\right.$

Melanolite ..... $\left\{\begin{array}{l} 1Fe_2(Si_3O_8)_2(FeH_2O_2)_2H_2 \\ +3Fe_2(SiO_4)_2(FeH_2O_2)_2H_2 \end{array}\right.$

Epichlorite ..... $\left\{\begin{array}{l} 1Mg_2(SiO_4)_2H_4+1Mg_2(Si_3O_8)_2H_4 \\ +3Mg_2(SiO_4)_2(AlH_2O_2)_2 \end{array}\right.$

Strigovite ..... $\left\{\begin{array}{l} 3Fe_2(SiO_4)_2(AlH_2O_2)_3H+ \\ 3Fe_3(SiO_4)_2(AlH_2O_2)_2 \\ +1Fe_3(Si_3O_8)_2(AlH_2O_2)_2 \end{array}\right.$

Epiphanite ..... $\left\{\begin{array}{l} Mg_3(Si_3O_8)_2(AlH_2O_2)_2 \\ +3Mg_3(SiO_4)_2(AlH_2O_2)_2 \end{array}\right.$

Here we find stilpnomelane and melanolite are orthochloritic in type; epiphanite is equivalent to aphrosiderite, and the other species are intermediate like most of the leptochlorites. The analyses discussed are these:

Stilpnomelane from Antwerp, N. Y., by Brush.
Melanolite, Somerville, Mass., by H. Wurtz.
Epichlorite, from the Hartz, by Rammelsberg.
Strigovite, Striegau, by Websky.
Epiphanite, Wermland, by Igelström.
The reduced analyses are as follows:

	Stilpnomelane.		Melanolite.	
	Found.	Calculated.	Found.	Calculated.
SiO_2	42·85	41·80	34·25	33·46
Fe_2O_3	24·74	26·01	29·32	29·74
FeO	23·69	23·41	26·48	26·76
H_2O	8·72	8·78	9·95	10·04
	100·00	100·00	100·00	100·00

	Epichlorite.		Strigovite.	
	Found.	Calculated.	Found.	Calculated.
SiO_2	43·94	45·50	29·51	30·20
Al_2O_3	17·75	16·58	24·78	24·25
FeO	.....	.....	36·05	36·24
MgO	27·38	28·17	.....	.....
H_2O	10·93	9·75	9·66	9·31
	100·00	100·00	100·00	100·00

For epiphanite Igelström's analysis needs no reduction, if we calculate with a ratio of Mg: Fe:: 7: 5.

	Found.	Calculated.
SiO_2	37·10	37·66
Al_2O_3	21·13	21·34
FeO	20·00	18·83
MgO	14·03	14·64
H_2O	7·83	7·53
	100·09	100·00

The agreements are sufficiently close to establish the validity of the hypothesis upon which the calculations rest, although they are not as good in all cases as might be desired. Still, the formulæ offered bring some order out of chaos, and are therefore entitled to consideration until something better is proposed.

As between Tschermak's theory and mine, both representing the known facts fairly well, experimental research must be the final arbiter. Until experiment has given grounds for decision either theory may properly be used as a guide. Mine is offered as a possible simplification of the problem; but both may be supplanted by something more general still. Neither theory exhausts all the possibilities of the question, and neither can claim to be much more than a step forward in the series of approximations by which the truth may be at last attained.

THE CONSTITUTION OF THE LITHIA MICAS.

By F. W. Clarke.

In a series of papers published during the past eight or nine years,[1] I have sought to develop the theory that the complex natural silicates are chemically to be considered as substitution derivatives of simple normal salts. For the micas in particular a theory has been worked out in detail, partly on general principles, and partly on the basis of experimental evidence, in which the starting point of the series is the normal aluminum orthosilicate, $Al_4(SiO_4)_3$, with occasional replacements of the orthosilicic group by the feldspathic group Si_3O_8. Thus we have the following systematic scheme:

Normal salt	$Al_4(SiO_4)_3$.
Muscovite	$Al_3(SiO_4)_3R'_3$.
Biotite	$Al_2(SiO_4)_3R''_3R'_3$.
Phlogopite	$Al(SiO_4)_3R''_3R'_3$.
Clintonite	$Al\begin{cases}O\\O\end{cases}R''$, $SiO_4 \equiv R'_3$

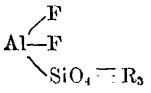
This scheme is modified, however, not only by the assumption that SiO_4 may be replaced by Si_3O_8, as in the feldspars, but also by other considerations due to the presence of fluorine in many micas, etc. In the cases of the lithia micas, lepidolite, zinnwaldite, cryophyllite, polylithionite, etc., such modification is absolutely necessary; and hitherto it has been covered by the supposition that the fluorine is represented by the univalent group AlF_2, among the components of R′.

Naturally, and almost necessarily, the development of any such theory is by process of evolution; in which details held provisionally at first are replaced by simpler conceptions, rendered possible by the acquisition of new evidence. A simplification of this order is the purpose of the present communication.

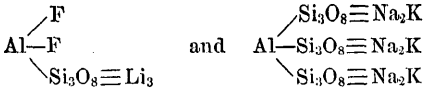
Structurally considered, the lithia micas are all characterized by two special features; an oxygen ratio lower than that of the orthosilicates, and the presence of fluorine. The first of these peculiarities has already

[1] Bulletins of the U. S. Geological Survey, Nos. 27, 42, 55, 60, 64, and 90.

been explained by the presence of the group Si_3O_8 replacing SiO_4, and the second is now rendered intelligible by assuming that the clintonite type may also be replaced by a molecule of the structure



or its equivalent in the corresponding polysilicate. For example, in the polylithionite described by Lorenzen, SiO_4 is entirely replaced by Si_3O_8, and the assumption of the latter group is thus fully vindicated. The analogy of the feldspars was strong evidence in its favor; but now we have what may fairly be regarded as positive proof. Polylithionite may now be considered as a mixture of the two molecules



in the ratio 5:1; whence we get the following comparison between observation and theory:

	Found, Lorenzen.	Calculated.
SiO_2	59·25	59·80
Al_2O_3	12·57	12·70
FeO	·93	.....
K_2O	5·37	5·85
Na_2O	7·63	7·72
Li_2O	9·04	9·34
F	7·32	7·93
	102·11	103·34
O=F	3·08	3·34
	99·03	100·00

The small amount of ferrous impurity and the low summation of the analysis fully account for all the variations between the two columns of figures both as regards their magnitude and their direction.

In the light of the foregoing evidence, and of the mica theory in general, the lepidolites proper, such as occur in Moravia and in Maine, become easily explainable. All of their variations in composition are covered by the supposition that these micas consist of mixtures in different proportions, of two typical molecules; one, the compound $AlF_2 . Si_3O_8 . R'_3$, with lithium as the principal constituent of R′, and the other a muscovitic molecule, $Al_3(SiO_4)_3R'_3$, in which R′ may be either K_2H, or KH_2. Two such mixtures may be considered here: first, the two molecules $AlF_2 . Si_3O_8 . Li_3$ and $Al_3(SiO_4)_3K_2H$, in the ratio 1:1; and second, the three compounds $AlF_2 . Si_3O_8 . K_3$; $AlF_2 . Si_3O_8 . Li_3$,

and $Al_3(SiO_4)_3KH_2$, commingled in the ratio 1:2:2. These mixtures correspond to the following percentage compositions:

	First.	Second.
SiO_2	49·05	50·39
Al_2O_3	27·79	25·70
K_2O	12·81	13·16
Li_2O	6·13	5·04
H_2O	1·22	2·01
F	5·18	6·38
	102·18	102·68
Less O	2·18	2·68
	100·00	100·00

For purposes of comparison with these figures, the following analyses of typical lepidolites are quite sufficient, as they cover all important variations: A, Rozena, by Berwerth. B, Schüttenhofen, by Scharizer. C, Paris, Maine. D, Hebron, Maine. E, Norway, Maine. F, Rumford, Maine. The last four analyses are by Riggs.

	A.*	B.†	C.	D.	E.	F.
SiO_2	50·98	49·25	50·92	48·80	49·52	51·52
Al_2O_3	27·80	25·27	24·99	28·30	28·80	25·96
Fe_2O_3	.....	.....	·30	·29	·40	·31
FeO	·05	·84	·23	·09	·24	.....
MnO	.....	·85	trace.	·08	·07	·20
CaO	.....	.....	trace.	·10	·13	·16
MgO	.....	.....	trace.	·07	·02	·02
Li_2O	5·88	5·38	4·20	4·49	3·87	4·90
Na_2O	.....	·35	2·11	·74	·13	1·06
K_2O	10·78	13·85	11·38	12·21	8·82	11·01
Rb_2O	.....		trace.		3.73	.....
Cs_2O	.....		trace.		·08	.....
H_2O	·96	1·76	1·96	1·73	1·72	·95
F	7·88	5·68	6·29	4·96	5·18	5·80
	104·33	103·23	102·38	101·86	102·71	101·89
Less O	3·32	2·39	2·64	2·02	2·18	2·44
	101·01	100·84	99·74	99·84	99·53	99·45

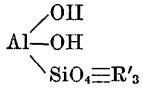
* Also contains 0·05 P_2O_5.

† Also contains 0·06 SnO_2.

In the first of these lepidolites, the mineral from Rozena, a slight variation from the scheme must be assumed, due to the excess of fluorine and the low proportion of alkalies. These peculiarities are easily accounted for by supposing a small admixture of the molecule $AlF_2 . Si_3O_8 . Al$, which corresponds to the type already indicated and which is justified by other evidence. In the mineral cookeite recently reanalyzed by Penfield[1] we find what appears to be the vermiculite of the lepidolite series, with nearly all the alkalies but lithia removed

[1] Amer. Journ. Sci., May, 1893.

and with fluorine replaced by hydroxyl. Penfield's analysis of it reduces easily to the type



and in detail to a mixture of the three molecules $Al(OH)_2 . SiO_4 . Li_3$; $Al(OH)_2 . SiO_4 . H_3$, and $Al(OH)_2 . SiO_4 . Al$, in the ratio 10:14:33. Reducing Penfield's analysis by uniting Fe with Al, the remaining bases with Li, and F with OH, and throwing out water lost at or below 300°, we get the subjoined comparison between observation and theory:

	Found.	Reduced.	Calculated.
SiO_2	34·00	35·01	34·68
Al_2O_3	45·06	46·71	46·53
Fe_2O_3	·45		
CaO	·04		
K_2O	·14		
Na_2O	·19		
Li_2O	4·02	4·29	4·56
H_2O below 300°	1·82		
H_2O above 300°	13·14	13·90	14·23
F	·46		
	99·32	100·00	100·00

In the lepidolite from Juschakova, analyzed by Rammelsberg, we find a connecting link between the lepidolites proper and the iron-lithia micas zinnwaldite and cryophyllite. The Juschakova mineral is easily represented as a mixture of molecules like the other lepidolites, except that a portion of the typical $AlF_2 . Si_3O_8 . R'_3$ is replaced by a similar molecule $AlF_2 . Si_3O_8 . Mn\ Li$. In detail it seems to contain the molecules $Al_3(SiO_4)_3\ K_2H$; $AlF_2 . SiO_4 . Al$; $AlF_2 . Si_3O_8 . Mn\ Li$; and $AlF_2 . Si_3O_8 . Li_2K$, in the ratio 2:1:3:6. Calculating its composition upon this basis, we get the following comparison with Rammelsberg's analysis:

	Found.	Reduced.	Calculated.
SiO_2	50·26	50·26	50·33
Al_2O_3	21·47	21·47	21·39
MnO	5·36	5·36	5·26
K_2O	11·08	11·08	11·60
Na_2O	·54		
Li_2O	4·88	5·14	5·55
H_2O	·66	·66	·44
F	8·71	9·33	9·38
Cl	1·16		
	101·12	103·30	103·95
Less O	3·92	3·92	3·95
	100·20	99·38	100·00

As for the iron-lithia micas, zinnwaldite and cryophyllite, a detailed discussion now would be premature, for the reason that alternative formulæ, agreeing equally well with the recorded analyses, are possible. The complication is due to the iron, which may be regarded either as belonging to a molecule of the type $AlF_2 . Si_3O_8 . Fe'' R'$; or to a biotitic molecule $Al_2 (SiO_4)_3 Fe''_2R'_2$. The zinnwaldite analyses of Berwerth and Rammelsberg are easiest interpreted as representing mixtures of $AlF_2 . Si_3O_8 . Fe Li$, and $Al_3 (SiO_4)_3 K_3$, in the ratio 5:2, approximately. Cryophyllite, on the other hand, according to analyses by Riggs, is most simply represented by the composition $Al_3X_3KH_2$, $+2\ Al_2X_3Fe_2H_2$, $+3\ AlF_2 . X . K_3$, $+4AlF_2 . X . Li_3$, in which X corresponds to the two acid groups SiO_4 and Si_3O_8 in the ratio 1:3. This interpretation is based in part upon the fact that cryophyllite occurs in margins upon plates of annite, which is a lepidomelane of the biotite type. The iron in cryophyllite, however, may also be regarded as present in the molecule AlF_2, Si_3O_8, $Fe''R'$, as in zinnwaldite; and between this interpretation and the other there are no adequate grounds for deciding. Taking the formulæ as given above, Rammelsberg's analysis of zinnwaldite and the mean of Riggs's three analyses of cryophyllite compare as follows:

	Zinnwaldite.		Cryophyllite.	
	Found.	Calculated.	Found.	Calculated.
SiO_2	46·44	47·55	51·86	51·95
Al_2O_3	21·84	21·19	16·50	18·13
Fe_2O_3	1·27	.....	2·98	.....
FeO	10·19	13·60	6·65	7·52
MnO	1·57	.....	·21	.....
CaO	.....	.....	·04	.....
MgO	·18	.....	·07	.....
Li_2O	3·36	2·84	4·89	4·71
Na_2O	·54	.....	·79	.....
K_2O	10·58	10·66	10·61	12·26
H_2O	1·04	.....	1·29	1·41
F	7·62	7·18	7·08	6·94
	104·63	103·02	102·97	102·92

In general it seems highly probable that the lithia micas are all characterized by the presence of the groups $AlF_2 . X . R'_3$, $AlF_2 . X . R''R'$, and $AlF_2 . X . Al$; in which X may be either SiO_4 or Si_3O_8, and with the fluorine replaceable by hydroxyl in the process of vermiculitization. In the original form of the mica theory the group AlF_2 was regarded as the equivalent of R' in a molecule of the muscovite type. It is now represented as belonging to a distinct molecule analogous to clintonite. So far as the evidence goes, this interpretation seems to be satisfactory; and it is an advance upon the earlier scheme in the direction of simplicity.

EXPERIMENTS UPON THE CONSTITUTION OF CERTAIN MICAS AND CHLORITES.

By F. W. Clarke and E. A. Schneider.

Shortly after the publication of our first joint paper upon the constitution of the natural silicates,[1] we received from Mr. A. Lösch, curator of minerals in the Imperial School of Mines at St. Petersburg, some highly important material bearing upon our researches. Our work upon leuchtenbergite, it will be remembered, was defective, on account of impurity in the specimens at our disposal; and Mr. Lösch therefore sent us a supply of the perfectly pure mineral, selected with extreme care, and in the very best condition for study. To this gift he added four other minerals which he thought would be of interest to us, and upon these five specimens our present communication is founded.

The minerals and the analyses are as follows:

A.—Xanthophyllite, var. Waluewite, from the Nikolai-Maximilian mine, district of Slatoust, Ural.

B.—Clinochlore from the same locality. Green, broadly foliated, closely resembling the mineral from West Chester, Pennsylvania.

C.—Leuchtenbergite from Slatoust.

D.—"Diallage serpentine" from the River Poldnewaja, district of Syssert, Ural.

E.—White mica from Miask, Ural.

	A.	B.	C.	D.	E.
SiO_2	16·85	30·84	30·00	42.55	44·17
TiO_2	trace	.....	.....	.....	.....
Al_2O_3	42·33	18·31	20·43	1·25	37·35
Fe_2O_3	2·35	1·94	1·68	1·56	1·29
FeO	0·20	1·08	0·14	1·52	0·20
MnO	.....	.....	.....	.....	0·10
CaO	13·30	.....	0·21	none	.....
MgO	20·77	34·38	34·26	40·05	.....
K_2O	.....	.....	.....	.....	10·00
Na_2O	.....	.....	.....	.....	1·14
Chromite	.....	.....	.....	0·37	.....
F	.....	.....	.....	.....	0·90
H_2O, 105°	0·04	0·55	0·55	0·21	1·06
H_2O, 250°–300°	0·12	0·49	0·35	0.11	0·53
H_2O, ignition	4·44	12·84	12·85	12·15	4·14
	100·40	100·43	100·47	99.77	100.88
Less O=F	.....	.....	.....	.....	·37
					100·51

[1] Bull. U. S. Geol. Survey, No. 78.

The molecular ratios deducible from these analyses, rejecting water given off below 300°, and the chromite contained in the serpentine, are as follows:

	A.	B.	C.	D.	E.
SiO_2	·281	·516	·500	·709	·736
R_2O_3	·430	·192	·211	·022	·374
RO	·759	·874	·861	1·022	·004
R_2O					·124
H_2O	·247	·713	·714	·675	·230
F					·050

Hence we get the following empirical formulæ, in which all R‴=Al, all R″=Mg, etc.

Waluewite $Al_{26}Mg_{76}H_{50}(SiO_4)_{28}O_{174}$
Clinochlore $Al_{32}Mg_{87}H_{143}(SiO_4)_{52}O_{113}$
Leuchtenbergite $Al_{42}Mg_{86}H_{143}(SiO_4)_{50}O_{121}$
Serpentine $Al_{1}Mg_{102}H_{135}(SiO_4)_{71}O_{35}$
Mica $Al_{75}K_{25}H_{46}(SiO_4)_{74}O_9F_5$

The last of these minerals is evidently an ordinary muscovite, possibly a little altered, and will receive no further consideration in this paper. The other minerals were examined more in detail, with very interesting results. As in our previous work, all experiments upon each mineral were made upon a uniform sample of the powdered material, so that direct comparisons with the analyses might be possible. The analyses themselves agree closely with the published analyses made by others, and are noteworthy only in the fractional determinations of the water.

Towards dry, gaseous hydrochloric acid, at the temperature interval 383°–412°, the minerals under investigation were somewhat refractory. From the waluewite, after nine hours heating in the gas, only 0·22 per cent of lime and 0·10 per cent of magnesia were extractable by water. Hence we may fairly infer that the species contains practically no -Mg–OH groups, a result which is in accordance with theory, as will be seen later. The chlorites and the serpentine, however, gave anomalous results, as follows, there being two experiments on each:

	Clinochlore.		Leuchtenbergite.		Serpentine.	
Hours heated	8½	13	16½	18½	28½	7
MgO extracted	7·34	5·48	7·33	5·62	3·66	2·66

In each case the heating was continued to constant weight, but the amount of action was much less than in the American clinochlore and serpentines which we formerly investigated. The leuchtenbergite behaves much like the impure material discussed in our earlier paper, from which 6·29 per cent of magnesia was removable; but more than double that amount is required to represent the MgOH which must be present under any recognized theory.

The irregularities in all these data remain to be explained. So far the results have only qualitative value. In those minerals which must contain the group MgOH, some action takes place, but in variable amount. But the magnesium silicates which can not contain MgOH are practically unattacked, and so far all the evidence is harmonious and clear. Contrary to our earlier expectations, however, we can not trust the dry hydrochloric acid reaction quantitatively, at least until its conditions and its nature are more fully understood. We can determine when the group MgOH is present as an essential part of a silicate, but not its actual amount. Probably the hydroxyl is first replaced by chlorine, converting the group –MgOH into the chlorhydrin-like group –MgCl. The latter, by continued action of the gaseous acids is then possibly split off as $MgCl_2$, but with secondary reactions to which the anomalous and irregular results may be due. The question is still open, and we hope by further experiments to get at something more conclusive. The problem is, to measure basic hydroxyl by its replacement with chlorine; and there seems to be no good reason why it should not be solvable.

By strong aqueous hydrochloric acid the chlorites and the serpentine were easily decomposed; but by previous ignition they were split up into soluble and insoluble portions. This splitting up is, in the case of serpentine, already well understood, the products being, as Daubrée has shown, olivine and enstatite. For the waluewite and the chlorites, however, the existing data were scanty, and accordingly new experiments were undertaken. In each case the powdered mineral was ignited over a blast for several hours. It was then digested with strong hydrochloric acid, and after evaporation to dryness and re-solution, the residue was filtered off. Then, after drying and ignition, it was boiled with aqueous sodium carbonate to remove the silica which had been released from the soluble silicates, and the final residue was weighed and analyzed. As this process was followed in our first investigation with the Pennsylvania ripidolite, the results are included here for comparison with the Siberian material. The percentages of insoluble residue were as follows:

	Waluewite.	Clinochlore.	Leuchtenbergite.	Ripidolite.
Found	45·01	17·56	19·24	19·74
Corrected	43·96	16·63	18·05	18·49

In the second line the silica found in the residues, being presumably extraneous, is deducted. The composition of the residues is given below:

	Waluewite.	Clinochlore.	Leuchtenbergite.	Ripidolite.
SiO_2	2·34	5·25	6·16	6·32
R_2O_3	71·12	67·20	68·52	67·81
MgO	26·75	27·89	25·12	25·67
CaO	trace.			
	100·21	100·34	99·80	99.80

In these analyses the silica ranges from 0·93 to 1·25 per cent of the original mineral, and the residue has quite sharply the composition of spinel. This point was noticed in our former paper, in the case of the West Chester ripidolite; but since then it has acquired new significance, and it is emphasized by the new analyses. Leaving the waluewite for separate consideration, it is to be noted that the three chlorites studied by us are all typical members of Tschermak's orthochlorite series; which, according to him, are mixtures of two end compounds, serpentine and amesite. How amesite may behave upon ignition we do not know, but serpentine splits up, as is well known, into olivine and enstatite, the latter being insoluble in hydrochloric acid. Under Tschermak's theory of the chlorites, a clinochlore of the composition SpAt, should, upon ignition, yield about 18 per cent of enstatite; or, in other words, the insoluble residue should contain *at least* one-third of all the silica in the mineral. Since no enstatite is actually formed, or practically none, it is plain that the three chlorites here considered contain no serpentine molecules; and hence, so far at least as these minerals are concerned, Tschermak's theory falls to the ground.

Approximately, but not exactly, the formation of spinel from the waluewite and the chlorites seems to follow a simple quantitative law. To illustrate this the empirical formulæ may be reproduced here.

Waluewite	$Al_{86}Ca_{24}Mg_{52}H_{50}(SiO_4)_{28}O_{174}$
Clinochlore	$Al_{38}Mg_{87}H_{143}(SiO_4)_{52}O_{113}$
Leuchtenbergite	$Al_{42}Mg_{86}H_{143}(SiO_4)_{50}O_{121}$
Ripidolite	$Al_{38}Mg_{86}H_{140}(SiO_4)_{50}O_{113}$

Upon ignition, of course, water is expelled, and the ignited residue is empirically as follows:

Waluewite	$Al_{86}Ca_{24}Mg_{52}(SiO_4)_{28}O_{149}$
Clinochlore	$Al_{38}Mg_{87}(SiO_4)_{52}O_{41}$
Leuchtenbergite	$Al_{42}Mg_{86}(SiO_4)_{52}O_{49}$
Ripidolite	$Al_{38}Mg_{86}(SiO_4)_{50}O_{43}$

Here we have in each mineral an excess of oxygen over SiO_4, and to that excess the amount of spinel residue is approximately proportional, thus:

	Found, corrected.	Calculated.
Waluewite	43·96	43·15
Clinochlore	16·63	14·80
Leuchtenbergite	18·05	17·62
Ripidolite	18·49	15·83

Considering the impurities in the original materials, and the unavoidable inaccuracies of manipulation, the agreement here is as close as could be expected. The calculation assumes that the excesses of oxygen represent, quantitatively, the amount of spinel formed, and all the errors of analysis are accumulated in the final result. If we deduct the spinel from the composition of each mineral, the soluble portion is

expressible as a mixture of olivine and magnesian garnet; two species which are among the commonest progenitors of the chlorite group. That olivine and garnet are actually formed is certainly not proved; but it seems highly probable that the chlorites studied do split up in the manner indicated, yielding water, spinel, garnet, and olivine as the final products of decomposition. Other chlorites may behave differently, and it is quite likely that the species or varieties rich in iron may diverge widely from the types considered here. Speculation upon this theme would be premature.

As to the chemical structure of the leuchtenbergite and clinochlore, the evidence now available is quite in harmony with the general theory of the chlorite group recently advanced by one of us.[1] Again including the Pennsylvania ripidolite, the three chlorites reduce to compositions as follows:

Clinochlore ..... $Mg_{50}(SiO_4)_{52}(AlH_2O_2)_{38}(MgOH)_{37}H_{30}$
Leuchtenbergite ..... $Mg_{49}(SiO_4)_{50}(AlH_2O_2)_{42}(MgOH)_{37}H_{22}$
Ripidolite ..... $Mg_{49}(SiO_4)_{50}(AlH_2O_2)_{38}(MgOH)_{37}H_{27}$

Condensing, by union of the univalent factors, these become—

Clinochlore ..... $Mg_{50}(SiO_4)_{52}R'_{105}$
Leuchtenbergite ..... $Mg_{49}(SiO_4)_{50}R'_{101}$
Ripidolite ..... $Mg_{49}(SiO_4)_{50}R'_{102}$

or, in general, all three examples have nearly identical composition and conform to the typical expression $Mg_2(SiO_4)_2R'_4$, in accordance with the theory which represents them as substitution derivatives of the normal salt $Mg_4(SiO_4)_2$. We may interpret the minerals in detail as was done in the case of our earlier discussion of the West Chester ripidolite, or we may regard them as mixtures of the two salts $Mg_2(SiO_4)_2(AlH_2O_2)_2(MgOH)_1H$ and $Mg_2(SiO_4)_2(AlH_2O_2)_1(MgOH)_2H$. In either case the juxtaposition of the groups AlH_2O_2 and $MgOH$ renders the formation of spinel intelligible.

In the waluewite, or more properly xanthophyllite, we have the first example of a true brittle mica met with in the course of our investigations. Being the most basic known member of the clintonite series, it has peculiar interest, and it deserves a somewhat detailed discussion. In the empirical formula deduced from our analysis, $Al_{86}Ca_{24}Mg_{52}H_{50}(SiO_4)_{28}O_{174}$, the most noticeable feature is the great excess of oxygen compared with the possible hydroxyl and the small amount of SiO_4. This excess is accounted for in part by the general formula which we have heretofore assigned to the clintonite group,

$$\begin{matrix} & /O\!\!> R'' \\ Al\!-\!O & \\ & \backslash SiO_4\!-\!R'_3; \end{matrix}$$

which formula, however, needs some extension along a new line. In that formula the group of atoms $-AlO_2R''$ appears, an equivalent

[1] See the first paper in this Bulletin.

obviously of the group AlO_2H_2; and this group may fairly be repeated among the components of R'_3. With such a group the extreme member of the clintonite series should have the composition $(AlO_2R'')_4SiO_4$; and a molecule of that type is theoretically capable of splitting up into olivine and spinel in the ratio of 1:2, when each mineral is given its lowest possible formula:

$$(AlO_2R'')_4SiO_4 = R''_2SiO_4 + 2R''Al_2O_4.$$

In the case of xanthophyllite, if such a molecule is contained in it, the olivine formed should be partly monticellite. At Monzoni monticellite is found associated with spinel, and brandisite, a member of the clintonite series, occurs in the same region. In fact, all three of the true clintonite micas are commonly associated with spinel, a fact of much interest when considered in its relations to our experiments. In the light of the foregoing argument the composition of waluewite and its manner of decomposition by heat may be represented as follows:

$$5Al\begin{cases}\diagup O \\ \diagdown SiO_4\end{cases}Ca = H_2 . AlH_2O_2 \qquad +5Al\begin{cases}\diagup O \\ \diagdown SiO_4\end{cases}Mg = (AlO_2Mg)_3$$

$$+1Al\begin{cases}\diagup O \\ \diagdown SiO_4\end{cases}Ca = (AlO_2Ca)_3$$

These three molecules are all of the general type heretofore assigned to the clintonite series, and two of them are presumably capable of yielding spinel. Reducing the original analysis to 100 per cent with consolidation of like bases as usual, we get the following comparison between experiment and theory, the calculated composition being in accordance with the structural formula above cited.

	Found, reduced.	Calculated.
SiO_2	16·97	17·02
Al_2O_3	44·14	44·71
CaO	13·50	13·00
MgO	20.92	20·63
H_2O	4.47	4·64
	100·00	100·00
Spinel formed	43·96	43·94

Reckoned on a similar basis, clintonite, according to the analyses published by Sipöcz, may be written—

$$AlO_2R''.SiO_4.H_3 + (AlO_2R'')_4.SiO_4$$

and brandisite is of the same general character, with a small admixture of the first of the three xanthophyllite molecules given in our structural expression. Whether chloritoid is a true member of this group, seems to be uncertain; but if it is, its composition may be written $AlO_2Fe.SiO_4.H.AlOH$; the last factor being a bivalent group related to the univalent AlO_2H_2.

As for the ultimate structure of the group AlO_2R'', it may be written in two ways, thus:

$$-Al<^{O}_{O}>R'' \quad \text{or} \quad -R''-O-Al=O$$

The first form corresponds to the group—$Al(OH)_2$. the second to the formula commonly assigned to spinel,

$$Mg<^{O-Al=O}_{O-Al=O}$$

In either case two of the groups AlO_2R'' coalesce to form one molecule of spinel, with removal of a single magnesium atom. Such a coalescence is easiest comprehended when the second form of the radical is chosen; but the first form is more harmonious with the constitution of the mica series in general. If the xanthophyllite compound $(AlO_2R'')_4SiO_4$ be regarded independently of the micas, it is most simply written as follows, with its splitting up into olivine and spinel as indicated:

$$Si\begin{cases} O-Mg-O-Al=O \\ O-Mg-O-Al=O \\ O-Mg-O-Al=O \\ O-Mg-O-Al=O \end{cases} \qquad Si\begin{cases} O \\ O \end{cases}\!\!>Mg \;\; \begin{matrix} \\ \end{matrix} Si\begin{cases} O>Mg \\ O>Mg \end{cases} \qquad \begin{matrix} Mg<^{O-Al=O}_{O-Al=O} \\ Mg<^{O-Al=O}_{O-Al=O} \end{matrix}$$

If, however, for the sake of preserving harmony with the mica formulæ we adopt the first expression for —AlO_2R'', then spinel would seem to have the constitution

$$Mg<^{O}_{O}>Al-O-Al=O$$

Although the last formula is somewhat novel, it is not altogether improbable; but between it and its alternative we cannot yet certainly decide. Another open question is furnished by the chlorites, in which the formation of spinel may possibly be due to the presence of AlO_2Mg groups. Upon this supposition, however, the chlorites do not reduce to simple formulæ, and therefore the suggestion has slight value. Apart from all theoretical considerations, the spinel reaction, as it may fairly be called, is one of an entirely new order in mineral chemistry, and it opens up a noteworthy line of attack upon the difficult problems before us.

NOTES ON THE ACTION OF AMMONIUM CHLORIDE UPON SILICATES.

By E. A. Schneider and F. W. Clarke.

In our investigations relative to the constitution of the natural silicates,[1] the action upon them of dry hydrochloric acid gas has played an important part. The reaction, however, as heretofore described by us, is very slow, and the operations involved in its application are long and tedious. In each experiment the powdered mineral must be heated for many hours in the stream of gas, and from time to time it is taken out and weighed. After each weighing the powder is stirred with a platinum wire to expose a fresh surface to action, and it then becomes liable to the absorption of hygroscopic moisture from the atmosphere, which introduces into the work a possible, though small, source of error.

In the hope of simplifying the reaction, and of avoiding the possible error just indicated, the experiments shortly to be described were tried. The results as yet are not wholly satisfactory, at least from a theoretical point of view; but we believe them to be novel, and that a preliminary notice will not be quite without value.

It is well known that when ammonium chloride is heated to 350° it is dissociated into $HCl+NH_3$. If, therefore, the salt is heated to that temperature with a silicate, the reaction of the latter with dry hydrochloric acid should take place. It is, of course, conceivable that in some cases the ammonia might act also; but we have so far observed nothing which would show this to be the case.

Our method of procedure has been as follows: The powdered mineral was mixed with about ten times its weight of pulverized ammonium chloride and heated in a platinum crucible to a temperature above 350°, but below the temperature at which dehydration takes place, until the added salt was completely volatilized. The residue was then leached out with water, and the portion rendered soluble was investigated. In some experiments the residue, before leaching, was treated with a second, and even a third, portion of ammonium chloride, in order to ascertain whether a single treatment was final. Our conclusions are best stated in connection with our results, which we subjoin with all

[1] Bull. U. S. Geological Survey, No. 78; and Amer. Journ. Sci., Sept., 1891, and April, 1892.

necessary detail. In each experiment approximately one gramme of mineral was taken.

Olivine (Mg_2SiO_4).—From Fort Wingate, New Mexico. By treatment with ammonium chloride only 0·44 per cent of magnesia was rendered soluble; i. e., converted into chloride. This result agrees with the data obtained upon heating olivine in dry hydrochloric acid gas. By aqueous acid the mineral is easily decomposed.

Serpentine ($Mg_3H_4Si_2O_9$).—The so-called "diallage" serpentine from the river Poldnewaja, district of Syssert, Urals. After a single treatment with sal ammoniac 4·93 per cent of magnesia was dissolved out by water, but the residue contained a little oxychloride, representing less than one per cent more.

In a second experiment the serpentine, after heating with ten grammes of ammonium chloride, was reheated with ten grammes more. Upon leaching, 14·30 per cent of magnesia went into solution. In a third experiment the mineral was thrice treated, and only 10·63 per cent of magnesia became soluble. In the last case the residue was boiled with a solution of sodium carbonate, which took up 3·82 per cent of silica. This fact, the splitting off of silica during treatment with ammonium chloride, may possibly shed some light upon the nature of the reaction. The same serpentine was completely decomposable by aqueous hydrochloric acid, but only moderately attacked by the dry gas. The irregularity of the results is manifest, but as yet unexplained.

Clinochlore ($Mg_7Al_3H_{11}Si_4O_{25}$).—From Slatoust, Urals. A double heating with ammonium chloride extracted 2·12 per cent of magnesia. A triple heating took out 3·80 per cent. The dry gas converted twice as much magnesia into chloride, but the mineral is much less attacked than the similar clinochlore from Pennsylvania.

Leuchtenbergite.—From Slatoust. Identical in composition with the clinochlore. A triple heating with ammonium chloride took out 3·98 per cent of magnesia. The residue contained a little oxychloride. Gaseous hydrochloric acid converted 5·62 per cent of magnesia into chloride.

Xanthophyllite, variety waluewite ($Al_{34}\ Ca_9\ Mg_{20}\ H_{20}\ Si_{11}\ O_{112}$).—From the Nikolai-Maximilian mine, district of Slatoust. Practically unattacked either by gaseous hydrochloric acid or by dissociating ammonium chloride, but completely decomposable by aqueous acid. A triple heating with ammonium chloride took out 0·48 per cent of lime and 0·61 of magnesia.

So far the silicates examined have all been characterized by the presence of magnesia. Two of them, olivine and waluewite, were not seriously attacked by the reagent, while the others were perceptibly affected. In the latter group the radicle —Mg—O—H almost certainly occurs; from the two unattacked minerals it is absent. The reaction, therefore, is *probably* valid as a rough test for MgOH; but how far it is trustworthy remains to be ascertained. The evidence is so far not absolutely conclusive. In the following experiments the minerals studied were nonmagnesian.

Natrolite ($Al_2Si_3O_{12}Na_2H_4$).—From Magnet cove, Arkansas. A triple heating with ammonium chloride took out 9·50 per cent of soda, out of a total percentage of 15·40.

Prehnite ($Al_2Si_3O_{12}Ca_2H_2$).—From the Fassathal, Tyrol. A triple heating with salammoniac removed 1·72 per cent of lime. The mineral contained 26·49 per cent of lime.

Wollastonite ($CaSiO_3$).—From Diana, New York.

Pectolite ($Ca_2NaHSi_3O_9$).—From Bergen Hill, New Jersey.

These minerals were so strongly attacked that the complete analyses are given to facilitate comparison.

	Wollastonite.	Pectolite.
SiO_2	50·05	53·11
CaO	47·10	33·88
Na_2O	undet.	8·62
Al_2O_3. Fe_2O_3	1·13	·40
MgO	·09	
MnO		·81
H_2O	·45	3·04
	98·82	99·86

The wollastonite was twice and the pectolite three times treated with the ammonium chloride. Upon leaching with water the following constituents were dissolved out:

	Wollastonite.	Pectolite.
CaO	36·98	20·50
Na_2O		6·95
MnO		·54

Here the action is quite independent of hydroxyl in the minerals, for wollastonite is anhydrous, and pectolite but slightly hydrated. By future experiments we hope to reach some explanation of the results here given, which may or may not indicate a complete breaking up of the silicate molecules. At present, however, we prefer to offer no solution of the problem.

Our chief purpose in these experiments has been to discover some reaction by which the basic hydroxyl of a silicate might be recognized and measured. We have not succeeded in carrying out that purpose; but the results obtained are novel and at least worthy of record. Incidentally we have also studied the action of dissociating ammonium chloride upon certain phosphates. Lazulite and turquois were scarcely attacked, except that a little copper was removed from the latter mineral. Upon dufrenite there was considerable action, some ferric chloride being volatilized, and still more being extractable by water. But these experiments were merely qualitative, and have no immediate significance.

THE PREPARATION AND SPECIFIC GRAVITY OF CRYSTALLIZED URANIUM DIOXIDE.

By W. F. Hillebrand.

Wöhler prepared uranium dioxide, UO_2, as a black crystalline powder, by evaporating uranyl chloride, UO_2Cl_2, with excess of sodium and ammonium chlorides and fusing the dry residue. Uhrlaub[1] fancied that the substance thus obtained might contain nitrogen, and, on the strength of a very unsatisfactory determination of that element, he suggested $U_{10}N_4O_{18}$ as its probable formula. This requires 2·05 per cent of nitrogen, whereas Uhrlaub found scarcely over 1 per cent in a single determination by the soda-lime method. The tube softened to such an extent during the long ignition as to interrupt the operation before all the nitrogen had been given off. Qualitatively the compound prepared by Wöhler's method gives off ammonia on fusion with potassium hydroxide, according to Uhrlaub.

In view of the presence of nitrogen in uraninite it became desirable to subject Uhrlaub's work to review, and the supposed oxynitride was therefore prepared a number of times by Wöhler's method, varying proportions of sodium and ammonium chlorides being used. The fusion was made in all but one or two cases in a large covered platinum crucible over a multiple (15) burner, and in some instances special precautions were taken to ensure entire exclusion of air during the whole operation of fusion, which in no case was continued over forty minutes. The amount of pure uranyl chloride employed for any single reduction, while never accurately gauged, ranged from seven to twelve grammes. The platinum crucible was somewhat affected by the chlorine liberated, but not to a great extent.

Without going too closely into details of the numerous experiments, it may be said that the color of the product of reduction, after thorough extraction by hot water and a little weak hydrochloric acid, ranges from different shades of rich brown to a most brilliant black, according to the degree of fineness of the octahedral crystals and the percentage of dioxide which they contain. In degree as air has had access to the interior of the crucible does the percentage of dioxide diminish and that of trioxide increase, and this change involves an increase in the opacity, a decrease in the specific gravity, and a change of color in the pulverized crystals from brown to dull greenish black. If the brilliantly reflecting crystals are relatively large, as was often the case, the color is black to the unaided eye whether the oxide, UO_3, is present in quantity or entirely absent, but under the microscope those free, or nearly so, from trioxide are deep brown by transmitted light, at least

[1] Die Verbindungen einiger Metalle mit Stickstoff, Inaugural Dissertation, Göttingen, 1861.

on the edges. When air has been entirely excluded the reduction is practically quantitative, and neither water nor hydrochloric acid extracts more than traces of uranium.

Notwithstanding the most careful qualitative tests, no trace of ammonia could be obtained by fusion with potassium hydroxide from any of the products of different reductions, nor was a sufficient amount of gas obtained by the methods used for the liberation of nitrogen from uraninite[1] to render qualitative tests for nitrogen applicable. A volume of 1·5cc of gas was obtained from 1·06 grammes of substance in one instance, but even this may have been of extraneous origin. It thus appears that the *oxynitride* of Uhrlaub has no existence. His *nitride*, U_3N_4, has not been examined, and it is improbable that any further work in this direction can be undertaken in the near future.

Nearly all the preparations obtained were assayed for UO_2, and in a few of them small quantities of insoluble matter and of platinum were estimated. Ignition in oxygen serves for all practical purposes for the estimation of UO_2,[2] but titration by potassium permanganate in sulphuric-acid solution is most accurate if solution has been perfect. The following determinations of dioxide were all made by the latter method unless otherwise stated. For the careful specific gravity determinations I am indebted to Mr. L. G. Eakins. These have been reduced to water at 4° C. and vacuo for the sake of better comparison. They are especially interesting as showing that the highest hitherto obtained specific gravity of uranium dioxide, 10·15, by Ebelmen, of the oxide prepared by ignition of uranium oxalate in absence of air, is much too low. The tabulation is in ascending order of specific gravity, the first column giving the order of preparation of the sample:

No.	Specific gravity.			UO_2 per cent.	
	Found.	Temperature.	Reduced to water at 4° C. and vacuo.		
X	10·18	(?)	10·15	56·96	
I	10·50	19·1	10·47	66·89	
III	10·67	22·2	10·64	.....	
VI	10·86	23	10·82	97·69	
V	10·88	28·5	10·83	94·61	97·9 by ignition in air.
XI	10·87	18·8	10·85	.....	
VII	10·895	22·2	10·86	97·02	
XII	10·94	30·3	10·88	98·42	No Pt. found.
IV	10·92	20·5	10·89	86·05!	
IX	11·00	27·6	10·95	99·38	Pt. found.
II	11·01	20·2	10·98	78·97!	77·46 by ignition in air. Pt. found.
VIII	.....	.....	.....	99·10	

[1] Bull. U. S. Geological Survey, No. 78, p. 56, 1889–1890. Chem. News, vol. 64, p. 245, 1891.

[2] Ignition *below redness* in air is usually quite as effective as strong heating in oxygen for the conversion of UO_2 to U_3O_8. For the conversion of large quantities, or of coarse powders, several oxidations, each except the last followed by reduction in hydrogen, may be required, but this is also true when the ignition takes place at redness in oxygen.

The table calls for a few explanations. In the first place, as to the effect on the specific gravity of the trifling amounts of platinum and silica found in some preparations. The silica (probably derived from the sodium and ammonium chlorides) never exceeded 0·05 per cent, and the proper correction for this amount raises the specific gravity by less than two units in the second decimal. On the other hand, the correction for the platinum sometimes found was insufficient to produce a maximum effect of more than two units in the same decimal place in the opposite direction. Their effect when found together is toward neutralization, and may in any case be disregarded.

A second point relates to the remarkable results shown by Nos. IV and II, for which no explanation offers itself. That two of the samples possessing the highest specific gravity should contain only 86 and 79 per cent of dioxide is, to say the least, surprising. They were among the earliest preparations made and were almost entirely consumed in various experiments before the anomaly was made apparent by examination of subsequent preparations, but the determinations of specific gravity in both cases and of UO_2 in No. II had been duplicated; hence there is no ground for doubting their substantial accuracy. In fact, the low results for the dioxide led to making the subsequent preparations, for it was thought that with such a high specific gravity for a material containing only 79 per cent of UO_2 the pure dioxide should possess a specific gravity much above 11. As the table shows, however, repeated efforts failed completely to secure such a result.

Still a third point may be mentioned in regard to Nos. X and I. The reduction in the case of X was made in an atmosphere of carbon dioxide derived from a cylinder of the liquid oxide, which, however, contained so much air that a large amount of oxidation took place. In both cases the greater part of the product was greenish to olive gray under the microscope, though the mass was metallic gray and brilliantly reflecting to the unaided eye. The greenish matter extinguished polarized light weakly but very distinctly, it was in flat plates of irregular outline, but sometimes showing a good angle, and the axis of extinction was such as to make the system apparently orthorhombic.

Besides this there was a good deal of black matter, like that of later reductions, but not well crystallized in octahedra. The green often contained inclusions of the black, and the appearance of both was but little altered by ignition in air. It is probable that Uhrlaub's experiments were made on material like this which had already suffered considerable oxidation, for he describes it as gray and iridescent after drying, but no ammonia could be obtained from the present material. The substance obtained by Zimmermann[1] in his preparation of alkaline uranates after *short* fusion in an open crucible was doubtless a similar mixture.

[1] Ann. d. Chem., vol. 213, pp. 291–292, 1882.

No. XI was made from Joachimsthal uraninite without preliminary separation of the numerous foreign substances known to occur in it, other than silica, lead, and sulphur. The silica was separated by evaporation to dryness after solution in nitro-hydrochloric acid and conversion into chlorides, the lead, bismuth, etc., and a small part of the arsenic were thrown out by hydrogen sulphide, and after boiling off the excess of this gas, the sulphuric acid was removed by barium chloride. Without removing the excess of the latter reagent the solution was then evaporated with sodium and ammonium chlorides and fused as usual. To avoid contamination with platinum a porcelain crucible is preferable to one of platinum, but is harder to heat. All the metallic chlorides which were not volatilized were then easily extracted by water and dilute hydrochloric acid, leaving the uranium dioxide in a state of great purity, as shown by examination and by the high specific gravity.

This mode of preparing the oxide is mentioned briefly in Gmelin-Kraut, vol. II, part 2, p. 381, as applied by H. Hermann to the separation from pitchblende, but I have not had access to the original paper and can find no other reference whatever in chemical literature to this particular point. The Jahresberichte der Chemie, while quoting Hermann's paper, omits mention of this topic. The method as outlined above seems admirably suited for obtaining large or small quantities of the dioxide quickly and almost absolutely pure and in a beautifully compact and attractive condition. It is obtained at once entirely free from alkali and is especially well adapted for the preparation of those compounds of uranium which do not contain an alkali metal.

Summary.—The results above detailed may be summarized as follows:

The oxynitride of uranium of Uhrlaub has no existence, or at least cannot be prepared in the manner described by him.

The specific gravity of crystallized uranium dioxide, UO_2, is much higher than heretofore supposed, being not less than 10·95 and possibly as high as 11 at 4° C. and in vacuo.

A FURTHER EXAMPLE OF THE ISOMORPHISM OF THORIA AND URANIUM DIOXIDE.

By W. F. HILLEBRAND.

Attempts to prepare something like an artificial uraninite by fusion of thoria, a uranium compound, and lead oxide with borax proved ineffectual, but the results of further experimentation without lead oxide were of some interest. Without following the order of experimentation, they were as detailed below.

The fusions were made over a blast lamp in a small platinum crucible set in a protective mantle to increase the heat. It was immaterial which of the oxides of uranium was employed, since the higher ones began to suffer loss of oxygen as soon as fusion commenced, as could be observed by the continual appearance of bright spots on the surface, caused by the rising of gas bubbles. The heating was continued for from eighteen hours to two or three days, according to the amount of borax to be volatilized, the progress of crystallization being noted from time to time by dipping in and withdrawing a platinum rod and examining the cooled drop adhering to it. After formation of a copious crop of crystals the cooled melt was soaked in water and dilute acetic or hydrochloric acid, which in time effected separation of everything soluble. The residue consisted always of jet-black crystalline forms, generally grouped in trellis-like shapes and sometimes distinctly crystallized in octahedra.

Two crops of crystals made by fusing only the oxide U_3O_8 with borax gave the following results:

I. 5 g. U_3O_8, 5 g. borax glass. Duration of fusion, twenty-four hours. Sp. grav. of product at 17° C., 10·70, or 10·676 reduced to water at 4° and vacuo.

Composition.

UO_2	94·50
UO_3	3·38
SiO_2	·06
Na_2O	·36
	98·30

II. 5 g. U_3O_8, 7 g. borax glass. Duration of fusion, twenty-four hours. Weight of product, 4 g. Sp. grav. at 20·6° C., 10·77, or 10·74 reduced to water at 4° and vacuo.

Composition.

UO_2	95·25
UO_3, etc	4·75
	100·00

The result of long fusion of an oxide of uranium with borax is thus seen to be practically the formation of crystallized uranium dioxide. The loss shown is probably to be largely accounted for by boric oxide, existing either as sodium or uranium borate inclosed by the crystals. The high specific gravity of the products is in conformity with the results communicated in the preceding paper on the preparation and specific gravity of crystallized uranium dioxide. The appearance of the crystals was in no wise changed by isomorphous admixture of thorium, but their solubility in nitric acid was markedly lessened as the percentage of this element increased, so much so that acid potassium sulphate had to be used to effect solution in one or two instances.

III. 7 g. UO_3, 0·71 g. ThO_2, 7 g. borax glass. Sp. grav. 10·57 at 17·5° C. or 10·55 reduced to water at 4° and vacuo.

Composition.

ThO_2	9·87
UO_2	74·44
UO_3	13·91
FeO	·07
Na_2O	·38
	98·67

IV. 7 g. U_3O_8, 1·4 g. ThO_2, ? borax glass. Sp. grav. 10·51 at 16·8° C., or 10·49 reduced to water at 4° and vacuo.

Composition.

ThO_2	17·25
UO_2	74·48
UO_3	6·71
FeO	·09
Na_2O	·34
SiO_2	·16
	99·03

V. 0·7 g. UO_3, 0·7 g. ThO_2, 3 g. borax glass. Duration of fusion thirty-six hours. Sp. grav. not determined.

Composition

ThO_2	47·6
UO_2	51·8
	99·4

This UO_2 was calculated from the weight of U_3O_8 found gravimetrically; there may have been UO_3 present. Other constituents were not looked for.

VI. 1 g. U_3O_8, 0·5 g. ThO_2, 0·5 g. PbO, 2 g. borax glass. This experiment is added to show the high percentage of thoria in the product.

Composition.

ThO_2	65.7
UO_2	15·9
UO_3	16.8
PbO	·6
	99·0

The results of these experiments furnish another proof of the isomorphism of thoria and uranium dioxide.

THE COMPOSITION OF ROWLANDITE AND MACKINTOSHITE.[1]

By W. F. HILLEBRAND.

I.—ROWLANDITE.

The specimen ot rowlandite, furnished by Mr. Hidden for analysis, was a portion of a mass somewhat resembling amorphous gadolinite. It had a glassy interior surrounded by an uneven thickness of reddish alteration substance, chiefly a carbonate, or carbonates, of the rare earths and lime. The glassy "rowlandite" showed, when broken up, reddish and dark stains in places, the latter being produced by minute black inclusions, perhaps of a titanium mineral. Numerous scarcely visible fissures, filled with foreign matter, traversed the glass. This rendered the selection of pure material an arduous task; the result of several days of labor, however, was a sample possessing a high degree of purity as shown by the microscope. A very small amount of impurity was still present, but much less, apparently, than the analysis seems to indicate. A slight cloudiness in some grains points to incipient change. Its density is the same as that found by Mr. Hidden, 4·513, at 15·5° C. The analysis is as follows:

			Mean.	
SiO_2	25·77	26·04	26·04*	
Xt†	·39	.....	·39	
ThO	·59	.....	·59	
Ce_2O_3‡	5·06	.....	5·06	
La group	9·34	.....	9·34	Mol. W. 336·8
Yt group	47·70	.....	47·70	Mol. W. 266·2
Fe_2O_3	·09	.....	·09	
FeO	4·39§	.....	4·39	
MnO	·70	·64	·67	
CaO	·60	·40	·50	
MgO	1·58	1·66	1·62	
Alk	·32	·24	·28	
H_2O	·24	.....	·24	
CO_2	·34	.....	·34	
Fl	3·87	.....	3·87	
P_2O_5	trace	.....	trace	
			101·12	
Less O for Fl	.....	.....	1·63	
			99·49	

*Certainly more nearly correct than 25·77, since the fluorine must have caused loss of silica on evaporation with hydrochloric acid.

†A mixture of undefinable earths with some uranium and a trace of titanium,

‡Cerium dioxide can not be present, if at all, in more than trivial amount, for otherwise much less ferrous oxide would have been found. For the same reason the manganese can not be present as Mn_2O_3.

§If the small and undetermined amount of uranium exists as dioxide, the ferrous oxide here given is correspondingly high, but the possible error can have no influence on the formula deduced.

[1]For the general description of these new minerals, by W. E. Hidden, see the Amer. Jour. Sci. for Aug. and Sept., 1893.

In calculating the molecular ratios a brief consideration shows that CaO and CO_2 may be neglected, and likewise, so far as their effect on the general formula is concerned, the ThO_2 and the group denominated X; also the trace of ferric oxide and the alkalies. For the present the water may also be disregarded. There result then the following molecular ratios:

SiO_2	26·04	÷ 60	=	·4340	3·91
Ce_2O_3	5·06	328·4	·0154		
La group	9·34	336·8	·0277	·2223	2·00
Y group	47·70	266·2	·1792		
FeO	4·39	72	·0610		
MnO	·67	71	·0094	·1109	1·00
MgO	1·62	40	·0405		
Fl	3·87	19		·2037	1.84

These furnish the following empirical formula, after deducting 10 atoms of oxygen for 20 of fluorine:

$$Si_{43}'''R_{44}''R_{11}F_{20}O_{154}$$

The silica is in all probability as much as half a per cent too low through loss occasioned by the presence of fluorine. Furthermore, it is possible that the fluorine, estimated by the Berzelian method, is a little too low; or, if not, that the small amount of water found is in part at least derived from hydroxyl replacing fluorine. The presumption is then strong that the composition of rowlandite is represented by the formula $Si_{44}'''R_{44}''R_{11}F_{22}O_{154}$, or in simplified form $Si_4'''R_4''RF_2O_{14}$.

Structurally this formula may perhaps be written in a number of ways, that which most readily suggests itself being

$$\begin{array}{c} '''RF \\ \| \\ ''R\!\left\langle \begin{array}{l} Si_2O_7\equiv'''R \\ Si_2O_7\equiv'''R \end{array} \right. \\ \| \\ '''RF \end{array}$$

in which the mineral is to be regarded as a derivative of the acid $H_6Si_2O_7$. Until, however, the whole group of rare earth silicates is carefully studied and their relations among themselves and to other better known silicates are ascertained, it would be premature to pronounce in favor of this or any other structural formula.

Reducing all the other earths to a hypothetical one having the molecular weight of the yttrium group as found, and the manganese and magnesia to their equivalents in iron, the composition of an ideal rowlandite would appear as in the first column below, while the second column shows the percentages required to conform to the above formula.

	Found.	Calculated for $Si_4Y_4FeFl_2O_{14}$
Si	12·73	12·93
Y	50·83	50·37
Fe	6·50	6·46
Fl	4·05	4·39
O	25·89	25·85
	100·00	100·00

The agreement is very close and becomes much more so if the suggested slight increase in silica and fluorine is allowed.

II.—MACKINTOSHITE.

Of the dull black mineral, named mackintoshite by Hidden, and supposed by him to be the parent of thoro-gummite but nine-tenths of a gram was available for analysis after careful hand-picking under the lens. It was almost entirely free from recognizable impurity and had a density of 5·43 at 21·4° C.

In powder the mineral is not entirely decomposed by any one acid so far as the necessarily restricted tests indicated. Sulphuric acid attacks it quite strongly, but the gelatinous silica set free protects a portion from further action. The addition of nitric acid then, however, causes speedy and complete solution. This behavior is perhaps susceptible of a different explanation, namely, that the mineral is not homogeneous, but consists of two different substances, the predominant one of which is decomposable by sulphuric acid, the other much less affected by it, but when once the latter has been opened up by removal of the former it is readily dissolved by nitric acid. Nitro-hydrochloric acid likewise dissolves it completely.

Considering that the limited sample had to be divided into three portions in order to estimate the constituents tabulated below, it is not perhaps surprising that the analysis should present a loss of three and one-half per cent. The presence of even the little phosphoric acid shown renders the analytical operations by which the silica and bases are determined extremely complicated, particularly when zirconia and yttria are present. Precipitates are then obtained which under similar conditions the other earth bases do not give, and thus separations and identifications are rendered more difficult and losses are almost inevitable. It is therefore not at all certain that the very considerable loss is to be sought in some constituent not enumerated; it is more probable that it should be distributed somewhat unevenly over a number of those given, silica and lead oxide excepted, they being without doubt nearly correct. The following observations, however, may be of importance in this connection. After sealing the tube in which was the sample serving for the estimation of the oxidizable constituents, a slow but long continued evolution of gas was observed, just as in the case of most uraninites when similarly treated, but owing to the very small quantity of powder in the tube—only ·15 gram—it could not be proven that the gas was nitrogen and not CO_2. The latter it should not be, for thoro-gummite, the direct alteration product of the mineral, is free from it according to Hidden and Mackintosh's analysis. In any event its amount is probably very small.

With respect to the oxidizable constituents it was found to be impossible to secure complete solution of the powder in the tube, even after several days' heating with dilute sulphuric acid, owing presumably

to the above-mentioned protective action of silica set free and of thorium sulphate thrown out. The amount of oxygen consumed indicated 16 per cent of oxidizable bases counted as UO_2; it may be therefore that all the uranium exists in that form and the iron in the ferrous state, as they are given in the analyses which follow. Of these *b* was made on a small sample selected grain by grain with the utmost care, but it was evidently not much purer than the first lot. There is at most an indication that FeO, CaO, alkalies, P_2O_5, and perhaps some water arise from impurities. Titanium, manganese, and fluorine are not present in the mineral.

	a	*b*	Thoro-gummite (H. & M.).		
SiO_2	13·90	13·92	SiO_2	13·085	
UO_2	22·40	†21·86	UO_3	22·43	
ZrO_2?	·88		ThO_2	41·44	
ThO_2 }	*45·30	Lost.	Al_2O_3	·965	
Ce_2O_3? }			Fe_2O_3	·845	
La_2O_3 } groups	1·86		$(Ce, Y)_2O_3$ etc.	6·69	(At. W. 135.)
Y_2O_3 }			PbO	2·16	
PbO	3·74	3·92	CaO	·41	
FeO	1·15	(‡)	P_2O_5	1·19	
CaO	·59	·44	H_2O	7·88	
MgO	·10	·13	Moisture	1·23	
K_2O	·42	·70		98·325	
$(Na, Li)_2O$	·68				
P_2O_5	·67	·46			
H_2O above 100° C.	4·31				
H_2O below 100° C.	·50	·35			
	96·50				

* The precipitate by potassium hydroxide was pure white after long action of chlorine. It may, however, have contained a trace of cerium.

† Would be slightly increased by uranium which was not separated from the earths.

‡ The estimation of iron miscarried, but the amount was unquestionably less than in *a*.

Taken by themselves these results are incapable of translation through the medium of molecular weights into any precise formula, but they become of interest when compared with the accompanying analysis of thoro-gummite by Hidden and Mackintosh.[1] It is then seen that the opinion of Mr. Hidden regarding the derivation of thoro-gummite from the present mineral was fully justified. It is in fact remarkable, considering the great molecular alteration that must have taken place, as determined by the totally different appearance of the two minerals, that so little loss of substance has occurred. Almost the sole change has consisted in an oxidation of uranous oxide and an increase in the hydration. These facts render not altogether safe the assumption above made that all uranium and iron in the new mineral exist there in the lower forms of oxidation, and they furthermore indicate that the black mineral itself may have already undergone

[1] Amer. Jour. Sci., xxxviii, 480, 1889.

oxidation and hydration without this being manifest to the eye—a supposition which is strengthened by the loss at 100° C. of half a per cent of water, and in fact by the intimate union which existed between the two minerals when received. Such material alteration without corresponding physical evidence of it seems to be common among uraninites. The original condition of the mineral may then have been one in which uranium and iron were entirely in the lower state of oxidation and in which water was possibly absent. It is to be hoped that opportunity may yet be afforded for a more thorough examination of this mineral, which, though apparently allied to thorite and uranothorite, is distinguished from them chiefly by greater content in uranium and by a higher degree of basicity.

ZINC-BEARING SPRING WATERS FROM MISSOURI.

By W. F. Hillebrand.

Zinc salts have been observed in the waters from La Malou in the south of France, according to Doelter,[1] and in those of certain hot springs of New Zealand;[2] perhaps also in those of other localities, but I have as yet been unable to find any data bearing upon their contents in such salts. Durand-Fardel's Dictionnaire des Eaux Minérales, 1860, fails to include zinc as a constituent of the waters of La Malou which had been analyzed up to that time. It is therefore improbable that this element is present there in any considerable quantity.

The spring waters herein described are, it is thought, unique, in that their chief salt constituent is zinc sulphate. The following information in regard to the location and surroundings of the springs from which they flow has been obtained from Mr. W. P. Jenney of the U. S. Geological Survey, who was led to suspect a peculiarity of composition from the strong metallic astringent taste left in the mouth after swallowing, and by the slimy white precipitate which covers the walls of the springs and all vegetable matter falling into the water about them.

On the road from Joplin to Seneca, in Newton County, southwestern Missouri, about a quarter of a mile north of Shoal Creek and four and a half miles southwest of Joplin is a low bluff, perhaps 18 feet high, formed by a portion of the Burlington chert beds. At the base of this bluff, in a shallow depression, is a series of springs extending for a distance of perhaps 150 feet and emptying their waters into the above-mentioned depression, wherein a sluggish current is produced and a deposition of a slimy white precipitate takes place. They vary in size, discharging from one-half to 3 gallons of water per minute, and about 30 gallons, or 150 to 160 liters, in the aggregate. So far as can be judged by the taste they vary also in composition, some waters being much stronger than others.

The two samples analyzed were taken by Mr. James A. Reeves, of Joplin, from springs about 90 feet apart, designated as the east spring and the west spring, which were not only the most powerful, but which also, judged by the taste, furnished the strongest water.

[1] Allgemeine chemische Mineralogie, p. 233.

[2] Trans. and Proc. New Zeal. Institute, 1870, vol. III.

The composition as given below is that of the water after having stood in sealed bottles for two or three weeks and having been then separated by filtration from a whitish flocculent deposit which was probably formed after collection of the samples, in which case the reported composition does not exactly represent that of the water as it issued from the spring. As received the waters were clear and limpid above the sediment, they were neutral to litmus paper, and their density differed but little from that of pure water, that of No. 1 being 1·0006 at 20½° C. The samples were too small and time was too valuable to admit of exhaustive examination or of duplication of determinations. The analyses are as follows:

	I. East spring. Parts in 1,000,000.	II. West spring. Parts in 1,000,000.
Pb	trace.	undet.
Cu	·2	undet.
Cd	·5	?
Zn	120·5	132·4
Fe	·6	·6
Mn	2·3	2·4
Al	·4	·5
Ca	61·1	63·1
Mg	3.8	4·2
K	2·5	2·5
Na	3·6	3·9
Cl	2·6	2·6
SO_4	284·9	287·6
CO_3	43·2*	56·8*
SiO_2	13·7	15·7
	539·9	572·3

* Calculated.

	I. East spring.		II. West spring.	
	Parts in 1,000,000.	Percentage composition.	Parts in 1,000,000.	Percentage composition.
$PbSO_4$	trace.	trace.	undet.	undet.
$CuSO_4$	·5	·09	undet.	undet.
$CdSO_4$	·9	·17	?	?
$ZnSO_4$	297·7	55·14	327·0	57·14
$FeSO_4$	1·6	·30	1·6	·28
$MnSO_4$	6·3	1·17	6·6	1·15
$Al_2(SO_4)_3$	2·5	·46	3·2	·56
$CaSO_4$	109.9	20.34	85·8	14.99
$MgSO_4$	19·0	3·52	21·0	3·67
K_2SO_4	5·6	1·04	5·6	·98
Na_2SO_4	5·9	1·09	6·8	1·19
NaCl	4·3	·80	4·3	·75
$CaCO_3$	72·0	13·34	94·7	16·55
SiO_2	13·7	2·54	15·7	2·74
	539·9	100·00	572·3	100·00

Besides the above tabulated constituents, the waters held a considerable quantity of organic matter, which was not estimated, a small amount of ammonia not exceeding one part per million and which if counted as sulphate would affect only slightly the relative proportions of calcium sulphate and carbonate, and in an unconcentrated state they gave no reaction with brucine or diphenylamine for nitrates or nitrites. Although cadmium was not found in the water from the west spring, it is possible, in view of the close similarity of the two waters, that it was somehow overlooked.

In analyzing these waters a peculiarity deserves to be mentioned, which may at the same time serve as a warning to any one who may in the future examine them. Although a portion of the calcium unquestionably exists as carbonate, as shown by the excess of bases over chlorine and sulphuric anhydride, it is nevertheless the case that *all* the carbon dioxide is expelled by simply boiling the water. The amounts found for the east and west springs respectively were 120·5 and 110·0 parts of CO_2 per million. No more was obtained by acidifying the water. At the same time a precipitation of a zinc compound free from carbon dioxide and from calcium began to take place in the water as soon as the boiling point was neared, which soon ceased after ebullition set in. This precipitation furnishes the explanation of the total escape of carbon dioxide, combined as well as free, from the unacidulated water; for as the calcium bicarbonate in solution becomes decomposed by heat the calcium carbonate at temperatures near the boiling point at once reacts with zinc sulphate, with the formation of calcium sulphate, zinc hydrate or a very basic sulphate, and carbon dioxide. A determination of total solid constituents by evaporation of the water to dryness would involve, therefore, a very serious error in addition to those usually encountered.

A few remarks are here necessary in connection with the above reaction, which in one particular is so contrary to the statements that have come under my observations in chemical and geological literature bearing on the reaction which takes place between zinc salts in aqueous solution and undissolved calcium carbonate at elevated temperatures. It is generally stated that a basic zinc carbonate is precipitated while calcium sulphate goes into solution, except by Demarçay, the discoverer of the reaction, who says[1] that zinc *oxide* is thrown down. It is not to be supposed that soluble calcium in the form of bicarbonate would in any way affect this reaction except to hasten its completion. While a zinc carbonate is undoubtedly thrown down from a solution of the chloride by calcium carbonate or by the bicarbonate, as I have satisfied myself by experiment, this does not seem to be the case with a solution of zinc *sulphate*. An experiment, tested by repetition, with zinc sulphate and calcium bicarbonate in about the proportions shown in the above waters, i. e., with insufficient carbonate to throw out all

[1] Ann. d. Chemie, vol. xi, p. 250, 1834.

the zinc, by observing which precaution no calcium carbonate can contaminate the precipitate, showed that the latter was absolutely free from carbonic acid and from calcium, but contained some sulphuric acid. If this is the normal reaction for the sulphate, it is the one to be chiefly considered by the geologist, for in nature the sulphate of zinc, and not the chloride, on which latter laboratory experiments seem to have been largely made, is the form in which that element is most likely to be found in solution.

The sediments from the bottles, which were very slimy, amounted when dried at 100° C. to approximately 17·0 parts per million of the water from the east spring and to about 40·3 parts per million of that from the west spring. They contained thus dried not less than 13 per cent of water and organic matter, while the ignition residue was about three-fourths silica, and the remainder zinc oxide with a little iron, alumina, and sulphuric acid. The sediments were undoubtedly a mixture of amorphous silica, with very basic sulphates of zinc, aluminum and iron, without calcium. They had in both cases probably formed after the water was bottled, for they continued to appear in that portion of the filtered water which was retained as a reserve till completion of the analysis. As the two waters were not analyzed simultaneously the analyses are not strictly comparable, for one had deposited more sediment than the other, but it is noticeable that the water richest in salts had also deposited more sediment, showing that the differences in the analyses are not solely or in the main due to the different lengths of time that had elapsed between bottling and analyzing, but to inherent differences in composition.

With the waters was sent in a separate bottle a sample of the precipitate deposited in the depression into which the springs emptied. It was contaminated by much decaying vegetable matter and admitted of no satisfactory quantitative examination, but after filtration and washing, qualitative tests showed it to be essentially the same as the deposit found in the bottles. Owing to its greater amount it was also possible to ascertain that cadmium, lead, and copper were to a certain extent concentrated in it.

The source of the metallic salt constituents of these waters is of course to be sought in one of the deposits of zinc blende so numerous in that part of Missouri and across the state boundary in Kansas, although there are no known indications of zinc ores within a quarter of a mile of the springs and no large producing zinc mines within two miles of them. The limestones and cherts of the region supply the calcium and silica, and the organic matter, if not originally of surface origin, may well have come from oxidation of the bitumen which is found in quantity in the limestone. The permanent water level thereabouts is very near the surface, and it is not to be supposed that the particular waters under discussion have come from a great depth or are other than surface waters. The amount of zinc sulphate in them,

however, is from two to three times as much as could have resulted under the most favorable conditions from oxidation of zinc sulphide either directly or indirectly by the sole agency of oxygen carried down by surface waters. It is probable, therefore, that the ore bed whence the supply of metals is derived lies very near the surface, above the permanent water level of the country, where the atmospheric oxygen has direct access to it through porosity of the earth's surface. The powerful influence of oxygen thus acting on moist ore bodies, which have been exposed by the opening up of mines, in changing the character of the waters of a region, is shown by E. Haworth[1] in writing of the mine waters of the adjoining county of Cherokee in Kansas: "The well and spring waters before the mines were opened were first class, * * * But as soon as the mines were opened all was changed, and the older the mines the worse the water. Animals of all kinds began being seriously affected," etc. He ascribes the high contents of the waters in metallic salts solely to the greater amount of oxidation rendered possible by exposure of masses of ore in the mine workings and on the dumps to atmospheric action, and gives instances to show how rapidly they succumb to it. He gives also a qualitative analysis of a mine water drawn from near the bottom of a shaft 130 feet deep which was nearly full of water at the time, and also the total weight of solids. The latter was over four times as high as in the spring waters above described, and there were found, in addition to the constituents already enumerated, ferric and ferrous sulphate in large quantity and free sulphuric acid. Carbonic acid, alkalies, and copper are not mentioned by him.

[1] A contribution to the Geology of the lead and zinc mining district of Cherokee County, Kansas, presented to the faculty of the Kansas State University, 1884, p. 34.

JOSEPHINITE, A NEW NICKEL-IRON.

BY W. H. MELVILLE.

History.—Several months ago Prof. F. W. Clarke submitted to me for examination a quantity of magnetic pebbles which were sent to this office by Mr. William H. Hampton, of Portland, Oregon, and by subsequent correspondence with this gentleman he obtained a larger amount, with full liberty to publish the results arrived at in the laboratory.

In the spring of 1891 Mr. Hampton discovered these pebbles in large quantities in the placer gravel of a stream in Josephine and Jackson counties, Oregon, which border on the south of Douglas county, where the nickel silicate[1] described by Prof. Clarke occurs. He analyzed with reference to nickel and iron an average sample of 20 pounds of the wash gravel from the placer diggings, and found that the metallic portion gave 60·3 per cent nickel and 26·7 per cent iron. From the nature of the gangue or stony portion Mr. Hampton concluded that these waterworn pebbles and bowlders—for some pieces weighed over 100 pounds—"came from an eruptive dike somewhere in the vicinity." The locality of this dike was not at that time ascertained.

Physical characters.—The pebbles are irregular in shape, but approximate the form of ellipsoids. Their smooth surfaces, polished by the action of water, are colored in general greenish black, interrupted by bright areas of the grayish white alloy of nickel and iron. The former portions consist of siliceous matter, and when cut by a knife yield a dull and light gray powder, but broken fragments show greenish yellow and deep green colors and resinous luster resembling noble serpentine. With this is associated in some pebbles a silicate whose hardness is between 5 and 6. It is compact and on the fresh fracture exhibits a light brown color and vitreous luster, while exposed surfaces are reddened by ferric oxide.

The texture of the metallic portion as it appears on fracture is granular. The metal is gray, malleable, and sectile, with hardness about 5.

The specific gravity of one lot containing forty-two pebbles was taken in a pycnometer at a temperature of 22° C. These pebbles ranged in weight from 0·3159 to 1·6447 grams, and were about the dimensions of

[1] Bull. U. S. Geol. Survey, No. 60, p. 21, 1887-'88.

a pea. The largest pebble in my possession weighed 4·2847 grams, and the specific gravity of this was taken by suspending it from a silk fiber. Two determinations furnished a mean specific gravity of 6·204.

The pebbles are strongly magnetic.

Analyses.—The analyses were conducted with the aim of separating the pebbles into their proximate principles and also their ultimate constituents. Two different lots of about twelve grammes each were pulverized in a steel mortar, a delicate and tedious operation, owing to the extreme malleability of the nickel-iron. Two complete analyses of these samples were made. The ratio between the nickel and iron in the metallic state was ascertained by deducting from the total amounts of each of these elements those quantities which were found in other combinations. The ordinary method of fusion with sodium hydrate and subsequent treatment of the residue with concentrated nitric acid failed to give the true contents of the metallic portion in the pebbles, because the nickel iron was not passive in this acid. The ratio between the nickel and iron, however, could be obtained by this method.

The stony matter was freed as far as practicable from the magnetic parts by a fractional process—that is to say, by the repeated use of an electro-magnet and by the decantation of the light particles suspended in water. The siliceous portion was then analyzed. A fresh sample was treated with diluted hydrochloric acid, and after repeated evaporations the soluble silica was separated from the insoluble residue and weighed. The insoluble residue was analyzed, and the percentage composition of soluble silicate was inferred from this analysis, the analysis of the total siliceous matter, and the total silica of the pebbles.

The mean composition of the pebbles is shown by the following numbers:

	Per cent.		Per cent.
Nickel free, Ni	60·45	Nickel combined	0·25
Cobalt, Co	0·55		
Iron free, Fe	23·22	Iron combined	1·79
Pyrrhotite, Fe_7S_8	0·55	Sulphur	0·22
Chromite, $FeO \cdot Cr_2O_3$ / Magnetite, $FeO \cdot Fe_2O_3$	0·12	Chromium	0·04
Copper, Cu	0·50		
Arsenic, As	0·23		
Chlorine, Cl	0·04		
Silicate (anhydrous)	12·26		
H_2O below 100° C	0·81		
H_2O above 100° C	1·12		
CO_2	trace.		
Volatile matter	0·70		
	100·55		

	Total silicate.	Insoluble silicate.	Soluble silicate.
SiO_2	5·14	0·23	4·91
Al_2O_3	0·33	0·03	0·30
Fe_2O_3	2·08	0·04	2·04
(Ni, Co)O	0·32	trace.	0·32
CaO	1·62	0·06	1·56
MgO	2·69	0·14	2·55
Na_2O	0·08	.....	0·08
H_2O above 100° C.	1·12	.....	1·12
	13·38	0·50	12·88

Composition.	Insoluble silicate.			Soluble silicate.		
	Per cent.	At. ratio.		Per cent.	At. ratio.	
SiO_2	45·63	3·04		38·23	2·55	
Al_2O_3	6·58	0.39		2·34	0·14	0·74
Fe_2O_3	8·77	0·33		15·88	0·60	
(Ni, Co)O	undetermined.		2·51	2·49	0·07	
CaO	11·03	0·39		12·14	0.43	
MgO	28·01	1·40		19·85	0·99	2·47
Na_2O	.....	.....		0·35	0·01	
H_2O above 100° C.	.....	.....		8·72	0·97	
Total	100·02	.....		100·00		

Silicates.—There are two silicates, then, the one soluble in hydrochloric acid being undoubtedly serpentine. This serpentine surrounds the metallic portion, and on polished sections its deep green color is well brought out. It has not penetrated into the metallic mass, and it would appear that the pebbles once formed a large aggregation and that fractures took place in directions of least resistance through the serpentine. Other characters of serpentine were noted—its resinous luster, its hardness of about 3, and its infusibility. In the closed tube water was given off. The atomic ratio of the combined bases and water to silica is 3·2:2·55 or 5:4, a ratio which is identical with that of serpentine. The ratio between bases and water, 7:3 instead of 3:2, is not the true ratio for these constituents in serpentine as it exists in the pebbles, because the analysis is calculated from figures obtained from material which was dried at 100° C. Again, the reddish brown coloration of this dried material indicated the presence of some impurity, probably oxides, and this could not be eliminated. The water is, therefore, too low and the iron oxide too high.

The insoluble silicate, however, can not be so clearly made out. Its atomic ratio, SiO_2: base = 6:5, brings it nearer an orthosilicate than a metasilicate. It is light brown, vitreous, hard, compact, and not cleavable. It does not fuse before the blow-pipe. It is not so hard as olivine and its insolubility in acid excludes this mineral. In physical and pyrognostic characters and to some extent, also, in composition it agrees fairly with bronzite (enstatite). The probable silicates to occur

in this association are pyroxene, olivine, enstatite, from which serpentine is derived, while a feldspar is not to be expected. I did not determine to which silicate the sodium-oxide belonged, owing to its small quantity and the small quantity of insoluble silicate in the pebbles. A mixture of a soda-lime feldspar and enstatite (or pyroxene) would answer the requirements of the ratio, but this is purely speculative. So far as the data go it is best to regard this silicate as an impure bronzite.

During attempts to purify the silicates it was noticed that on the removal of the metallic part by a neutral concentrated solution of either cupric sulphate or mercuric chloride that the silicate was more or less attacked. Magnesia was removed, and one analysis showed that out of 2·69 per cent MgO in the pebbles only 0·43 per cent remained in the purified silicate. Curiously no iron or lime was removed. Pulverized olivine and serpentine were each digested with copper sulphate on the water bath two or three hours; a yellow copper salt was deposited and a large quantity of magnesia was taken out of both silicates. A basic copper sulphate was produced, and the liberated sulphuric acid (SO_3) combined with magnesia to magnesium sulphate. In the presence of olivine or serpentine this treatment for the purification of the silicate is inadmissible.

Chromite.—Under the microscope a minute quantity of black metallic grains can be seen in the siliceous portion, which do not precipitate copper from a sulphate solution. These grains consist of chromite with a very few strongly magnetic particles of magnetite. 0·04 per cent of chromium was found in the pebbles, while the per cent of chromium, corresponding to 0·12 per cent of chrome iron, is 0·036. The presence of chromite is naturally expected in the serpentine.

Magnetite.—The few grains mentioned under chromite were dissolved by protracted heating in hydrochloric acid. Other particles of magnetite were not recognized with certainty.

Two magnetic pebbles were found among those which carried the large percentage of nickel, and a small amount of fibrous serpentine (not chrysotile) adhered to this magnetite. It is probable that magnetite occurs in the original deposit from which the nickel pebbles were transported. The high percentage of iron obtained by Mr. Hampton was probably due to the presence of some magnetite-pebbles in the average sample which he studied.

Pyrrhotite (*troilite*).—The monosulphide of iron could not be separated from the other principles with sufficient purity for analysis. The amount of this mineral, formula Fe_7S_8, was calculated from the total sulphur, 0·22 per cent. Hydrogen sulphide was liberated in considerable quantity when the powdered pebble was treated with diluted chlorhydric acid. Millerite does not act thus.

Copper.—The copper is not a constituent of the pyrrhotite, but belongs to the nickel iron. Copper minerals were not detected under magnifying power.

Arsenic.—Arsenious oxide was condensed in the cool parts of a tube through which air was allowed to pass, as also in all the tubes used for the determination of volatile matter. No sulphide of arsenic dissolved by digesting in the cold with ammonium carbonate, nor could niccolite (nickel arsenide) be detected. Arsenic forms a part of the metallic portion of the pebbles.

Chlorine.—The chlorine was determined in a nitric-acid solution of the original powder, a blank experiment with the use of the same quantity of reagents being run parallel with that. In an aqueous solution were found iron, nickel, magnesium, sodium, and chlorine, and this fact, together with the small available quantity of chloride, caused the difficulty in determining with which element chlorine was combined. The presence of iron and nickel, since pyrrhotite carries nickel, can be accounted for in the aqueous solution by the easy oxidizability of the sulphide with free access of air. Green ferrous chloride could not be detected in the powder, nor any soluble salt possessing that color. The permanence of the pebbles in air is also a presumption in favor of the absence of lawrencite. Nickel chloride has not before been observed, but may possibly exist in these specimens. It is more probable that the chlorine is united with sodium 0·04 per cent requiring 0·026 per cent Na or 0·035 per cent Na_2O. The magnesium is in the form of carbonate.

Water and volatile matter.—The powdered substance in a platinum boat was heated in a glass tube in a stream of dry carbonic anhydride, and the water, both hygroscopic moisture and water of constitution, was weighed in a chloride of calcium tube. Another portion was heated in hydrogen gas, and hence the oxygen in the oxides was known, although this amount might have included some, if not all, of the oxygen combined with iron in the ferric state in the silicates. After burning in a current of dry air and then reducing in hydrogen the total loss was ascertained from the difference in weight of the contents of the boat before and after the operation. In all cases except when burnt in air a brownish cloud possessing an empyreumatic odor was driven off without leaving a brown black sublimate in the tube. It was a volatile organic substance whose nature was not discovered. The pulverized pebbles when treated with dilute hydrochloric acid at the temperature of the water bath gave the odor characteristic of the decomposition of a carbide, so that the volatile matter given in the analysis consists of organic matter, namely, combined carbon and probably a hydrocarbon. All loss arising from the volatilization of arsenic, sulphur, and chlorine have not been included in the per cent given for volatile matter.

Nickel-iron.—Of special interest is the metallic portion. Two analyses gave—

	(1)	(2)	At. ratio
Fe	23·36	23·09	0·41
Ni	60·47	60·43	1·03

From this ratio is deduced the formula Fe_2Ni_5.

The following table gives a comparison of a few examples of nickeliferous iron, which form an instructive series:

	Catarinite.*	Octibbehite.†	Awaruite.‡	Josephinite.
Iron	63·69	37·69	31·02	23·22
Nickel	33·97	59·69	67·63	60·45
Atomic ratio Fe : Ni	1. 14 : 0·58	0·66 : 1·02	0·55 : 1·17	0·41 : 1·03
			$2(FeNi_2)$	
Formula	Fe_2Ni	Fe_2Ni_3	Fe_2Ni_4	Fe_2Ni_5

* Encyclopédie chimique, Fremy, Metalloids, Tome ii, par M. Stanislas Meunier.

† Am. Jour. Sci., II, xxiv, p. 293, Taylor.

‡ Am. Jour. Sci., vol. xxxiii, p. 244, G. H. F. Ulrich; analysis by W. Skey. A. Sella described a nickel iron from the auriferous sands of the stream Elvo, near Biella, Piedmont; Fe 26·6 per cent; Ni (Co) 75·2 per cent; formula $(2FeNi_3) = Fe_2Ni_6$. C. R. cxii, 171; also Am. Jour. Sci., III, p. 252, 1891.

The question naturally arises whether the origin of these pebbles is cosmic (meteoric) or terrestrial. Catarinite and octibbehite have been considered meteoric falls, while awaruite has been traced from the drift in the Awarua river on the western side of the middle island of New Zealand to a "mountain of peridotite, an olivine-enstatite rock more or less serpentinized," and is undoubtedly terrestrial. In the drift are found gold, platinum, cassiterite, chromite, and magnetite. The placer gravel, in which josephinite is found, is like that of New Zealand with the exception of the occurrence of platinum[1] and cassiterite so far as known at present.

There is one element, phosphorus, which is almost universally found in meteorites and combined with nickel and iron to form the mineral schreibersite, which has no representative among terrestrial minerals. After evaporating to dryness a nitric acid solution of a sample of the pebbles, and fusing the residue with sodium carbonate and potassium nitrate, phosphoric acid was not detected in the acid filtrate, and thus was proved the absence of phosphorus both as terrestrial phosphate and meteoric phosphide. In the published analysis of awaruite by W. Skey no phosphorus is given. Catarinite and octibbehite contain 0·05 per cent and 0·10 per cent respectively.

By etching with nitric acid Widmannstätten figures can not be produced upon a polished surface of the nickel-iron. The metal seems to be homogeneous, and the little sulphide occurs in the fissures. Awaru-

[1] Platinum occurs in the region of Rogue river, Oregon.

ite is passive toward an acid solution of copper sulphate, and only with difficulty and long heating is the nickel-iron from Oregon completely dissolved with replacement of the copper in a sulphate solution. This passive state is uncommon with the ordinary nickel-iron of meteorites, but the high percentage of nickel may account for this property. Concentrated nitric acid dissolves the alloy.

Daubrée[1] points out that meteorites and analogous terrestrial rocks differ in that the former contain in a reduced state certain substances which appear in the latter in the state of oxides. This idea could be extended to include metamorphism in its broadest sense. Serpentine is rarely found in meteorites, although Wöhler has recognized it in some carbonaceous meteorites. In the two cases of awaruite and josephinite, serpentine is the principal silicate, derived in the former from olivine and enstatite. Daubréelite is metamorphosed into chrome iron, and this may possibly be the explanation of the origin of the latter: that the double sulphide of chromium and iron existed in the ferromagnesian silicates before or at the time of their serpentinization, and was then oxidized to chromite.

The evidence cited in the previous paragraphs points to the terrestrial origin of the pebbles which form the subject of this paper, and here the question of origin must rest till the nickeliferous iron is found in situ.

The name josephinite is given in honor of the county, its locality, in accordance with the custom in use for naming analogous substances.

[1] Etudes synthétiques de géologie expérimentale, par A. Daubrée, 1879, p. 578.

A NEW METEORITE FROM HAMBLEN COUNTY, TENNESSEE.

By L. G. Eakins.

This meteorite, which was found in September, 1887, on a ridge about six miles WSW. from Morristown, Hamblen County, Tennessee, was first recognized and brought to notice by Prof. J. M. Safford, of Nashville, who in course of an inspection of a collection of iron ores recognized some fragments as undoubtedly meteoric.

Professor Safford at once took steps to secure these pieces, and visited the locality where they were found. Here he succeeded in finding a few more fragments, which had the appearance of having been buried in the soil and afterwards turned up by the plow. These various pieces now in Professor Safford's possession have a total weight of about 36 pounds, two of them weighing respectively 11 pounds and 13 pounds.

A specimen sent by Professor Safford to the U. S. National Museum, and now in its collection, furnished the material for this investigation.

Most of the pieces show much surface oxidation; a fresh fracture showing a gray color, with numerous metallic particles of nickel iron.

The analysis was made in the usual way for this class of meteorites, that is, by separating the metallic and siliceous portions, both by picking and by the magnet, and analyzing separately the nickeliferous iron, the silicates soluble in hydrochloric acid and those insoluble in the acid.

The metallic and siliceous portions of this meteorite are, approximately, equal in amount, the iron being quite malleable and unusually tough.

The analysis is as follows:

Nickeliferous iron.

Fe	90.92
Ni	7.71
Co	.80
Cu	trace.
P	.19
S	.04
	99.66

Siliceous portion.

	Soluble in HCl.			Insoluble in HCl.		
	Analysis.	Calculated to 100 per cent.	Molecular ratios.	Analysis.	Calculated to 100 per cent.	Molecular ratios.
SiO_2	16·79	45·61	·760	31·47	50·67	·844
Al_2O_3	8·33	22·62	·222	9·25	14·89	·146
Cr_2O_3	.....	.....	.....	·82	1·32	·009
FeO	4·88	11·73	·163	6·55	10·55	·147
NiO	·39	1·06	·014	.....	.....	.....
MnO	.....	.....	.....	·47	·76	·010
CaO	5·19	14·09	·252	2·24	3·61	·064
MgO	1·34	3·64	·091	11·16	17·98	·449
K_2O	.....	.....	.....	·02	·03	.....
Na_2O	.....	.....	.....	·12	·19	·003
P_2O_5	·46	1·25	·009	.....	.....	.....
S	·25	.....	.....	.....	.....	.....
	37·63	100·00	.....	62·10	100·00	.....

In calculating the analysis of the soluble portion to 100 per cent, the S and an amount of iron (.56 per cent FeO) sufficient to form FeS are first deducted.

In many stony meteorites olivine is a considerable constituent, generally forming the bulk of the soluble silicate; but in this case the analysis shows olivine to be present in but small proportions, if at all. It is interesting to see that both the soluble and insoluble portions have practically the same molecular ratios, the soluble portion reducing itself essentially to $R\,Al_2\,SiO_6$, in which, R=Ca, Fe; and the insoluble part to the same formula, where R=Mg, Fe; both being equivalent to aluminous enstatite or pyroxene.

At the time this analysis was made it was impracticable to supplement the work with the proper microscopical examination of sections, which doubtless, in conjunction with the chemical evidence, would have satisfactorily determined the minerals present. Without this microscopical knowledge, however, little that is definite can be said, except that there seem to be present two similar molecules, the one in which lime predominates being soluble, and the other, magnesian, being insoluble, in hydrochloric acid. The other alternative is to assume a complex molecule which is split into two sections by the action of the acid.

ON THE CATALYTIC ACTION OF ALUMINUM CHLORIDE ON SILICIC ETHERS.

By H. N. Stokes.

If a little powdered anhydrous aluminum chloride be added to some ethyl trichlorsilicate, $SiCl_3(OC_2H_5)$, which is cooled by ice, it dissolves, but no reaction is observed; on removing from the ice, bubbles of gas soon appear, and the reaction often becomes violent, attended by heating of the liquid. The gas, which burns with green-edged flame and formation of hydrochloric acid, is obviously ethyl chloride. If now the liquid be gently heated it gradually becomes thick, then solid, and finally the entire amount of aluminum chloride sublimes unchanged.

If instead of trichlorsilicate, tetraethylsilicate, $Si(OC_2H_5)_4$, be used, the reaction is in many respects the same, including the formation of ethyl chloride and the thickening of the liquid; but if the test-tube be connected with a condenser, it is seen that much ethyl ether is also produced. It may also be noticed that a relatively much greater amount of aluminum chloride than in the first case is required to produce the solid residue, while, unless a very considerable quantity has been added, none sublimes out on further heating.

It will be shown below that the action of the aluminum chloride on the trichlorsilicate is a case of so-called *catalytic action* (this being defined as a change brought about by a substance which at the end remains unaltered), while its action on the tetraethyl ether is one which is purely proportional to the relative amounts of the reagents, the aluminum remaining finally in combination with silica. It will also be seen that the monochlorsilicate, $SiCl(OC_2H_5)_3$, is intermediate in its behavior, a mere trace of aluminum chloride being sufficient to carry the decomposition to an end, when all the aluminum is found in fixed form. From these observations may be deduced the explanation of each case, including the catalytic action of the chloride on the trichlorsilicate. The details of the experiments, which were roughly quantitative, will be found in a separate section.

The only hypothesis which explains the facts observed is that in each case the substances react in a truly chemical sense, ethyl chloride and aluminum silicate compounds, Si—O—Al, being formed, but that in case of the chlorsilicates these bodies are exceedingly unstable, and

decompose at once with regeneration of aluminum chloride, which is thus able to act again, and thus produce total decomposition when present even in traces.

The cause of this regeneration I take to be due, in part at least, to the tendency of the silicon to monopolize the oxygen, at the expense of the aluminum, forming Si=O, Si—O—Si, etc., whereby the metal is unable to remain combined with oxygen as long as this tendency of the silicon is not fully satisfied. If it happens that the latter is partly combined with chlorine (silicon chlorine), it at once exchanges it for an equivalent of oxygen. This, however, holds only in the aliphatic series of ethers, and in those cases where the chlorine is not the only constituent of the silicon compound. As I shall show elsewhere, silicon, when completely saturated with chlorine, as in silicon tetrachloride, does not show this tendency, neither does it exist in case of the aromatic silicates. From the latter, aluminum chloride, if in excess, takes all the oxygen and the silicon becomes completely chlorinated.

The formation of *ethyl ether* I can explain only by assuming in silicon a well-known property of carbon, which is manifested in the ortho-ethers of carbonic and other organic acids, namely, that the highest basicity is shown only when all the basic radicle are organic, while the metallic salts are of a lower degree of saturation, and the mixed organic metallic ortho-salts are so unstable as to be scarcely capable of existing under ordinary conditions. Assuming this analogy to exist, we should expect to find transformations like the following occurring:

$$Si\begin{matrix}OR\\OR\\O\\O\end{matrix}>AlCl = SiO<\begin{matrix}O\\O\end{matrix}>AlCl + R_2O,$$

$$2\,Si\begin{matrix}OR\\O_3Al\end{matrix} = O<\begin{matrix}SiO_3Al\\SiO_3Al\end{matrix} + R_2O.$$

Strictly speaking, the tendency is not to form, as in the case of carbon, meta compounds containing Si=O, the analogue of carbonyl, but groupings in which two silicon atoms are united by oxygen, Si—O—Si, or $(SiO)x$. This tendency is so strong, as has been pointed out by others,[1] that it is obviously the explanation of the fact that nearly all silicon compounds containing the analogue of carbonyl are not volatile, or volatile only at high temperatures, when by analogy with carbon, the reactions producing them should give volatile bodies of low molecular weight. This tendency to condensation and polymerisation by means of oxygen is the rule in the silicon series, and forms one of the most marked differences in the chemical behavior of these two elements, and the chief obstacle to producing by any simple means definite derivatives of silicic acid. I wish to be distinctly understood, therefore, as using the following formulas and equations only as typical ones reduced to the simplest possible form, the actual ones being vastly more complex and of almost infinite variety. Where R is used it stands,

[1] e. g. Mendelejeff, Grundlagen der Chemie, deutsche Aufl., p. 767.

for sake of simplicity, for ethyl. That the quantitative experimental results do not conform with absolute strictness to the theoretical explanation is not surprising, for aluminum chloride is an extremely reactive body, tending to produce all sorts of secondary changes, while it is not to be expected that the transformations could be carried quantitatively to an end by heating the viscous and finally solid masses which result.

Ethyl trichlorsilicate, $SiCl_3(OR)$, is readily and completely decomposed by aluminum chloride, and the reaction is quite independent of the amount used, even a trace being sufficient. The products are ethyl chloride, free from ethyl ether, free aluminum chloride unchanged in amount, and finally a solid residue of the empirical composition $SiO.Cl_2$, but which in reality consists of a mixture of all sorts of complex silicon oxychlorides with free silica, the general result being expressed by the equation

$$SiCl_3(OR)+xAlCl_3=SiO.Cl_2+RCl+xAlCl_3,$$

a typical case of catalytic action.

These oxychlorides are for the most part not volatile, but undergo at a high temperature transformation into oxychlorides richer and those poorer in chlorine,[1] the result being that they lose weight on ignition. The reactions by which they can be formed in the present case are very numerous, and only a few typical ones are given. The first steps in the process are

$$SiCl_3(OR)+AlCl_3=SiCl_3.OAlCl_2+RCl,$$

or

$$2SiCl_3(OR)+AlCl_3=\begin{matrix}SiCl_3O\\SiCl_3O\end{matrix}>AlCl+2RCl.$$

These bodies, being for reasons above given very unstable, at once react with fresh portions of trichlorsilicate:

$$SiCl_3.O.AlCl_2+SiCl_3(OR)=SiCl_3.O.SiCl_2(OR)+AlCl_3,$$

and

$$\begin{matrix}SiCl_3O\\SiCl_3O\end{matrix}>AlCl+SiCl_3(OR)=\begin{matrix}SiCl_3O\\SiCl_3O\end{matrix}>SiCl(OR)+AlCl_3.$$

The regenerated aluminum chloride acts further, thus:

$$SiCl_3.O.SiCl_2(OR)+AlCl_3=SiCl_3.O.SiCl_2.O.AlCl_2+RCl,$$

which latter repeats the process, or may decompose thus:

$$SiCl_3.O.SiCl_2.OAlCl_2=SiCl_3.O.SiO.Cl+AlCl_3,$$

and so on in every possible way ad infinitum, the aluminum chloride being continually regenerated, while the tendency of silicon to such condensations leads to increasing size of the molecules, which tend to the limit $(SiO.Cl_2)_x$, but seldom reach it before a high degree of complexity is attained. The increasing viscosity of the liquid interferes with the complete conversion of RO into RCl at a temperature below which other changes set in, which are manifested by more or less evolution of hydrochloric acid and gaseous hydrocarbons, with some carbonization. There is, however, always an excess of silicon chlorine,

[1] Troost and Hautefeuille, Ann. chim. phys. [5], 7, 469.

which regenerates aluminum chloride, enabling it to act in minute amounts, and to reappear unchanged at the end.

It may be objected that these reactions are purely hypothetical, and that no such compounds as $SiCl_3.O.AlCl_2$ have been shown to exist. In the following cases it will be shown that there is strong evidence of their existence, the aluminum being caught in the act, so to speak, and found ultimately, not as chloride, but in combination with oxygen.

Ethyl monochlorsilicate, $SiCl(OR)_3$.—Aluminum chloride, in acting on this compound, produces a similar series of changes, even if used in relatively small amount, with this difference, that as there is not enough silicon chlorine to carry the regeneration through to the end, the aluminum remains finally as Al_2O_3, and probably also as AlCl, combined with silica. The process is also complicated in certain cases by the formation of ethyl ether, which was explained above.

If we suppose the aluminum chloride to act by contact or influence merely, the decomposition would be expressed by the equation

$$SiCl(OR)_3 + xAlCl_3 = SiO_2 + RCl + R_2O + xAlCl_3,$$

and the result would be practically independent of the amount of chloride used, which could be finally recovered unchanged. It is found, however, that while a mere trace is sufficient to bring about total decomposition in nearly the sense of the last equation, by increasing the amount more ethyl chloride and less ethyl ether are formed; when a certain proportion is reached, the ethyl ether vanishes, and also up to this point all aluminum remains fixed in the residue. If more than this amount of chloride be taken, some remains unchanged, and may be recovered by sublimation. We may consider three distinct cases, with differing proportions of the reagents, namely, when

$$Si:Al \begin{cases} >3:2 & (1) \\ =3:2 & (2) \\ <3:2 & (3) \end{cases}$$

The first case includes that where aluminum chloride is present only in traces, when the complete reaction, reduced to the simplest form and neglecting aluminum, would be

(*a*) $$SiCl(OR)_3 = SiO_2 + RCl + R_2O.$$

By increasing the proportion of chloride we have, for example,

$$20SiCl(OR)_3 + 2AlCl_3 = (SiO_2)_{20}(Al_2O_3) + 26RCl + 17R_2O,$$
$$6SiCl(OR)_3 + 2AlCl_3 = (SiO_2)_6\,(Al_2O_3) + 12RCl + 3R_2O, \text{ etc.}$$

It will be noticed that the relative amount of R_2O decreases and that of RCl increases as we approach the ratio Si: Al=3: 2. Reaching this point, which is case (2), we have

(*b*) $$3SiCl(OR)_3 + 2AlCl_3 = (SiO_2)_3(Al_2O_3) + 9RCl.$$

The experiment shows that with this ratio no R_2O is formed, and that all aluminum remains in fixed form in the residue. Any further in-

crease in the proportion of chloride belongs under case (3), where $Si:Al<3:2$. For example, if the ratio be that of equality, or 3:3, we might have

(*c*) $$3SiCl(OR)_3+3AlCl_3=(SiO_2)_3(Al_2O_3)+AlCl_3.$$

In fact when this proportion is taken, unchanged aluminum chloride sublimes out of the residue. Owing, however, to the tendency of the silicon to monopolize the oxygen or to take the metasilicate form, this proportion admits of another reaction:

(*d*) $$SiCl(OR)_3+AlCl_3=Si\begin{matrix}Cl\\O\\O\\O\end{matrix}\!\!\diagdown\!\!\diagup\!\!Al+3RCl,$$

and

$$Si\begin{matrix}Cl\\O\\O\\O\end{matrix}\!\!\diagdown\!\!\diagup\!\!Al=SiO<\begin{matrix}O\\O\end{matrix}>AlCl,$$

the residue being a chloraluminum metasilicate, or at least some similar form in which the preference of silicon for oxygen before chlorine is satisfied. The chlorine and aluminum in this form are practically fixed, as such a body as this would probably give off aluminum chloride, if at all, only at a high temperature, the effect being that the volatile chloride falls below the theoretical amount required by equation (*c*).

Finally, if $Si:Al=1:2$—

(*e*) $$SiCl(OR)_3+2AlCl_3=SiO_3Al_2Cl_4+3RCl.$$

If we write the formula of the product

$$SiO<\begin{matrix}OAlCl_2\\OAlCl_2\end{matrix}$$

it appears that in this form also the aluminum might be fixed, but that if more chloride be present, leading to the formation of

$$SiCl(OAlCl_2)_3,$$

such a body would, by virtue of the silicon chlorine present, decompose at once into $AlCl_3$ and $SiO(OAlCl_2)_2$. Two atoms aluminum are therefore the most that can possibly be held by one atom silicon reacting as monochlorsilicate; any further amount must remain finally as unchanged chloride. The stability of such bodies as $SiO(OAlCl_2)_2$ is, however, made improbable by the experiments, which show that even with the ratio 1:1 only a part of the aluminum remains fixed.

These equations do not explain the semicatalytic action of aluminum chloride in decomposing indefinitely large amounts of monochlorsilicate. The reason is obvious when we consider that, as the experiments show, the greatest amount of aluminum which can be held fixed by 1 mol. wt. monochlorsilicate, lies between $\frac{2}{3}$ and 1 at. wt. (equations *b* and *d*). Any greater amount of monochlorsilicate will, by virtue of its silicon chlorine, regenerate aluminum chloride, and be destroyed thereby,

until the above proportion is reached. At this point further reaction results only in the sense of *b* and *d*, the regeneration of the chloride ceases, and all aluminum remains fixed.

It will be observed that in these reactions the chlorine going to form ethyl chloride comes proximately from the aluminum chloride, but ultimately, in part, from the chlorsilicate, and that the equations

$$SiCl_3(OR) = SiOCl_2 + RCl,$$
$$SiCl(OR)_3 = SiO_2 + RCl + R_2O$$

are not strictly true, the aluminum acting as the agent by which Cl is transferred from Si to R. The hypothesis might perhaps be further tested by substituting aluminum bromide for the chloride. If the decomposition is due to *influence* only, $SiCl_3(OR)$ should give $SiO.Cl_2$, and RCl and $AlBr_3$ only, but on the above hypothesis $SiO.Cl_2$ with either RBr and $AlCl_3$ only, or a mixture of RCl, RBr, $AlCl_3$ and aluminum chlorobromides, according to the proportions and the nature of the intermediate products. As this would involve previously studying the question whether a *direct* interchange of chlorine and bromine might occur, the experiment was postponed.

Ethyl dichlorsilicate, $SiCl_2(OR)_2$, from similar considerations, should decompose thus—

$$SiCl_2(OR)_2 = SiO_2 + 2RCl,$$

and it is not possible to devise any probable reaction by which aluminum should remain permanently combined. Therefore the apparent catalytic action should be as obvious here as in the case of the trichlorsilicate. The experiments were, however, defective, probably owing to impure material, and no satisfactory conclusion could be drawn from them.

Ethyl orthosilicate, $Si(OR)_4$.—This body shows a radically different behavior from that of the chlorsilicates, the decomposition being strictly proportional to the relative amount of aluminum chloride used, and in this lies the explanation of the whole series of observations.

We may consider the following cases:

$$Si:Al \begin{cases} <3:4 & (1) \\ =3:4 & (2) \\ >3:4 & (3) \end{cases}$$

the ratio 3:4 being that in which the aluminum chloride contains just enough chlorine to convert all ethyl into ethyl chloride.

(*a*) $$3Si(OR)_4 + 4AlCl_3 = Si_3O_{12}Al_4 + 12RCl.$$

From considerations mentioned while speaking of the monochlorsilicate, it is obvious that this proportion may result in a certain amount of chlorine remaining combined with the aluminum up to the limit—

(*b*) $$3Si(OR)_4 + 4AlCl_3 = Si_3O_{10}Al_4Cl_4 + 8RCl + 2R_2O.$$

For practical reasons given below, the substances could not be made to react in this proportion, the result being a formation of ethyl ether,

ethyl chloride, and sublimation of some unchanged aluminum chloride. For the same reason a reaction in the sense of case (1) was practically not to be brought about.

If the reaction were in any sense catalytic, it would follow that by reducing the aluminum chloride below the proportion Si:Al=3:4, the decomposition would still be complete, but the amount of ethyl ether would increase relatively, while that of ethyl chloride would decrease, the limit being, with a trace of aluminum chloride—

$$Si(OR)_4=SiO_2+2R_2O.$$

The actual result was that while with Si:Al=3:1 the decomposition was complete, and approximately in the sense

(*c*) $$6Si(OR)_4+2AlCl_3=(SiO_2)_6(Al_2O_3)+6RCl+9R_2O,$$

the slightest diminution of the amount of chloride below this ratio was followed by some of the silicate remaining totally unchanged. With Si:Al=3:0.9 for instance, it was possible to recover some of it, and with Si:Al=150:1 the merest trace of decomposition was discernible. This proportion in the case of the monochlorsilicate resulted easily in total decomposition. The only possible explanation of this difference is that in the case of the chlorsilicates the apparent contact action is due to constant regeneration of aluminum chloride by silicon chlorine. The tetraethyl ether contains no silicon chlorine, aluminum chloride is not regenerated, and therefore acts only in proportion to the amount originally taken.

An experiment was made which shows the peculiar stability of silicon tetrachloride as compared with the chlorsilicates. It was supposed that since

$$SiCl_3(OR)+\text{trace } AlCl_3=SiO.Cl_2+RCl+\text{trace } AlCl_3,$$

by adding to tetraethyl silicate some silicon tetrachloride in the proportion required by the equation

$$Si(OR)_4+3SiCl_4=4SiCl_3(OR),$$

the chlorine of the tetrachloride would regenerate aluminum chloride, with the final result that solid silicon oxychloride and ethyl chloride would be formed. With even Si:Al=5:1 and in sealed tubes at 100° no solid was formed. Only after heating at 170°, at which temperature the tetrachloride acts on the ether, did total decomposition occur.

Anhydrous ferric chloride acts on both the tetraethyl silicate and the trichlorsilicate, but with much greater difficulty than aluminum chloride. Only at near the boiling point (105°) of the trichlorsilicate was any marked reaction, with formation of ethyl chloride, visible. The tetraethyl silicate reacted easily on heating, giving off ethyl ether and ethyl chloride and leaving a solid residue. The reactions were not further studied.

Anhydrous zinc chloride is without action on the tetraethyl silicate at its boiling point (165°).

EXPERIMENTAL DETAILS.

Only carefully fractioned silicates and freshly sublimed aluminum chloride were used. The apparatus and method of working were as follows:

A thin-walled glass tube of about 2 cm. diameter was drawn out into the shape shown in the figure. The constriction *E* served when necessary as a support for the small weighed test-tube *G*, in which the ethyl ether collected. Some aluminum chloride was placed in a boat, inserted into *AB*, and carefully sublimed over into *CD* in a current of dry hydrogen. In this way it was obtained in a finely divided state, rendering solution more rapid. The hydrogen was then replaced by air, *BC* drawn out and melted off at *B*, and the weight of the sublimed chloride determined to a centigram. *CD* was then placed in ice, the calculated weight of silicate or chlorsilicate introduced through *F*, the tube *G* inserted when necessary, and the apparatus attached to an inverted condenser which ended in a U-tube with two cocks, placed in a freezing mixture, and serving to condense the ethyl chloride and any ethyl ether that might be carried over. By gently agitating the tube, the solution of the chloride was effected. On removing it from the ice, the reaction usually began

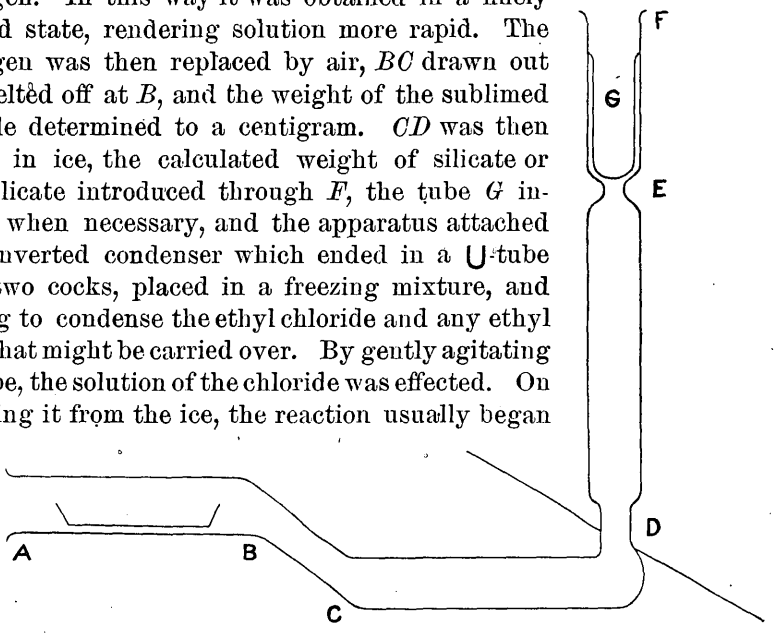


Fig. 1. Apparatus used in experiments upon silicic ethers.

of itself, and often had to be moderated by cooling. After the evolution of ethyl chloride had slackened, *CD* was gently heated, the ethyl ether then distilling and collecting in *G*. After the collection of ether had ceased, *G* was gently warmed, whereby practically all ethyl chloride was driven over, the ether condensing and running back. After removing *G*, the point *B* was broken off and the residue heated in a current of hydrogen until no further effect was observed, any aluminum chloride condensing in *DE*, or sometimes in part being carried over into the condenser. The hydrogen was then displaced, *DF* melted off at *D*, when necessary, and all products determined by weighing. Some of the liquid in the U-tube was brought into a graduated tube over mercury, and any ethyl ether determined by absorption with a drop or two of strong sulphuric acid, the residue being ethyl chloride.

Ethyl trichlorsilicate.—Taken $SiCl_3(OR)$ 7·66 grams (3 mol. wts.) and $AlCl_3$ 1·91 grams (1 mol. wt.).

On removing the ice from *CD*, the evolution of ethyl chloride began almost at once and the liquid grew so warm that cooling had to be resorted to to prevent the contents from boiling over. Presently a large quantity of a colorless, apparently crystalline substance separated, nearly filling the liquid. Its nature was not determined, but it was found to fuse on gently heating. After the evolution of ethyl chloride had moderated, its formation was promoted by a gentle heat. The liquid then became gradually thick, and finally almost solid. *B* was then broken off, and the residue heated in a stream of hydrogen until no further sublimation of aluminum chloride was observed. Absolutely no ethyl ether was formed. The residue was somewhat discolored, solid, transparent, and frothy. As explained above, the reaction occurs in accordance with the equation

$$SiCl_3(OR) + xAlCl_3 = SiO.Cl_2 + RCl + xAlCl_3,$$

as is borne out by the following data, which in this, as in all following experiments, are given in percentage of the total material used:

	Found.	Calculated.
Residue	46·3	51·2
Sublimate ($AlCl_3$)	20·9	19·9
Distillate, RCl	22·5	28·8

The results are naturally only approximate, but quite as near as could be expected. The viscosity of the liquid towards the end interferes with the smoothness of the reaction, and it is impossible to condense the ethyl chloride completely, or to prevent some being carried off by the current of hydrogen. If the reactions given are correct, the residue is not really $SiO.Cl_2$, but a mixture of oxychlorides in which there remains a small amount of ethyl, which will not go off at a temperature below that at which carbonization and other secondary changes take place, and which are still greater in the cases below mentioned. Troost and Hautefeuille[1] have shown that the result of heating oxychlorides is an approximation towards SiO_2 and $SiCl_4$. This is doubtless the reason why in this case the weight of the residue is slightly too low and that of the sublimed aluminum chloride a little too high. The former, on extracting with alcohol, left a little silica in gelatinous form, while the latter was found to contain a small amount of volatile silicon compounds. In fact, the residue on heating in a test tube to redness gave off a considerable amount of volatile oxychlorides, but no aluminum chloride.

[1] Loc. cit.

In experiment 2 the proportions taken were the same and the observations essentially similar.

	Found.	Calculated.
Residue	38·9	51·4
$AlCl_3$ (sublimed)	21·2	19·8
RCl	22·4	28·8

The residue consisted mostly of oxychlorides, soluble in alcohol, and considerable silica, insoluble in alcohol. A portion of the same residue gave—

	Found.	Calculated for $SiO.Cl_2$.
Si	27·08	24·35

The excess of silicon is due, as before, to a partial volatilization of oxychlorides with a low percentage of silicon. This residue also contained a very small amount of aluminum, which was completely extracted by alcohol, and therefore present as chloride, not as silicate or oxide. No ethyl ether was formed.

In experiment 3 the residual aluminum was determined in the residue after heating to dull redness in hydrogen. The amount found, calculated as chloride, was only 3·5 per cent of the total chloride used. A small amount was to be expected, as it is practically impossible to expel it completely from the solid frothy residue. The conclusion that the chloride remains unchanged at the end of the reaction may therefore be accepted without hesitation.

Ethyl dichlorsilicate.—This calls for the reaction

$$SiCl_2(OR)_2+xAlCl_3=SiO_2+2RCl+xAlCl_3.$$

Two experiments were made, one with Si:Al=50:1, the second with Si:Al=3:1. In both cases the decomposition was readily brought about, in the first almost as easily as in the second, but only in the second could any aluminum chloride be recovered, and then not the whole amount used. A small amount of ethyl ether was also formed in each case. As there were reasons for suspecting the sample to contain monochlorsilicate (which would explain the discrepancy) and as no more was available the quantitative data are omitted.

Ethyl monochlorsilicate.—Four experiments were made in which the following proportions were observed:

$$Si:Al=\begin{cases} 3:3 & (1) \\ 3:2 & (2) \\ 3:1 & (3) \\ 150:1 & (4) \end{cases}$$

For case (1) the following equations hold, according as the chlorine

of the aluminum chloride is completely given off as ethyl chloride, or as it remains in part as $\begin{matrix}O\\O\end{matrix}>AlCl$.

(*a*) $3SiCl(OR)_3 + 3AlCl_3 = Si_3Al_2O_9 + 9RCl + AlCl_3$.

(*b*) $3SiCl(OR)_3 + 3AlCl_3 = 3(SiO_3AlCl) + 9RCl$.

Taken, 6·21 grams $SiCl(OR)_3$ and 4·19 grams $AlCl_3$, or equal mol. wts.

The course of the reaction was essentially the same as with the trichlorsilicate, except that no solid was deposited. The liquid became gradually thicker, with evolution of ethyl chloride, and then quite suddenly stiff at about 75°. On heating in a current of hydrogen, a considerable volume of uncondensible hydrocarbon gas was given off, whereby some aluminum chloride was carried into the condenser and receiver. This was collected and determined. The amount of aluminum fixed in the residue was also determined. No ether collected, and none could be found by absorption over sulphuric acid.

	Found.	Calculated for (*a*).	Calculated for (*b*).
Residue	37·5	28·4	45·9
Al in residue	7·3	5·4	8·1
$AlCl_3$ (sublimed)	3·5	13·5	.....
R_2O	.....	.....	.....

The reaction occurs, therefore, in a form combining (*a*) and (*b*), the residue probably consisting in part of aluminum silicates, in part of chloraluminum silicates.

For case (2) where Si : Al = 3 : 2, there are also two ultimate equations possible:

(*a*) $3SiCl(OR)_3 + 2AlCl_3 = Si_3O_9Al_2 + 9RCl$.

(*b*) $3SiCl(OR)_3 + 2AlCl_3 = Si_3O_8Al_2Cl_2 + 7RCl + R_2O$.

Taken, $SiCl(OR)_3$, 12·93 grams; $AlCl_3$, 5·80 grams; or exactly 3 : 2 mol. wts. The reaction was essentially similar to that in the last experiment, and took place quite as readily as when more chloride was used. The same gradual thickening and sudden stiffening of the liquid were noticed. On finally heating to dull redness in hydrogen, gas was evolved, and a somewhat carbonaceous black vitreous residue was left, but no aluminum chloride sublimed. A small amount of ethyl ether was formed, which was determined by absorption.

	Found.	Calculated for (*a*).	Calculated for (*b*).
Residue	36·0	32·7	39·1
Al in residue	6·1	6·2	6·2
$AlCl_3$ (sublimed)	.....	.....	.....
R_2O	2·5	.....	8·6
RCl	33·5	67·3	52·3

Here, too, the reaction is intermediate between (*a*) and (*b*), some R_2O is formed, but all aluminum remains in the residue.

Case (3), where Si: Al=3:1, also admits of two equations:

(*a*) $6SiCl(OR)_3+2AlCl_3=Si_6Al_2O_{15}+12RCl+3R_2O.$

(*b*) $6SiCl(OR)_3+2AlCl_3=Si_6Al_2O_{14}Cl_2+10RCl+4R_2O.$

Taken, $SiCl(OR)_3$, 14·72 grams; $AlCl_3$, 3·30 grams, or 3:1 mol. wt. The same thickening, and sudden stiffening at 75° were observed. The reaction began at the same low temperature, and was nearly as rapid as with more chloride. Ethyl ether collected in the tube *G* in abundance, and was identified by its boiling at 30°–35°. The solid residue was nearly colorless, and only on high heating did discoloration ensue. No chloride sublimed. The ether was determined by weighing that collected, and absorbing the small amount found in the distillate as before.

	Found.	Calculated for (*a*).	Calculated for (*b*).
Residue	43·1	31·7	38·4
$AlCl_3$ (sublimed)			
R_2O	20·0	15·2	22·0

Although the residue was somewhat too large, the amount of ether showed that the reaction was mainly in the sense of (*b*).

Case (4). In this experiment, 1 mol. wt. aluminum chloride was made to act on 150 mol. wts. monochlorsilicate, or almost a mere trace of the former (taken, 13·38 grams silicate to 0·06 gram chloride). The facts noted were the same as in the other experiments, including the sudden solidifying of the residue. The only difference was that the reaction took place rather more slowly, owing to the small amount of chloride present, and that the residue left at red heat was of purplish color, showing very little carbonization. The ease with which the decomposition took place indicated that a much smaller amount of aluminum chloride would have been sufficient. The ethyl ether showed the correct boiling-point.

The equation for a trace of aluminum chloride is practically

$$SiCl(OR)_3=SiO_2+RCl+R_2O.$$

The actual results were:

	Found.	Calculated for Si: Al=150: 1.
Residue	30·8	30·3
R_2O	32·7	36·8
RCl	11·2	33·0

The amount of ether was 89 per cent of the theoretical.

Tetraethyl silicate.—Four experiments may be mentioned into which the following proportions entered:

$$\text{Si:Al} = \begin{cases} 3:4 & (1) \\ 3:1 & (2) \\ 3:0{\cdot}9 & (3) \\ 150:1 & (4) \end{cases}$$

The hypothetical equations for (1) and (2) are given under the general considerations on the decomposition of the tetraethyl silicate (*a*, *b*, and *c*).

For experiment (1) were taken 5·95 grams $Si(OR)_4$, 5·09 grams $AlCl_3$, or 3:4 mol. wts. It was not possible to cause the chloride to dissolve completely in this amount of ether, and the result was a mixture of varying composition, from which no definite result should be expected. The general course of the reaction was the same as in other cases. Some ethyl ether was formed, but a little aluminum chloride also sublimed, indicating an excess in one part of the mass and a deficiency in another.

In experiment (2) with Si:Al=3:1 the mixture evolved ether and ethyl chloride, and finally became solid, and on further heating gave off gases, but no aluminum chloride. Only about one-half the theoretical amount of ether was obtained, the remainder appearing as hydrocarbon gas and empyreumatic substances.

In experiment (3) with Si:Al=3:0·9 it was noticed that some unchanged silicate distilled at the end of the operation. It appears, therefore, that the least amount of aluminum chloride required to effect total decomposition is 1 mol. wt. to 3 mol. wts. of the silicate. This is strikingly seen in the next experiment (4), which at the same time shows the radical difference in their behavior towards aluminum chloride of the silicates and chlorsilicates.

Taken, 16.37 grams $Si(OR)_4$, 0·07 $AlCl_3$, or 150:1 mol. wts. Even on boiling strongly for an hour at about 165° no marked reaction was noticed. The liquid remained clear and limpid, and not over 0·1 gram ethyl ether collected. At the end of an hour the silicic ether was distilled off unchanged, leaving but a trace of solid residue. It was therefore clear that only a trace had been decomposed, corresponding to the trace of chloride used.

The decomposition of monochlorsilicates by a trace of aluminum chloride might perhaps be utilized to obtain other ethers than ethyl ether. It is known that the continuous process for obtaining ethyl ether from alcohol by means of sulphuric acid does not apply to the alcohols above propyl alcohol.[1] Isobutyl alcohol, for instance, does not give a trace of isobutyl ether. The silicates of the monatomic aliphatic alcohols, as far as has been investigated, are easily prepared, and of all the chlorsilicates, the monochlorsilicates are the most easily made. By adding

[1] Norton and Prescott, Am. Chem. Jour., vol. 6, p. 241.

to 1 mol. wt. silicon tetrachloride 3 mol. wts. of the alcohol, boiling the product or heating to 170° under pressure, and finally distilling with a trace of aluminum chloride, a product should be obtained, consisting of a mixture of ether and chloride, which could be easily separated. From ethyl monochlorsilicate 89 per cent of the theoretical yield of ethyl ether was thus obtained.

On the isolation of the intermediate products.—Aluminum chloride is insoluble in carbon bisulphide; if, however, a mixture of about 1 vol. tetraethyl silicate and 4 vols. carbon bisulphide be boiled with some aluminum chloride, the latter liquefies and partly dissolves, while there is an evolution of permanent gas, presumably ethyl chloride. On decanting the warm liquid a considerable amount of oil separates. This oil is not volatile, and on heating gives a solid residue resembling that obtained by the direct action of the chloride on the silicic ether. The carbon bisulphide solution, if concentrated out of contact with moisture, deposits on cooling a mass of well-formed rectangular crystals, or on evaporation in vacuo over paraffin shavings leaves a perfectly dry crystalline mass. A portion of such a bisulphide solution was decomposed by ammonia and the ratio of Si: Al: Cl determined. It was found to be 1: 2·1: 3·9, or very nearly 1: 2: 4, a result which may, of course, have been accidental. The oil which separates is soluble in a fresh portion of hot carbon bisulphide, but it appears readily to change, for a greater amount is required than that from which it separated, and by boiling out with small quantities of bisulphide a residue is left which is finally almost solid. These facts seem to indicate the possibility of isolating some of the intermediate products, but this has not yet been attempted.

ON THE ACTION OF PHOSPHORUS OXYCHLORIDE ON AROMATIC SILICIC ETHERS.

By H. N. Stokes.

In a paper on the action of phosphorus oxychloride on ethyl silicates and chlorsilicates[1] (chlorhydrines), I have shown that this reagent converts ethyl orthosilicate completely into ethyl chloride and silicopyrophosphoryl chloride, $SiP_2O_6Cl_2$, and that the ethyl orthochlorsilicates yield under the same conditions these bodies and silicon tetrachloride, the amount of the latter being proportional to the amount of chlorine in the silicon compound used, the trichlorsilicate yielding most, while tetra-ethyl silicate gives none.

$$4SiCl_3(OC_2H_5)+2POCl_3=3SiCl_4+SiP_2O_6Cl_2+4C_2H_5Cl.$$
$$Si(OC_2H_5)_4+2POCl_3= \quad SiP_2O_6Cl_2+4C_2H_5Cl.$$

It was not thought worth while to repeat these experiments with other silicic ethers of the aliphatic series, as similar results were to be expected.

In view of the different properties in general of aromatic bodies, the action of phosphorus oxychloride on silicates of this class could not be foreseen. I have therefore treated *phenyl orthosilicate*[2] with phosphorus oxychloride, and have obtained results which show in a striking manner the difference between aliphatic and aromatic silicates.

The proportion selected was that required by the equations—

$$Si(OC_6H_5)_4+2POCl_3=SiP_2O_6Cl_2+4C_6H_5Cl,$$

or

$$Si(OC_6H_5)_4+2POCl_3=SiCl_4+2PO\begin{matrix}Cl\\(OC_6H_5)_2\end{matrix}.$$

The mixture, after being heated three to four hours at 170°–180° (the temperature at which the ethyl silicates react with phosphorus oxychloride), was distilled. No indication whatever of a reaction could be discovered, the oxychloride being recovered unchanged, and proved to be absolutely free from silicon compounds. After being heated sixteen hours at 240°, the liquid was somewhat discolored, but perfectly clear. On fractioning, it was easily separated into silicon tetrachloride (b. p. 59°), phosphorus oxychloride (b. p. 109°), and chloride of phenyl-phosphoric acid,

[1] Amer. Chem. Journal, 13, 244; Ber. d. chem. Ges., 24, 933.

[2] Hertkorn: Ber. d. chem. Ges., 18, 1679.

$POCl_2(OC_6H_5)$ (b. p. 240°–243°), with a residue consisting of chloride of diphenyl-phosphoric acid, $POCl(OC_6H_5)_2$, and phenyl phosphate.

The fraction of b. p. 59° gave—

	Calculated for $SiCl_4$.	Found.
Si.....	16·47	16·24

The amount of tetrachloride was approximately equivalent to the quantity of phenyl silicate used, while the higher-boiling portions and the residue were found to be practically free from silicon, thus proving the conversion into tetrachloride to be complete. Not a trace of chlorbenzene or silico-phosphoryl chloride was formed.

It will be noticed that while the ether is completely converted into chloride, the reaction does not proceed strictly according to the second of the above equations, but that a mixture of phenyl phosphate with the chlorides of the two phenyl-phosphoric acids results, some of the oxychloride remaining unchanged.

By means of this reaction and that described previously,[1] it is easy to convert aromatic or aliphatic orthosilicates into silicon tetrachloride. The aromatic ethers, heated with phosphorus oxychloride, give the tetrachloride directly; the aliphatic ethers yield silico-pyrophosphoryl chloride, which is readily converted into silicon tetrachloride by heating with phosphorus pentachloride[2] at 100°. Phosphorus pentachloride, used directly, effects the transformation only with great difficulty. Friedel and Crafts[3] have shown that the pentachloride readily converts ethyl orthosilicate into ethyl monochlorsilicate, $SiCl(OC_2H_5)_3$. I have found that this reaction can not readily be pushed farther than the trichlorsilicate, $SiCl_3(OC_2H_5)$. This body holds the ethoxyl very firmly, and even after heating many hours at 140° with pentachloride but little silicon tetrachloride is formed. If heated much higher, the pentachloride liberates chlorine, causing total destruction of the ether. Acetyl and benzoyl chlorides effect complete conversions into tetrachloride, but only when used in large excess and on heating at over 200° for a very long time.

I am studying the action of various metallic haloid salts, especially those of aluminum, on silicic ethers, and have observed a similar difference; aluminum chloride, for example, readily converting the aromatic ethers into silicon tetrachloride, while its action on aliphatic ethers is entirely different and much more complex, the products depending on the nature of the ether taken and the proportional amount of aluminum chloride used. The results will be described in a separate paper.

[1] Amer. Chem. Journal, 13, 248.
[2] Ibid., 13, 247.
[3] Ann. chim. phys. [4], 9, 14.

NOTE ON BENZYL SILICATE.

By H. N. Stokes.

As is known, both ethyl alcohol and phenol, if perfectly anhydrous, produce with silicon tetrachloride the corresponding *ortho*-silicates in nearly theoretical amount, the chief difference being that while ethyl alcohol acts violently, with reduction of temperature,[1] phenol requires prolonged boiling for complete conversion into the ether, the evolution of hydrochloric acid being scarcely noticeable at ordinary temperature.[2]

Anhydrous *benzyl* alcohol, as was to be presumed, behaves towards silicon tetrachloride as an aliphatic alcohol, not as a phenol, violent action with fall of temperature occurring. The reaction is not smooth, however, as in the case of ethyl alcohol. A large amount, perhaps one-fourth, is converted into *benzyl chloride*, either by direct action of the hydrochloric acid evolved, or indirectly by action of the latter on the benzyl silicate. As a result, if the calculated amount of alcohol be taken, much remains unchanged, and the tetrachloride is largely converted into polysilicates. On distilling the mixture under atmospheric pressure, some benzyl silicate passes over, but this is completely broken up by one or two redistillations. The products of decomposition consist of water, toluene, stilbene, anthracene, and high-boiling products of undetermined nature. As no particular interest attaches to benzyl silicate, no further attempt was made to isolate it.

This formation of benzyl chloride recalls the action of benzyl alcohol on boron trichloride,[3] when the chief product is benzyl chloride.

[1] Ebelmen: Ann. Chem. (Liebig), 57, 334.
[2] Hertkorn: Ber. d. chem. Ges. 18, 1679.
[3] Councler: Jour. prakt. Chem. [2] 18, 396.

ON AMIDOPHOSPHORIC ACID.

By H. N. Stokes.

By replacing the hydroxyls of orthophosphoric acid successively by amido groups, three amides may be derived, namely, amidophosphoric acid, $PO.NH_2(OH)_2$, diamidophosphoric acid, $PO.(NH_2)_2.OH$, and phosphoryl triamide, $PO(NH_2)_3$, and from these, by abstraction of water or ammonia, an imido acid, PO.NH.OH, an imido amide, $PO.NH.NH_2$, and a nitrile, PO.N. Of these, amido and diamido phosphoric acids have not yet been described. In the dictionaries of Fehling[1] and of Ladenburg[2] the formula $PO.NH_2.(OH)_2$ is given to a body described by Schiff[3] and called by him *phosphaminsaeure.* This rests on an error of the compilers, as Schiff gives to his acid the formula PO.NH.OH, with which his analyses agree, while they differ widely from that of amidophosphoric acid. Moreover, as will be shown, amidophosphoric acid is a body of entirely different properties.

Schiff[4] also describes the triamide, $PO(NH_2)_3$. Although his analyses agree quite well with this formula, the existence of the body is called in question by Gladstone,[5] who, in repeating Schiff's method of preparation, treating phosphorus oxychloride with dry ammonia, was unable to replace the third chlorine atom at any temperature below that at which further decomposition occurs (above 300°). The correctness of the formula PO.NH.OH assigned by Schiff to his phosphamic acid is also questioned by Gladstone and Holmes,[6] who point out the general resemblance of its properties, as described, to those of pyrophosphodiamic acid, obtained by them. They regard it as a mixture of the latter with metaphosphoric acid. The identity of Schiff's acid with pyrophosphodiamic acid (diamidopyrophosphoric acid) has also found acceptance in some handbooks.[7]

The imido amide, $PO.(NH).NH_2$, was described by Gerhardt[8] under the name phosphamide, and was obtained by treating phosphorus pentachloride with dry ammonia and then with water. Its nature has not been questioned.

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[1] Neues Handwörterbuch der Chemie, 5, 423.
[2] Handwörterbuch der Chemie, 9, 100.
[3] Ann. Chem. (Liebig), 103, 168.
[4] Ann. Chem. (Liebig), 101, 300.
[5] Journ. Chem. Soc., [2] 7, 18.
[6] Journ. Chem. Soc., [2] 2, 229, 235.
[7] Gmelin-Kraut: Handbuch der anorg. Chemie, 1, 2 Abth. 529; Graham-Otto: Anorg. Chem. (Michaelis), 2, 401.
[8] Ann. chim. phys., [3] 18, 188.

The body PO.N, described by Gerhardt[1] as biphosphamide, by Schiff[2] as monophosphamide, and by Gladstone[3] as phosphonitryle, is the final product of heating the triamide, the imidoamide, or the amido chlorides. Its constitution is not known, but is probably much more complex than is represented by the formula given.

In addition to the above, Gladstone and Holmes[4] have obtained a series of complex amides, derivable from pyro and tetra phosphoric acids.

The difficulty in preparing amido orthophosphoric acids lies in part in the impossibility of regulating the decomposition by water or acids of the products of the action of ammonia on phosphorus pentachloride and oxychloride. Gerhardt's imidoamide and Schiff's triamide seem to be capable of giving ammonia and phosphoric acid only; at least no mention is made of intermediate products. The bodies derived from phosphorus oxychloride by partial replacement of chlorine by amido groups are so decomposed by water as to give the amidopyrophosphoric acids of Gladstone, and further action results in the separation of ammonia before the pyrophosphoryl group is broken up. The reason for this, as will be seen below, lies in the great ease with which amidophosphoric acid passes over into ammonium phosphate. As phosphorus pentoxide is a derivative of pyrophosphoric acid, it is not to be expected that it would give orthophosphoric amides with ammonia.

I have overcome these difficulties in part by acting with ammonia on phosphoric ethers, and in this way have obtained the primary amide, $PO.NH_2.(OH)_2$. Attempts to obtain other amides by the same method are in progress.

By dissolving the chloride of diphenylphosphoric acid, $PO.Cl.(OC_6H_5)_2$, in alcohol and adding alcoholic ammonia, diphenylamidophosphate, $PO.NH_2.(OC_6H_5)_2$, a beautifully crystalline substance, is at once formed. This, on saponifying with ammonia or baryta, gives phenylamidophosphoric acid, $PO.NH_2.(OC_6H_5).(OH)$, and with caustic potash or soda, amidophosphoric acid. The free acid, obtained by decomposing the lead salt by sulphuretted hydrogen and precipitating with alcohol, is a well characterized body, forming fine microscopic crystals. It forms two series of salts, acid and neutral, of which the acid salts are invariably, the neutral often, crystalline, and in many cases the forms are characteristic. Boiled in aqueous solution, either alone or with an acid, it decomposes almost instantly into ammonia and orthophosphoric acid. Its cold aqueous solution may be kept a short time without much decomposition, but quickly passes into primary ammonium orthophosphate. Dilute mineral acids in the cold effect the change much more rapidly, but in either case the first product is not orthophosphoric acid, but an acid or mixture of acids giving white

[1] Ann. chim. phys., [3] 18, 188.
[2] Ann. Chem. (Liebig), 101, 304.
[3] Jour. Chem. Soc., [2] 7, 18.
[4] Quar. Journ. Chem. Soc., 3, 353; Journ. Chem. Soc., [2] 2, 225; [2] 4, 1,290; [2] 6, 64,261; [2] 7, 15.

amorphous precipitates with silver nitrate. At 100° the dry acid passes without loss of weight into an ammonium salt, giving a white silver salt. This is possibly metaphosphate, or a mixture of the different metaphosphates,

$$PO\begin{matrix}NH_2\\OH\\OH\end{matrix}=PO_3(NH_4),$$

but the nature of the product has not yet been established. The acid salts on heating give off ammonia and leave metaphosphates. Such of the neutral salts as contain crystal water pass first into ammonium salts, and on further heating into pyrophosphates. The neutral silver salt, which is anhydrous, is an exception. At 180° it gives off one-half its nitrogen as ammonia, apparently forming a very stable *pyrimidophosphate*,

$$NH\begin{matrix}PO(OAg)_2\\PO(OAg)_2,\end{matrix}$$

which stands a red heat without further change, or at least without loss of weight. Other salts which are especially characteristic are the acid sodium salt, almost insoluble in water, and the neutral magnesium salt, isomeric with crystallized ammonium magnesium phosphate. In the absence of any experimental evidence to the contrary, the constitution of the acid is regarded as $PO\begin{matrix}NH_2\\(OH)_2,\end{matrix}$ in accordance with the usually assumed structure of acid amides, rather than as $P(NH)(OH)_3$, in harmony with the most recent views on the nature of organic amides.

DESCRIPTIVE PART.

Diphenylamidophosphate, $PO\begin{matrix}NH_2\\(OC_6H_5)_2.\end{matrix}$—1 mol. wt. phosphorus oxychloride and 2 mol. wts. phenol are boiled in a flask fitted with return condenser until no further evolution of hydrochloric acid occurs. The product is a mixture of $PO(OC_6H_5)_3$, $PO.Cl.(OC_6H_5)_2$, $PO.Cl_2.(OC_6H_5)$ and unchanged oxychloride. It is not necessary to isolate the diphenylphosphoric chloride. The liquid is diluted with absolute alcohol, and alcoholic ammonia is added slowly, with cooling, to alkaline reaction. The product is mixed with several volumes of water, whereby ammonium chloride dissolves and crystalline amidophosphate separates, mixed with oily phenylphosphates. This is sucked out in a funnel as far as possible, washed with water, dried on porous plates to remove the oil, again washed, dried and recrystallized two or three times from alcohol, or better, chloroform. The yield is about 35 per cent of the theoretical.

	Calculated for $PO.NH_2.(OC_6H_5)_2$.		Found.	
P	12·46		12·37	
N	5·67	5·70	5·64	5·67

Phosphorus was determined as magnesium pyrophosphate after evaporating first with alkali, then with acid; nitrogen as ammonia after evaporating with hydrochloric acid; both as ammonium chloroplatinate and by titration, after distilling.

The ether fuses at 148°, and on cooling solidifies to a crystalline mass with a surface of brilliant facets. At 180° there is a very slow evolution of ammonia and phenol, which becomes quite rapid at 230°, when it is accompanied by sublimation of unchanged substance. The non-volatile product of decomposition is first an oil, later a solid substance containing phosphorus.

Phenylamidophosphoric acid, $PO\begin{matrix}NH_2\\OH\end{matrix}OC_6H_5$.—The free acid could not be obtained in the solid state. On decomposing the lead salt in the cold with sulphureted hydrogen a solution is obtained which is not precipitated by alcohol. On evaporating in vacuo over sulphuric acid, the acid takes up water and is converted into the acid ammonium salt of phenylphosphoric acid, which contains only traces of amido acid, which were isolated as the silver salt described below.

Acid ammonium phenylphosphate is easily soluble in water, and crystallizes in long prisms. It also crystallizes from alcohol, in which it is difficultly soluble, as pearly rhombic plates or flat needles, fusing at 140°–145° with decomposition. Silver nitrate gives a precipitate of radiating flat prisms, consisting of the neutral silver salt, (*a*) which is anhydrous. By neutralizing the filtrate with ammonia a further precipitate of the same salt (*b*) is obtained.

	Calculated for $PO\begin{matrix}(OAg)_2\\OC_6H_5\end{matrix}$	Found.	
		a.	*b.*
Ag	55·64	54·88	55·44

Phenylphosphoric acid therefore resembles phosphoric acid in that its acid salts give directly the neutral silver salt, and differs from amidophosphoric acid, which gives either acid or neutral silver salt according as acid or neutral salt be used as precipitant.

Ammonium phenylamidophosphate, $PO\begin{matrix}NH_2\\ONH_4\end{matrix}OC_6H_5$, obtained by saponifying the diphenyl ether with aqueous ammonia, is easily soluble in water, and the solution may be evaporated without decomposition.

Silver phenylamidophosphate, $PO\begin{matrix}NH_2\\OAg\end{matrix}OC_6H_5$, from the ammonium salt, after recrystallizing from water, forms scales or long, narrow, pointed plates of pearly luster. It is difficultly soluble in cold, moderately in

boiling water, and has a strong tendency to separate as a crystalline scum on the surface. It is unaffected by light.

	Calculated for $PO(NH_2)(OC_6H_5)(OAg)$.	Found.		
P	11·09	.....	11·11	.....
N	5·02	.....	5·08	.....
Ag	38·53	38·31	.....	38·19

Barium phenylamidophosphate is formed by boiling the ether with baryta water until nothing crystallizes out on cooling, and removing the excess of baryta by carbon dioxide. It forms scales, is quite soluble in water, and resembles the silver salt in forming a crystalline scum on the surface.

Lead phenylamidophosphate, from the barium salt by lead acetate, forms brilliant scales, nearly insoluble in water.

Amidophosphoric acid, $PO\overset{NH_2}{(OH)_2}$.—The alkali salts of this acid are readily obtained by saponifying the ether with a strong solution of caustic potash or soda. The chief difficulty in obtaining them pure is in separating them from the small quantity of phosphate formed at the same time. In the case of some of the salts this may be effected by methods mentioned below. The conversion into phosphate by boiling alkali is very slow. A weighed amount of ether was boiled with concentrated caustic potash, and the ammonia determined in the distillate by titration. An hour's boiling showed a decomposition of only 3 per cent.

Acid potassium amidophosphate, $PO\overset{NH_2}{OK}\overset{}{OH}$.—If a lump of caustic potash be placed on some of the diphenyl ether and a few drops of water be added, a somewhat violent reaction occurs. On boiling with an excess of concentrated caustic potash the saponification is complete in ten minutes. The oily solution is acidified with strong acetic acid, care being taken to keep it cool with ice water. On adding several volumes of alcohol the acid salt is at once precipitated. It is purified by washing with alcohol, dissolving in a little water and reprecipitating by alcohol. It can not be recrystallized from hot water, as its solution is rapidly converted by heating into acid potassium ammonium phosphate. A weighed amount of acid potassium salt was dissolved in water and boiled ten minutes; $\frac{1}{10}$ n. caustic soda was added in excess, and the solution again boiled to remove ammonia. The loss of alkalinity due to the escape of ammonia indicated that by ten minutes' boiling, 98 per cent of the amide was converted into ammonium salt. The same change occurs in a few days in the cold aqueous solution. The salt forms six-pointed stars, or sometimes rhombohedra, readily soluble in cold water, insoluble in

alcohol. Its solution is neutral towards litmus, methyl orange, and phenolphthaleïn. On ignition it gives off ammonia and leaves potassium metaphosphate.

The analysis of two air-dried preparations (*a* and *b*) gave—

	Calculated for $PO.NH_2.OK.OH$.	Found.	
		a.	*b*.
P	22·96	22·76	.....
N	10·39	10·26 10·20	10·35

The loss on ignition gave—

	Calculated for $PO.NH_2.OK.OH$.	Found.
NH_3	12·61	13·83

The excess found is due in part to a small amount of water which the salt retains, in part to a little acid potassium ammonium phosphate which can not be removed by precipitating with alcohol. The amount of ammonium salt may be determined by distilling off the ammonia with alkali solution, and determining it in the distillate, making a slight correction for the decomposition of the amide itself as above determined (3 per cent per hour). In this way the amount of ammonium salt in preparation (*a*) was found to be 4·75 and 5·10 per cent, in (*b*) 4·15 per cent. As the acid potassium salt is used for preparing other salts, this small amount of phosphate must be taken into consideration, as the latter would otherwise be contaminated with phosphate. Its presence may be obviated by methods below mentioned.

Neutral potassium amidophosphate is extremely soluble in water, and not appreciably decomposed by boiling.

Acid sodium amidophosphate, $PO\begin{matrix}NH_2\\ONa\\OH\end{matrix}+xH_2O(?)$.—This is prepared by boiling the ether ten minutes with strong caustic soda, cooling and acidifying with acetic acid. It separates at once without adding alcohol, as a crystalline powder, which is washed with dilute alcohol, dissolved in ammonia, and reprecipitated by acetic acid or carbon dioxide. It forms a heavy sandy powder consisting of well-defined crystals belonging to the hexagonal system, occurring sometimes as hexagonal plates or prisms without pyramids, occasionally as very symmetrical double pyramids without prism surfaces. It is scarcely soluble in cold water, insoluble in alcohol. If boiled with water it dissolves and is at once converted into acid sodium ammonium phosphate. The same change occurs slowly at ordinary temperature under water. Like all other amidophosphates, it is instantly converted into phosphoric acid by warm dilute acids. On ignition it loses ammonia, and leaves a

vitreous residue of sodium hexametaphosphate. It contains small but varying amounts of water. The analysis of one preparation gave—

	Calculated for $PO.NH_2ONa.OH + \frac{1}{4}H_2O$.	Found.
P	25·11	25·08
N	11·36	11·49 11·34
Residue ($NaPO_3$)	82·54	82·43

Other samples contained less water. This water is accounted for in part by the presence of a small amount of acid sodium ammonium phosphate, but the latter, when determined as in the acid potassium salt, was found to be only 2 to 2·5 per cent, while the whole amount of water present, if assumed to be in the form of ammonium salt, would make the amount 16·8 per cent. The water is therefore present mainly as such. It does not act on the amido group at 100°, as the quantity of ammonia expelled by alkali after heating at this temperature is not increased, and there is no loss of weight. At 150° it reacts, converting a portion of amide into ammonium salt, which at the same time loses ammonia, the residue being found to contain less nitrogen. The acid sodium salt dissolves rather difficultly in excess of ammonia, probably forming the sodium ammonium salt; from this solution it is reprecipitated by carbon dioxide, or even by expelling the ammonia by an air current or spontaneous evaporation. In this respect it resembles the neutral phosphates containing ammonia.

Neutral sodium amidophosphate, $PO\begin{matrix}NH_2\\(ONa)_2\end{matrix}$, is readily made by treating caustic soda solution with excess of acid salt, the excess remaining undissolved. It forms bunches of needles or prisms, extremely soluble in water, but not deliquescent. By the action of carbon dioxide, even that in the air, it is decomposed into acid salt and sodium carbonate. Alcohol precipitates it as a sirup from aqueous solution.

Acid lithium amidophosphate is precipitated by lithium chloride from a strong solution of the acid potassium salt, in the form of difficultly soluble crystalline granules. On boiling it is converted into phosphates of lithium.

Acid ammonium amidophosphate is formed by decomposing either the acid or neutral silver salt with ammonium sulphide and precipitating by alcohol. It forms a beautiful network of needles, crossing at angles of 60°, and is very soluble in water, and permanent in the air. As it is formed by precipitating an ammoniacal solution by alcohol, it appears that the neutral salt is very unstable, if capable of existence.

Potassium ammonium amidophosphate is precipitated by alcohol from an ammoniacal solution of the acid potassium salt as a sirup, which is decomposed by washing with alcohol into acid potassium salt and ammonia.

Acid hydroxylamine amidophosphate, obtained by precipitating a

moderately strong solution of the acid potassium salt with hydroxylamine hydrochlorate, is difficultly soluble in water, and forms brilliant rhombic plates and prisms. Its crystallizing power is greater than that of any other salt obtained. A neutral salt could not be prepared.

The preparation of salts of the earths and heavy metals from the acid potassium salt is interfered with by the contamination of the latter with a small amount of phosphate. The contamination of the precipitate in the case of the salts is best avoided by adding to the ice-cold solution of the acid potassium salt, before precipitation, a very little dilute nitric acid, which effectively holds all phosphate in solution. In making neutral salts, it is not so easy to get rid of the phosphate; the ways in which this was accomplished are given in special cases below.

Acid barium amidophosphate, $\left(\begin{matrix}NH_2\\PO\ OH\\O-\end{matrix}\right)_2 Ba + 2\frac{1}{4}H_2O$, is obtained by adding to an ice-cold solution of acid potassium salt, faintly acidified with nitric acid, barium chloride in excess. It thus forms a supersaturated solution, which crystallizes only on rubbing with a glass rod. The precipitate is washed with a little water and alcohol. It forms groups of radiating microscopic plates, and once formed is quite difficultly soluble in water. On boiling its solution a scaly crystalline precipitate of acid barium phosphate, $BaHPO_4$, at once forms. It contains about $2\frac{1}{4}$ mols. crystal water, the greater part of which is lost at 100°, but this can not be directly determined, owing to its tendency to pass into ammonium salt with loss of ammonia. On ignition it fuses to a glass of barium hexametaphosphate.

	Calculated for $Ba(PO_2NH_2)_2 + 2\frac{1}{4}H_2O$.	Found.
Loss ($2NH_3 + 2\frac{1}{4}H_2O$)	20·17	19·82

The residue gave—

	Calculated for $Ba(PO_3)_2$.	Found.
Ba	46·43	47·12
P	21·03	21·38

Neutral barium amidophosphate, $PO\begin{matrix}NH_2\\O\end{matrix}>Ba + H_2O$.—By mixing a dilute solution of acid potassium salt with ammoniacal barium chloride solution, and filtering quickly from the small amorphous precipitate of barium phosphate, the salt soon crystallizes. It forms very characteristic hard and brittle rhombic plates, often with truncated angles, often superposed in coincident or partly turned position, sometimes also as

fine prisms with many sharply defined faces. It is unchanged at 100°, but at 150° the crystal water is taken up to form ammonium salt, which at once loses ammonia, forming acid barium phosphate, which on ignition leaves a residue of pyrophosphate, giving off but little ammonia.

	Calculated for $\begin{matrix}NH_2\\PO\\O\end{matrix}>Ba+H_2O$.	Found.
Loss of 1 mol. NH_3 at 150°	6·80	6·84
Total loss on ignition, $NH_3+\frac{1}{2}H_2O$	10·40	10·70

The residue gave—

	Calculated for $Ba_2P_2O_7$.	Found.
Ba	61·17	61·80
P	13·84	14·44

The salt is very difficultly soluble in water. Its solution, or the liquid from which it has not yet crystallized, gives on boiling, even in the presence of an excess of ammoniacal barium chloride, a scaly precipitate of acid barium phosphate.

	Calculated for $BaHPO_4$.	Found.
Loss on ignition $\frac{1}{2}H_2O$	3·86	4·65

The residue gave—

	Calculated for $Ba_2P_2O_7$.	Found.
Ba	61·16	61·76

The salt shows a peculiar behavior when formed in the presence of strong ammonia. By mixing a solution of the acid potassium salt with strongly ammoniacal barium chloride an amorphous precipitate is formed, which dissolves (excepting traces of phosphate) on adding water. Strong ammonia reprecipitates it, and more water dissolves it. This process may be repeated several times. The solution soon deposits crystals of the neutral salt, and the precipitate itself soon turns to scales of the same substance. Filtered off and washed with ammonia, it gave on analysis figures corresponding to those of the neutral salt.

Acid calcium amidophosphate, obtained like the barium salt, is much less soluble than the latter, and forms spherical aggregations of needles.

Neutral calcium amidophosphate is formed like the neutral barium

salt, but is much less soluble. Its crystallizing power is also much less. From very dilute solutions it separates gradually in the form of microscopic groups of flat-pointed prisms; from concentrated solutions as an amorphous precipitate which does not become crystalline, while from solutions of intermediate strength it is at first amorphous but gradually becomes crystalline.

Acid magnesium amidophosphate, $\left(\begin{matrix}NH_2\\POOH\\O-\end{matrix}\right)_2 Mg + 3\frac{1}{4}H_2O$.—On mixing an ice-cold strong solution of acid potassium salt, acidified slightly with nitric acid, with magnesium chloride, nothing separates, even after many hours. On rubbing with a glass rod crystallization starts at once. Once separated it is almost insoluble in water, and forms microscopic granules consisting of radiating needles or prisms. It is insoluble in ammonium chloride. At 100° it retains 2 mols. water; on ignition it gives off ammonia and water, and leaves magnesium metaphosphate.

	Calculated for $Mg(PO_3NH_3)_2 + 3\frac{1}{4}H_2O$.	Found.
Loss ($2NH_3 + 3\frac{1}{4}H_2O$).....	33·71	33·86

The residue gave—

	Calculated for $Mg(PO_3)_2$.	Found.
Mg	13·18	12.85
P	34·10	33·88

Neutral magnesium amidophosphate, $POO\begin{matrix}NH_2\\O\end{matrix}>Mg + 7\ H_2O$.—This salt has the same empirical composition as crystallized ammonium magnesium phosphate, $MgNH_4PO_4 + 6H_2O$, but differs entirely in its properties. It forms at once on adding magnesia mixture to a solution of acid potassium salt, or better, by precipitating neutral sodium salt with a magnesium salt. Any phosphoric acid present is first thrown down by a little of the precipitant, either as magnesium or magnesium ammonium phosphate; even when phosphoric acid is in excess it is completely thrown down by magnesia mixture before any amidophosphate forms, and the change can easily be followed by observing the crystals under the microscope. From solutions containing ammonium chloride (as when magnesia mixture is used) it crystallizes in very characteristic plates, often nearly rectangular, but more frequently with truncated angles, forming oblong octagonal plates. In the absence of ammonium salts it forms thick prisms, in either case easily distinguishable from ammonium magnesium phosphate. It is difficultly but perceptibly soluble in water, and quite readily in dilute ammonium chloride solution, and may be separated from any accompanying am-

monium magnesium phosphate in this way. From its aqueous solution ammonia precipitates magnesium hydroxide. On boiling its aqueous solution, ammonium magnesium phosphate is at once formed. It dissolves in acetic acid; from its solution in nitric acid, alcohol precipitates acid salt. Even when free from ammonium salt, caustic potash causes more or less evolution of ammonia in the cold. Over sulphuric acid it quickly loses most of its crystal water, but the last two or three molecules are given off very slowly, and constant weight could not be obtained. At 100° it loses somewhat more than 5 mols., but this can not be accurately determined, as at this temperature partial decomposition of the amide with loss of ammonia occurs, as shown by analysis of the residue. On ignition it leaves magnesium pyrophosphate.

	Calculated for $MgPO_2NH_2 + 7H_2O$.	Found.	
P	12·67	12·59	
N	5·73	6·53	6·27
Mg	9·79	9·77	
Loss on ignition	54·70	54·79	

Acid manganese amidophosphate, prepared like the acid magnesium salt, forms faintly pinkish microscopic crystals or granular and lenticular forms. It contains crystal water, is difficultly soluble, and shows no tendency to form supersaturated solutions.

Neutral manganese amidophosphate, from the neutral sodium salt, is an amorphous white precipitate.

Acid zinc amidophosphate is difficultly soluble in water; soluble in acetic acid and in ammonia. It crystallizes readily in small but finely-formed rhombic prisms with pyramids, or in hexagonal plates.

Neutral zinc amidophosphate is an amorphous white precipitate perceptibly soluble in water. Both salts are converted into phosphate by boiling.

Cobalt amidophosphates.—The *acid* salt forms readily from the acid potassium salt with a cobalt salt after adding a drop of nitric acid. It is difficultly soluble in water; soluble in ammonia, and forms pink granules. The *neutral* salt is an amorphous pink precipitate.

Nickel amidophosphates.—The *acid* salt has a great tendency to supersaturation, and can only with great difficulty be made to crystallize. Once formed, it consists of minute crystalline granules, difficultly soluble in water. The *neutral* salt is an amorphous, nearly colorless precipitate, soluble in acetic acid and in ammonia.

Ferrous amidophosphates.—The *acid* salt, formed as above, crystallizes very readily in nearly colorless microscopic crystals, apparently of the regular system, and consisting of the dodekahedron, or combinations of cube and octahedron. It is nearly insoluble in water or ammonium chloride; soluble in ammonia. The *neutral* salt is a dirty greenish, amorphous precipitate, soluble in much water, in acetic acid, and in ammonia.

Ferric amidophosphates.—Both acid and neutral alkali salts give, with a neutral solution of ferric chloride, white, amorphous precipitates, soluble in excess of amidophosphate and in ammonia; insoluble in acetic acid.

Aluminum amidophosphate.—Neutral sodium salt gives, with alum, a white, amorphous precipitate, completely soluble in ammonia.

Chromic amidophosphate, from neutral sodium salt, is a very nearly colorless amorphous precipitate, soluble in ammonia on warming.

Cupric amidophosphates.—The *acid* salt crystallizes in rosettes and dumb-bell-like forms, nearly insoluble in water. The *neutral* salt is an amorphous precipitate, slightly soluble in water, and converted into phosphate by boiling.

Mercuric amidophosphates.—Neither acid nor neutral salts are precipitated by mercuric chloride. On boiling, mercuric phosphate is formed.

Cadmium amidophosphates.—By mixing solutions of acid potassium amidophosphate and cadmium chloride, crystalline precipitates somewhat soluble in water are obtained. These differ in form according as one or the other reagent is in excess; with excess of cadmium chloride a double salt is formed which gives off ammonium chloride on heating.

Lead amidophosphate.—Acid potassium salt and lead acetate give a precipitate consisting of groups of radiating plates, slightly soluble in water, presumably acid salt.

Acid silver amidophosphate, $PO\begin{matrix}NH_2\\O\\OH\end{matrix}Ag$.—This may be obtained by precipitating the acid potassium salt with silver nitrate, but, thus obtained, it contains too much silver (about 2 per cent), due perhaps to a small amount of neutral salt or to a trace of phosphate. By previously adding a very little nitric acid to the cold solution it is obtained pure. As it is somewhat soluble in water, the theoretical yield can not be obtained. It is also formed by dissolving the neutral salt in cold dilute nitric acid and precipitating by alcohol or by adding alcohol to a solution of the free acid and silver nitrate. It forms a heavy crystalline powder, consisting of short needles, or, oftener, of very thick, short, hexagonal prisms with pyramidal ends, united into groups or twins; also, by precipitating with alcohol, as hexagonal stars. The forms are very characteristic. It is difficultly but appreciably soluble in water, easily in dilute nitric or acetic acid, and in ammonia; from the latter solution it crystallizes on evaporation. The aqueous solution is at once converted into phosphate by boiling. Light does not discolor it. The air-dried salt is anhydrous. Analysis gave:

	Calculated for $PO\begin{matrix}NH_2\\O\\OH\end{matrix}Ag$.	Found.
P.....	15·22	15·23
Ag.....	52·90	53·35

On ignition it loses ammonia and leaves an easily fusible glass of silver hexametaphosphate.

	Calculated for $PO\begin{matrix}NH_2\\OAg.\\OH\end{matrix}$	Found.
Loss (NH_3)	8·36	8·17

Neutral silver amidophosphate, $PO\begin{matrix}NH_2\\(OAg)_2\end{matrix}$.—This is obtained either by adding silver nitrate and then ammonia to the filtrate from the acid salt, or (with much loss) by dissolving the acid salt in very dilute nitric acid and adding silver nitrate and ammonia. It forms at first a turbidity, which in a few moments turns to a quickly subsiding crystalline precipitate. The ammonia must be added cautiously and stopped as soon as the salt ceases to subside quickly. At this point a nearly white amorphous substance of unknown composition is formed, which remains in suspension and may be redissolved by a drop of nitric acid. Further addition of ammonia to the filtrate gives the same amorphous salt, which is faintly yellow and rapidly blackens in the light. It may also be obtained from the neutral sodium salt, but this method is not to be recommended, as the product is slightly yellow. The best method is the first mentioned, and if very dilute solutions of acid potassium salt have been used nearly all the acid silver salt remains in solution and can be converted into neutral salt as described. The neutral salt forms characteristic microscopic rhombic plates, with angles of nearly 60°, often united to bunches. It is colorless and unaffected by light. The crystalline powder is soft, and can thus be distinguished from the acid salt, which is gritty. It is almost insoluble in water; soluble in nitric acid, from which solution alcohol precipitates acid salt; soluble in ammonia, and deposited unchanged on spontaneous evaporation. The air-dried salt is anhydrous.

	Calculated for $PO.NH_2(OAg)_2$.	Found.	
P	9·98	10·03	9·87
N	4·52	4·51	
Ag	69·40	69·18	69·15

It remains unchanged at 150°; at 180° it loses weight, the loss corresponding to one-half the total nitrogen calculated as ammonia. On heating to constant weight at 180°—

	Calculated for $2PO.NH_2(OAg)_2—NH_3$.	Found.
Loss	2·74	2·82

The residue is brownish, but may be fused over the blast with but slight loss, whereby a little oxygen escapes, and a small amount of

metallic silver is formed. In the above case this was weighed and found to be only 5·61 per cent out of a total of 69·40 per cent. The loss between 180° and red heat was 0·34 per cent, and this is exactly the amount of oxygen which would be given off by the silver oxide corresponding to 5·61 per cent silver. The residue on ignition consists, besides metallic silver, of a yellow glass, soluble in ammonia. Probably there is formed at 180° the silver salt of *pyrimidophosphoric acid*,

$$NH<^{PO(OH)_2}_{PO(OH)_2},$$

which is not decomposed by fusion. Attempt will be made to isolate the free acid.

If the salt be heated at once over the blast, without previous heating at 180°, the decomposition is markedly different, much more metallic silver being formed.

	Calculated for ½N as NH_3.	Found.
Loss	2·74	4·63
Free silver	.....	25·75

This amount of silver corresponds to 1·91 per cent oxygen, which, with 2·74 per cent ammonia, makes 4·65 per cent loss, the amount actually found. The formation of silver oxide is due to the liberated ammonia, which splits off silver oxide and water, forming a higher amide. The action of dry ammonia gas on the salt is scarcely appreciable at 180°, as was found by experiment, hence the salt may be heated at this temperature without the ammonia which is given off liberating any considerable amount of silver oxide, as in the first case. At 200° and higher, dry ammonia forms large amounts of silver oxide and water, and therefore on heating rapidly, as in the second case, the liberated ammonia is able to act, and the large amount of silver formed is accounted for. The products of the action of dry ammonia on this salt will be described in a future article, when it will also be shown that amidophosphates may be made from neutral silver phosphate in this way. Experiments towards forming other inorganic amides by this method are also in progress.

Free amidophosphoric acid.—The isolation of the free acid is attended with difficulties, owing to its unstable nature. It has not yet been obtained perfectly pure, and the yield is always far below the theoretical. The silver salts may be decomposed by hydrochloric acid in the cold, and the solution precipitated by alcohol, but a deficiency of acid causes the solution to be contaminated with acid salt, and an excess destroys the amido acid completely, or at least prevents its precipitation. The decomposition of the silver salts by sulphureted hydrogen gives better, but unsatisfactory results. The best results are obtained

by suspending the lead salt in a little ice water, and decomposing by sulphureted hydrogen. It is essential to have the latter in excess, as otherwise the solution contains some lead salt. The filtrate is run into four or five volumes of alcohol, whereby the acid is at once precipitated in the form of microscopic crystals. These consist sometimes of thick plates, sometimes of forms which appear to be cubes, but which are anisotropic. It is insoluble in alcohol, easily soluble in water, the solution having a sweetish taste. It gives no precipitate with silver nitrate, unless on addition of ammonia or alcohol. It evolves no ammonia with caustic alkalies, and is easily converted into the characteristic sodium, magnesium, barium, and silver salts, hence there can be no question as to its nature. It may be exposed to the air for a long time without change, but gradually alters, becoming pasty, in which condition it precipitates silver nitrate directly, and hence has become converted into an ammonium salt. The precipitate is white and amorphous, hence not phosphate. Its solution, if boiled but a moment, also gives a white silver precipitate, but, on boiling several minutes, it is completely converted into phosphate. It does not lose weight at 100°, but is slowly converted into ammonium salt, giving a white silver precipitate direct. Whether the product is one of the isomeric ammonium metaphosphates has not yet been determined. At 150° it also loses nothing, but fuses partially, and on higher heating it gives off ammonia. The silver salt from the acid which has been heated just to fusion becomes pasty under boiling water, like silver hexametaphosphate. The free acid obtained as above did not give satisfactory results on analysis, and such data are therefore postponed.

The alcoholic filtrate from the free acid contains an abundance of ammonium salts, giving amorphous, white, silver precipitates.

The action of amidophosphoric acid towards indicators is not sharp. The free acid gives acid reaction, the acid alkali salts have neutral reaction, but no sharp transitions can be obtained either with litmus, methyl orange, or phenolphthaleïn. It also differs from phosphoric acid in the uniformity with which its acid alkali salts precipitate acid salts and its neutral alkali salts give neutral salts. No exception to this was observed. Soluble acid phosphates, as is well known, give, with silver and many other metals, precipitates of neutral salt.

The investigation will be continued in the directions indicated.

ON SOME ORGANOSOLS.

By E. A. Schneider.

It is well known that Graham succeeded in the course of his work on diffusion in substituting organic liquids for the water in colloidal solutions. I mention here only that he prepared colloidal solutions of silicic acid in alcohol, ether, and even in carbon bisulphide.[1] Similarly to his nomenclature for water soluble colloids—hydrosol for the water-soluble colloid, hydrogel for the coagulated colloid—he formed names like alkosol and alkogel, glycerosol and glycerogel, etc.

After having investigated somewhat this field, it appears to me very probable that the water in colloidal solutions may be replaced by many organic liquids. Should we accept without reserve Graham's nomenclature we would find it difficult to form in all cases clear and euphonious names. I propose, therefore, to retain the excellent expressions "hydrosol" and "hydrogel" for the water-soluble and the water-insoluble forms of colloids and to call the solutions of colloids in organic liquids "organosols," while adding the chemical formula of the colloid and that of the solvent in parenthesis. Graham's experiments on organosols have not been repeated so far as I can make out from the existing literature. For this reason alone it appeared to me desirable to extend them to the large class of colloidal inorganic sulphides, which have become known only recently, and also to colloidal silver. The preparation of such solutions appeared to me also desirable, because we may hope that a detailed investigation of their physical properties will shed some light on the nature of solution.

Organosol Au_2S_2 (Ethyl alcohol).—Among the numerous known colloidal sulphides the best suited for the first experiments in this field appeared to be the colloidal sulphides of gold,[2] which have already been studied by me. They possess the advantage over other sulphides that they are not subject to oxidation on contact with the air, an advantage which should not be underestimated, if the length of time which dialysis requires is taken into account.

The organosol was obtained by dialyzing an aqueous solution of auroauric sulphide mixed with alcohol into absolute alcohol. To 50 c. c.

[1] Ann. de Chim. et de Phys., 4 ser., 3, 1864.
[2] Berichte, XXIV, 2241.

of a solution which contained in the liter 1·514 grams Au_2S_2 and only traces of impurities (prepared by the action of potassium cyanide on precipitated auroauric sulphide), 150 c. c. absolute alcohol were added; no sign of coagulation became visible. The mixture was poured into a parchment tube and the latter suspended in a tall narrow beaker which was filled with absolute alcohol. The dialysis was carried on under a bell jar which fitted air-tight on a ground glass plate. If an attempt is made to dialyze the hydrosol of the sulphide into absolute alcohol without mixing it first with a sufficient quantity of alcohol the contents of the dialyzers become coagulated and hardly any liquid is left in the dialyzer after the lapse of twelve hours, for the rapidity of diffusion of water through the parchment into absolute alcohol is much greater than the opposite movement.

After twenty-six days of dialysis, during which time the alcohol in the outer vessel was frequently renewed, a liquid was obtained which did not show any difference, so far as color and optical behavior are concerned, from the hydrosol of the auroauric sulphide.

The analysis of the organosol was carried out in the following manner: 100 grams were distilled from a fractionating bulb at the temperature of the water bath; at the same time a stream of dry carbonic acid was conducted into the flask in order to accelerate distillation. The specific gravity of the distillate was determined very accurately by means of the pycnometer. The residue in the fractionating bulb was dissolved in aqua regia and the gold was determined in the usual way; 100 parts by weight of the organosol contained—

	Parts by weight.
C_2H_5OH	98·90
Au_2S_2	0·0676
H_2O	1·03
	99·99

Equal volumes of the hydrosol and of the organosol which contain the same quantity of auroauric sulphide do not show any difference in depth of coloration or transparency.

The organosol is very stable, apparently more stable than the hydrosol, which on standing a long time deposits sediment.

Organosol Au_2S (Ethyl alcohol).—Up to this time I have not succeeded in preparing a sufficiently concentrated organosol of aurous sulphide in alcohol; the probable reason is that the hydrosol was not sufficiently pure. It was possible to mix the latter in all proportions with alcohol, but on dialyzing such a mixture coagulation always took place. The strongest alcoholic solution which I obtained by mixing the hydrosol with alcohol contained 99 per cent alcohol, but only 0·001 per cent aurous sulphide. Its color was yet perceptibly straw-yellow and it appeared clear in transmitted as well as in reflected light.

Organosol Ag. (Ethyl alcohol).—I have prepared the organosol of silver in ethyl alcohol according to two methods. It can be obtained

easily and conveniently by the dialysis of the hydrosol into absolute alcohol.

The product of a twenty-seven days' dialysis was analyzed with the following results: 100 parts by weight of the organosol contained—

	Parts by weight.
C_2H_5OH	99·30
Ag	0·1716
H_2O	0·53

This organosol is completely opaque in layers 2 mm. thick. Diluted with a sufficient quantity of alcohol or water it appears in transmitted light chlorophyll green with a bluish tinge; on further dilution the color becomes yellow-green. It is perfectly transparent in transmitted light; viewed by reflected light it appears violet-brown and decidedly turbid.

It is worth while to mention that on distilling off the alcohol silver is deposited on the bottom of the fractionating bulb as a beautiful gold-colored mirror.

The succession of colors in the hydrosol, in the case of transmitted light, reminds one very much of Newton's rings, for here also the order proceeds from brown-red to blue-green, while the thickness of particles is probably increasing. This analogy, however, is incomplete, for we are dealing here not with the colors of thin plates, but at the most with diffraction phenomena.

As far as the color of the solid colloid is concerned it can be explained by pure absorption. Still the peculiar correlation of the complementary colors—hydrosol, red-brown; solid mirror of the same, blue-white; organosol, green; solid mirror of the same, golden-yellow—is remarkable and needs further explanation.

If the probability is kept in view that it may be possible to explain the changes of color of the silver solution on the basis of well-known laws of optical physics, the assumption of allotropic modifications of silver, which has been made by Carey Lea, becomes unnecessary.

The organosol of silver in ethyl alcohol may be also prepared in another very easy manner, which is interesting because it illustrates the general application of the laws according to which colloidal solutions are formed.

If to the silver hydrosol, as it is obtained according to Carey Lea's prescription, absolute alcohol is added, coagulation begins as soon as a certain degree of concentration is reached. The black finely divided precipitate is now separated from the solution by means of a Pasteur filter. It settles on the walls of the latter as a crust with a beautiful bronze luster. This precipitate is soluble in water as well as in absolute alcohol, because the original impurities have been reduced to a minimum.[1]

[1] Compare article on the preparation of the pure hydrosol of silver, pages 99–101, this bulletin.

Two portions of 100 c. c. each of an organosol which had been prepared in this manner were subjected to analysis. The silver was coagulated with hydrochloric acid in alcoholic solution.

Previous to analysis the organosol had been allowed to stand for two months, and a sediment had separated out.

The analysis gave the following results:

	I.	II.
	grams.	*grams.*
Ag	0·1240	0·1225

Consequently a hundred parts by weight of the organosol contain, if we assume that the strength of the observed alcohol has decreased owing to absorption of moisture from the air, to 99 per cent by volume:

	Parts by weight.	
	I.	II.
Ag	0·1552	0·1533

Starting from the alcoholic organosols, it appears to me possible to prepare many organosols of the inorganic sulphides and of silver.

ON THE PREPARATION OF A PURE HYDROSOL OF SILVER.

BY E. A. SCHNEIDER.

In a previous communication on this subject the peculiar behavior of colloidal solutions of silver or, if we use Graham's terminology, of the hydrosol of silver, towards hydrochloric acid has been discussed.[1] It was shown that on addition of increasing quantities of hydrochloric acid, increasing quantities of silver chloride were formed and that at the same time neither the liberation of oxygen nor of hydrogen was noticeable. In order to find a plausible explanation for these facts it was necessary to prepare first of all a pure solution of silver hydrosol. Neither Carey Lea[2] nor Prange[3] have worked with the pure substance and, in my former experiments, I also used impure solutions. After prolonged experiments I have been able to work out a method by which it is possible to prepare solutions that possess the highest degree of purity attainable with this class of bodies. Experience has taught us that it is not possible to remove the last traces of crystalloids from colloidal solutions; this applies particularly to the hydrosols of silicic hydrate and of ferric hydrate, as has been observed by Graham[4] and other investigators.[5] My method is founded chiefly on the application of the Pasteur filter, of unglazed porcelain, and on the behavior of the silver hydrosol towards alcohol. The material used at the outset is made, according to the excellent prescription of Carey Lea, in the following manner: We prepare (1) 500 c. c. of a 10 per cent silver nitrate solution; (2) 500 c. c. of a 30 per cent ferrous sulphate solution (150 grams crystallized ferrous sulphate in 500 c. c. liquid); (3) 700 c. c. of a sodium citrate solution which is obtained by dissolving 280 grams crystallized sodium citrate in the necessary quantity of water. Any deviation from this prescription leads to very unsatisfactory results.

[1] Berichte XXIV, 3370.

[2] Am. Journ. of Science, 37, 481, 1889.

[3] Rec. des Trav. Chim. des Pays Bas, 9, 125.

[4] The hydrosol of ferric hydrate which Graham prepared contained 1 Eq. hydrochloric acid to 30.3 Eq. Ferric oxide. Ann. Chem. Pharm., 121, 46.

[5] Becquerel subjected some hydrosols to electrolysis. He remarks "During the experiment a rather considerable quantity of hypochlorous acid is formed, particularly from the solution of silicic acid; this shows that these solutions still contain chlorine, notwithstanding they are neutral. Ann. Chem. Pharm., 126, 303. Compte rendu, 56, 237.

The ferrous sulphate solution is mixed with the citrate solution and the resulting liquid is poured into the silver nitrate solution; the whole should be well stirred. To exclude daylight, as Prange recommends, is entirely unnecessary. It is advisable to divide the solutions into five equal parts, because the handling of smaller quantities at a time is much quicker and easier.

After standing half an hour the colloidal silver has usually settled completely. The supernatant liquid should be drawn off as much as possible, which is perhaps done best by means of a pipette, and the solid colloid is now thrown on the filter.

With the proper use of the Bunsen pump and of the right kind of filters it becomes possible to remove the greater part of the mother liquor from the colloid, without losing much of the latter by passage through the filter. The magnificently blue-violet iridescent colloid should now be rinsed off from the filter by means of a stream of water, and instant solution takes place. If care is taken to use the water very cautiously solutions may be easily obtained which contain 20 grams silver to the liter. Their color is dark brown-red; viewed in reflected light they appear turbid, in transmitted light, however, in thin layers or if largely diluted, completely transparent.

The impure hydrosol which has been thus obtained is brought into a flask and absolute alcohol added to it, with continuous agitation, until coagulation of the silver particles becomes apparent. It is not necessary to wait until the precipitate has settled (this sometimes takes several days), for it may be filtered off by means of a Pasteur filter tube. The filter tube should be connected with a powerful Bunsen or Chapman pump capable of producing a vacuum of 10 to 20mm, and placed in a glass cylinder, which is filled from time to time with the solution. The pure colloid is now deposited as a magnificently iridescent crust on the exterior wall of the filter. After some time the effectiveness of the filter is impaired owing to the fact that its pores become clogged and it is necessary to rinse of the crust by means of a stream of water. This should be done after the filter tube has been taken out of the cylinder and after the pump has been allowed to work a few minutes until the crust appears entirely dry. It is unfortunately not possible to wash the solid colloid with dilute alcohol. Just as other colloids, particularly the metallic sulphides, on washing with water go into solution after removal of the crystalloids, so also the colloidal silver, when free from impurities goes into alcoholic solution.

It should be mentioned that instead of the Pasteur filter, paper filters may also be used. But in this case the filtering takes a very long time, since no pressure can be employed, and it becomes impossible to work with large quantities.

To explain the working of this method, it is sufficient to point out the very considerable solubility of the sesquisulphate of iron and of ferrous citrate in alcohol and the insolubility of colloidal silver which

still contains some of these impurities, in alcohol. The data which are given below illustrate the effectiveness of the method.

I. A hydrosol which contained in the liter 17·034 grams silver and 0·362 gram iron, the latter in combination with sulphuric and citric acids, was treated as described above.

A. A hydrosol was obtained which contained in the liter 12·248 grams silver and 0·038 gram iron. Consequently the percentage of iron, calculated on the total amount of silver, has decreased from 2·12 to 0·31 per cent.

B. By the same method, using, however, ordinary paper filters and another hydrosol, the original proportion of 100 Ag: 2·7 Fe was changed to 100 Ag: 0·33 Fe.

A number of other solutions were prepared according to the same method. Their contents of iron averaged from 0·3 to 0·5 per cent (calculated on the total amount of silver), and this percentage was rarely exceeded.

After this method was found to yield the silver hydrosol so nearly pure, it became possible to explain its peculiar behavior towards hydrochloric acid.

CONTRIBUTION TO THE KNOWLEDGE OF COLLOIDAL SILVER.

By E. A. Schneider.

If hydrochloric acid is added to silver hydrosol the precipitate which is instantaneously formed always contains, besides silver, varying quantities of silver chloride; a fact which has been mentioned in a preliminary notice on this subject.

Two possibilities may be considered in attempting to explain this fact: Either the hydrosol contains small quantities of a silver oxide compound, or the silver combines with the chlorine of the hydrochloric acid and hydrogen is set free.

The first assumption appeared the more plausible since *an evolution of gas had never been noticed* on addition of hydrochloric acid. In order to carry out in the most approved way a test for silver oxy-compounds in the hydrosol, 75 c. c. of an almost absolutely pure preparation, which contained in the liter 12.248 grams silver and 0.038 gram iron, were distilled to dryness in a current of carbonic acid and the residue was heated to redness. The water which distilled off was collected in a well cooled receiver, and the gases, which were set free, in a eudiometer tube over caustic potash. In this way 4 c. c. (766 mm. B. and 16°) of a gas were obtained which yielded to pyrogallol only 0·6 c. c. We have here consequently to deal with air whose composition has been somewhat changed by absorption in the hydrosol. If we take into account the rather long time which the experiment required, then the capacity of the whole apparatus, and lastly the fact that the carbonic acid was prepared from marble, we are perfectly justified in ascribing a considerable part of the air collected to these sources of error.

At any rate by this experiment the absence of silver oxy-compounds in the hydrosol is proved absolutely.

The possibility of the reaction $Ag + HCl = AgCl + H$ has now to be considered. For this purpose *the electrochemical behavior of the hydrosol* was investigated. In order to obtain some information concerning the accumulation of hydrogen on the silver particles which are coagulated on addition of hydrochloric acid, the degree of the hydrogen polarization was measured by means of a compensation method.

Two equally large insulated silver crucibles connected with each other by means of a siphon were filled with the liquid to be investi-

gated; the system was manipulated as indicated in the table below. The wires of the measuring apparatus were connected with the outside surfaces of the silver crucibles and care was always taken that no current passed the liquid, with the exception of the weak, instantaneous one, which was needed for the measurement. Changes of the contents of the silver crucibles were always effected while the chain was kept open. Jarring, etc., was avoided. In the table are given the time of the measurement, the observed electromotive force e (degree of the hydrogen polarization), and the actual change δe of the latter, which is originated by hydrochloric acid in its action on colloidal silver.

Values of the electromotive force e.

	Time m.	$e \times 10^3$ volt.	$\delta e \times 10^3$.
a.			
Water on both sides		− 81	0
HCl, left hand		+277	358
HCl, both sides		− 18	376
b.			
Silver hydrosol		+ 9	0
HCl, left hand	0	+376	+367
	15	382	373
	60	386	377
	100	389	380
	1,200	381	372
	2,600	364	352
HCl on both sides	0	+ 95	
	30	+100	0
Silver hydrosol, left hand.*	0	+165	65
	5	161	61
	35	161	61
	145	157	57
	1,400	146	46

* These forces are to be added to 370, because each electrode is already charged with hydrogen.

The tables are divided into two parts and the experiments supplement each other. In *a* the system was first filled with water, then hydrochloric acid was poured first into the left hand crucible and after the measurement into the right-hand crucible. The polarization is here $\delta e = 0{\cdot}367$ volts on the average. The system was then thoroughly cleaned and the silver hydrosol placed in it. Experiment *b* shows forces which first increase, then decrease, but which on the whole exceed but little the values found in experiment *a*. On the basis of this experiment we would hardly be justified in assuming that the coagulated silver particles are more strongly charged with hydrogen than the silver foil (crucibles) treated in the same manner.

Much more sensitive and decisive are experiments *c*, which were carried out thus: The system was first filled with hydrochloric acid and then the hydrosol was poured cautiously into the left-hand crucible. Here an increase of the hydrogen polarization amounting to 0·060

volts is clearly discernible. From these experiments we can conclude: (1) That hydrogen must be accumulated on the silver particles; (2) that the quantity of hydrogen which thus condenses upon coagulation of the hydrosol with hydrochloric acid is a little larger than on silver foil; (3) that the silver particles which are charged with hydrogen gradually lose a part of their charge.

It was not possible to prove directly, that is, by collecting and measuring, the presence of hydrogen in the coagulated silver. Some experiments which were carried out in this direction, for instance amalgamation of the coagulum with mercury under water, did not yield decisive results. The quantity of hydrogen in the silver must be consequently very small. From this we can conclude that the quantity of silver chloride which is formed according to the reaction

$$Ag+HCl=AgCl+H$$

can not be large. This result is somewhat surprising, since it contradicts all outward appearances. The freshly coagulated silver is spongy and voluminous, and reminds one vividly of amonium-amalgam.

It is evidently necessary to find an explantion for the formation of the larger part of the silver chloride without simultaneous liberation of hydrogen.

An old experiment, which Becquerel[1] had made while experimenting upon the photography of colors, together with some observations which had been gathered in the course of this investigation, facilitated this task.

In order to prepare thin layers of silver chloride very sensitive to light, Becquerel dipped polished silver plates into solutions of metallic chlorides such as ferric chloride. A reaction takes place in the following way:

$$Ag+FeCl_3=AgCl+FeCl_2.$$

In the course of my analyses of silver hydrosols I noticed that the richer they are in iron the more silver chloride is formed on addition of hydrochloric acid. The suspicion that the iron salts which are present may be the cause of the whole phenomenon was obvious.

An experiment proved the correctness of this assumption. Two portions of 100 c. c. each of a silver hydrosol which contained in this volume 1·6834 grams Ag to 0·0112 grams Fe_2O_3 were mixed with varying quantities of neutral ferric chloride solution.

I. 100 c. c. silver hydrosol were mingled with 5 c. c. ferric chloride solution (=0·1268 grams Fe_2O_3).

	Grams.
Ag precipitated as metal	1·5566
Ag precipitated as chloride	0·1248
	1·6814

[1] Ann. d. Chim et Phys., 3 serie XXV, 448.

II. 100 c. c. silver hydrosol were mingled with 150 c. c. ferric chloride solution (=3·804 grams Fe_2O_3). The silver hydrosol was allowed to flow slowly into the chloride solution while the whole was shaken.

	Grams.
Ag precipitated as metal	———
Ag precipitated as chloride	1·6800
	1·6800

These experiments also show the influence of mass action.

The color of the precipitated silver chloride was a beautiful pink-red shading into violet; a tint I had not previously observed in the case of this compound. The silver chloride thus obtained appears to be very sensitive to direct sunlight.

A number of analytical examples are now given in order to better demonstrate the statements contained above.

Three portions of a strongly contaminated hydrosol, such as is obtained by the method of Carey Lea, and one portion of a hydrosol purified by the alcohol method were coagulated each with varying quantities of hydrochloric acid. The precipitate obtained was thoroughly digested with ammonia, the ammoniacal extract boiled in order to drive off the excess of the reagent, and the solution ultimately acidulated with nitric acid. The filtrate from the silver chloride thus obtained gave in some cases, on addition of hydrochloric acid, a further weighable quantity of the same compound. This behavior indicates the presence of silver subchloride in the precipitate which is formed by hydrochloric acid in the hydrosol. The formation of this silver chloride can be explained by the action of the (nascent) liberated hydrogen on a part of the precipitated silver chloride.

ANALYSIS OF THE IMPURE HYDROSOL.

(*a*) 50 c. c. of the hydrosol were coagulated with 1 c. c. hydrochloric acid (1 part fuming hydrochloric acid to 1 part water). The precipitate contained—

Ag	0·7641 g.	0·7641 g. Ag
AgCl	0·1082 g.	0·0814 g. Ag
AgCl[1]	0·0087 g.	0·0065 g. Ag
		0·8520 g. Ag

In the filtrate from the precipitate by hydrochloric acid were found—

	Grams.
Fe_2O_3	0·0259
SO_3	0·0099

0.0259 grams Fe_2O_3 correspond to 0·0464 grams AgCl if we start from the equation $FeCl_3+Ag=AgCl+FeCl_2$. If we subtract this quantity (0·0464 grams) from the total weight of silver chloride present—0·1082 grams—there remain still 0·0618 grams AgCl to be accounted for.

[1] In the filtrate from the ammoniacal extract as previously described.

Now 0·0618 grams AgCl correspond to 0·0004306 grams H=4·81 c. c. if we assume the equation

$$Ag+HCl=AgCl+H$$

to be true.

If we assume now that the coefficient of absorption of silver hydrosol for air is equal to that of water, 50 c. c. of the hydrosol must absorb 0·29 c. c. oxygen. This quantitv is sufficient to oxidize 0.0000517 grams hydrogen = 0·57 c. c. to water.

Further, according to Bunsen 100 c. c. water at a temperature of 0° to 20° absorb 1·93 c. c. hydrogen. If we assume now again for the silver hydrosol the same coefficient of absorption as for water, 50 c. c. absorb 0·96 c. c. hydrogen.

Ultimately a quantity of hydrogen is used in order to form 0·0152 grams Ag_2Cl. Two molecules of silver chloride require one atom of hydrogen in order to form one molecule of silver subchloride, which is indicated in the analysis by 0·0087 grams silver chloride.

According to the equation $2\times143\cdot5: 1=0\cdot0174:x$, the quantity of hydrogen which was used up to form silver subchloride = 0·0006 grams = 0·70 c. c. Consequently we can subtract from 4·81 c. c. hydrogen 0·57 c. c.+0·96 c. c.+0·70 c. c.=2·23 c. c. hydrogen. There remain thus 2·58 c. c. hydrogen which have to be accounted for.

If we take now into account the electrochemical behavior of the hydrosol in presence of hydrochloric acid, which has made probable the accumulation of hydrogen on the silver particles; and if we consider further that the liquid contains citric acid and perhaps other easily reducible organic compounds, the absence of gas bubbles on addition of hydrochloric acid to the hydrosol need not appear strange.

I will bring forward a few more examples, but this somewhat complicated calculation will not be repeated in detail, for a new element of uncertainty has still to be taken into account. The coeffieient of absorption of hydrochloric acid for air has not been determined experimentally so far as I know, and the question remains open whether or not hydrochloric acid may absorb more oxygen from the air than can be expected according to the well-known laws of absorption of gaseous mixtures by liquids.

(*b*) 50 c. c. of the same hydrosol were coagulated with 50 c. c. of fuming hydrochloric acid.

There was precipitated—

Ag	0.7408 g.	=0.7408 g. Ag
AgCl	0.1456 g.	=0.1096 g. Ag
		0.8504 g. Ag

(*c*) 50 c. c. of the same hydrosol were mixed with 150 c. c. fuming hydrochloric acid.

There was precipitated—

Ag	0.7406 g.	=0.7406 g. Ag
AgCl	0.1499 g.	=0.1121 g. Ag
		0.8527 g. Ag

The hydrosol of this composition was purified according to the method described in a previous paper and analyzed by the same method as the crude hydrosol. The concentration of the purified hydrosol has naturally decreased owing to the process of purification to which it had been subjected.

(A) 50 c. c. of the hydrosol were mixed with 1 c. c. hydrochloric acid (1 part hydrochloric acid to 1 part water).

There was precipitated—

Ag	0.5715 g.	=0.5715 g. Ag
AgCl	0.0479 g.	=0.0360 g. Ag
AgCl*	0.0028 g.	=0.0021 g. Ag
		0.6096 g. Ag

In the filtrate from the precipitate by hydrochloric acid were found—

Fe_2O_3	0·0027 g.
SO_3	trace.

0·0027 grams Fe_2O_3 correspond, on the basis of the equation $FeCl_3 + Ag = AgCl + FeCl_2$, to 0·0048 grams silver chloride. If we subtract this quantity from 0·0479 grams, representing the total quantity of AgCl, the hydrogen has to be accounted for which corresponds to 0·0431 grams AgCl. This quantity of hydrogen weighs 0·0003 grams and its volume amounts to 3·35 c. c. From this volume we may substract 0·57 c. c.+0·96 c. c. hydrogen=1·53 c. c. hydrogen, as has been shown above. 1·82 c. c. hydrogen remain consequently to be accounted for. To form the subchloride of silver a certain quantity of hydrogen has been used up. Two molecules of silver chloride need one atom of hydrogen in order to form one molecule subchloride of silver, whose presence is indicated by the 0·0028 grams AgCl found in the analysis.

According to the equation $2 \times 143{\cdot}5 : 1 = 0{\cdot}0056 : x$, the quantity of hydrogen which has been used up in the formation of subchloride of silver amounts to 0·00002 grams=0·22 c. c. Consequently the whole quantity of hydrogen whose functions can not be determined with certainty=1·60 c. c.

(B) 50 c. c. of the hydrosol were precipitated with 50 c. c. fuming hydrochloric acid.

There were thrown down—

Ag	0·5639 g.	=0·5639 g. Ag
AgCl	0·0628 g.	=0·0472 g. Ag
		0·6111 g. Ag

*In the ammoniacal extract as previously noted.

(C) 50 c. c. of the hydrosol were precipitated with 200 c. c. fuming hydrochloric acid.

There were precipitated—

Ag	0.5587 g.=0·5587 g. Ag
AgCl	0·0729 g.=0·0548 g. Ag
AgCl *	0·0040 g.=0·0030 g. Ag
	0·6165 g. Ag

If this particular case which has yielded the maximum of silver chloride is compared with the analogous case, in which we had to deal with the crude hydrosol, we can easily perceive that the proportion of the quantity of silver which is precipitated as silver chloride to the quantity of silver which is precipitated as metal is smaller in the hydrosol containing little iron than in the hydrosol containing much iron.

If this result is expressed in percentage calculated on the total quantity of silver the following numbers are obtained:

The hydrosol contained 3 per cent Fe_2O_3 . 0·4 per cent Fe_2O_3.

There were precipitated as AgCl 13·1 per cent=9·3 per cent Ag.

Shortly expressed, the results of this and of the two other investigations pertaining to the silver hydrosol are:

1. The crude hydrosol can be purified by precipitation with alcohol and by dissolving again the precipitated colloid in water.

2. The almost pure colloid is soluble in absolute alcohol and forms an organosol.

3. The behavior of the silver hydrosol differs from that of ordinary finely divided silver not in nature but in degree.

4. This becomes evident from the electro-chemical behavior of the hydrosol on contact with hydrochloric acid. The finely divided silver becomes charged in a higher degree with hydrogen than silverfoil. The same follows from the behavior of the hydrosol towards ferric chloride. If the latter is present in sufficient quantity all the colloidal silver present is changed into silver chloride according to the equation

$$FeCl_3+Ag=AgCl+FeCl_2.$$

Under the same circumstances silverfoil is covered only with a thin coating of silver chloride.

5. The peculiar differences in the color of the hydrosol, of the organosol (ethyl alcohol), and of the solid colloid are probably due to interference phenomena depending upon the size of the particles.

6. It is consequently unnecessary to assume an allotropic condition of silver so long as the physical properties of solid colloidal silver are not fully known.

* In ammoniacal extract as before.

MISCELLANEOUS ANALYSES.

THE MOUNT JOY METEORITE.

An iron found near Two Taverns post-office, in the neighborhood of Gettysburg, Pa.

[Analyzed by L. G. Eakins.]

Fe	93·80
Ni	4·81
Co	·51
Cu	·005
P	·19
S	·01
	99·325

A NICKEL-IRON SULPHIDE FROM CANADA.

From the Worthington Mine, Sault Branch Canadian Pacific Railroad, 25 miles west of Sudbury, Ontario. Grayish, with a cast of yellow. Not pyrrhotite. Possibly a mixture of pyrite and polydymite.

[Analysis by W. F. Hillebrand.]

Fe	38·36
Ni	4·57
Mn	·10
S	45·11
SO_3	·95
CO_2	*1·49
CaO	1·91
MgO	·41
Insoluble	4·80
Moisture at 100°	·55
	98·25

BEAUXITE FROM ALABAMA.

From near Jacksonville, Calhoun county. Two samples—A, red; B, white.

[Analyses by W. F. Hillebrand. Lime, magnesia, and alkalies not looked for.]

	A.	B.
H_2O at 100°	·65	·45
H_2O ignition	20·43	23·41
SiO_2	10·25	21·08
TiO_2	2·53	2·52
Al_2O_3	41·00	48·92
Fe_2O_3	25·25	2·14
P_2O_5	trace.	trace.
	100.11	98·52

* Calculated to saturate CaO.

ANORTHITE FROM RAYMOND, MAINE.

White crystals, associated with idocrase, cinnamon garnet, pyroxene, and scapolite.

[Analysis by W. H. Melville.]

SiO_2	43·13
Al_2O_3	30·95
Fe_2O_3	1·04
FeO, MnO	traces.
CaO	19·71
MgO	·31
K_2O	1·29
Na_2O	·69
Li_2O	trace.
H_2O at 100°	·22
H_2O ignition	2·80
	100·14

The locality is near the boundary between the towns of Raymond and Gray, and is perhaps in the latter. It adjoins the northern end of Little Sebago lake.

FELDSPARS FROM JONES'S FALLS, BALTIMORE, MARYLAND.

[Collected by G. H. Williams; analyzed by W. F. Hillebrand.]

A, white albite; B, flesh-colored microcline; C, greenish microcline.

	A.	B.	C.
SiO_2	63·72	65·06	*68.48
Al_2O_3	†22·26	†18·41	16·11
Fe_2O_3	.....	.....	·20
FeO	.....	.....	·17
CaO	3·58	·26	·23
SrO	trace.	trace.	trace.
BaO	.....	·13	·05
MgO	·06	·04	·03
K_2O	·76	14·30	12·99
Na_2O	8·98	1·60	1·27
Li_2O	trace.	trace.	trace.
H_2O at 100°	·09	·04	·06
H_2O above 100°	·43	·26	·26
	99.88	100·10	99.85

*Quartz not wholly separated. †Including trace of iron.

OTTRELITE FROM MARYLAND.

Separated by G. H. Williams from the ottrelite-phyllite rock occurring at Liberty, Frederick county.

[Analysis by L. G. Eakins.]

SiO_2	23·40
TiO_2	1·19
Al_2O_3	39·31
Fe_2O_3	5·14
FeO	21·94
MnO	trace.
CaO	trace.
MgO	2·18
K_2O	·20
Na_2O	·20
H_2O	6·81
P_2O_5	trace.
	100·37

PIEDMONTITE FROM MARYLAND.

From rhyolite found at Pine mountain, near Monterey station.

[Received from G. H. Williams; analyzed by W. F. Hillebrand; contains a little admixed quartz.]

SiO_2	47·37
Al_2O_3	18·55
Ce_2O_3	·75
Other X_2O_3, mol. wt. @ 295	1·28
Fe_2O_3	4·02
Mn_2O_3	6·85
MnO	1·92
PbO	·14
CuO	·11
CaO	15·82
MgO	·25
K_2O	·68
Na_2O	·23
Li_2O	trace.
H_2O at 100°	·14
H_2O above 100°	1·94
P_2O_5	trace.
	100·05

ZOISITE FROM NORTH CAROLINA.

From James's mica mine, Yancey county. Color, rose red.

[Analyzed by L. G. Eakins. Sp. gr. 3·352, 27°.]

SiO_2	38·98
Al_2O_3	31·02
Fe_2O_3	4·15
MnO	·23
CaO	23·80
H_2O	2·03
	100·21

PREHNITE FROM FASSA, TYROL.

Analyzed by E. A. Schneider in connection with the experiments described on p. 36, of this bulletin.

SiO_2	43·32
Al_2O_3	25·50
Fe_2O_3	trace.
CaO	26·49
H_2O, 105°	·17
H_2O, 250°–300°	·14
H_2O ignition	4·70
	100·32

MINERALS FROM ITALIAN PEAK, GUNNISON COUNTY, COLORADO.

Analyzed by L. G. Eakins. A, pyroxene; B, garnet; C, epidote; D, scolecite.

	A.	B.	C.	D.
SiO_2	47·53	36·88	37·22	45·90
Al_2O_3	9·68	10·34	24.09	26·51
Fe_2O_3	1·79	17·51	12·80	.....
FeO	·91	.....	·79	.....
MnO	trace.	.....	·11	.....
CaO	25·46	34·85	23·36	14.17
MgO	14·43	·43	trace.	trace.
Na_2O	trace.	trace.	·06	trace.
H_2O	·30	·21	1·61	13·79
F	.....	.....	·06	.....
	100·30	100·22	100·10	100·37
Sp. gr	3·312, 16°·7	3·721, 17°·2	3·452, 17°·	2·247, 17°·2

XENOTIME FROM NORTH CAROLINA.

From the gold washings at Brindletown.

[Analyses by L. G. Eakins.]

	Green.	Brown.
SiO_2	3·46	3·56
ZrO_2	1·95	2·19
UO_2	4·13	1·73
ThO_2	trace.	trace.
Al_2O_3	·77	1·57
Fe_2O_3	·65	2·79
$(LaDi)_2O_3$	·93	·77
$(YEr)_2O_3$, mol. wt. 260	56·81	55·43
CaO	·21	·19
P_2O_5	30·31	29·78
F	·06	·56
H_2O	·57	1·49
	99·85	100·06
Sp. gr	4·68, 24°·2	4·46, 24°·4

WATER OF CALEDONIA SPRING, CALEDONIA, NEW YORK.

[Analyzed by H. N. Stokes.]

	Parts per million.	Per cent total solids.
Ca	180·3	17·36
Mg	30·1	2·90
K	3·2	·31
Na	98·3	9·45
H (in bicarbonates)	3·6	·35
SO_4	292·6	28·17
Cl	206·1	19·85
CO_3	217·0	20·88
SiO_3	7·6	·73
	1038·8	100·00

WATER FROM NASHVILLE, ILLINOIS.

The "American Carlsbad Spring."

[Analysis by George Steiger. In parts per million.]

	Found.	Per cent total solids.	Hypothetical combination.		Per cent total solids.
SiO_2	12·40	·29	NaCl	40·27	·95
SO_4	1694.58	39·76	Na_2SO_4	2052·44	48·15
CO_3	1142·12	26·80	$MgSO_4$	383·78	9·01
Cl	24·44	·57	$MgCO_3$	701·97	16·47
Al_2O_3	3·60	·08	$CaCO_3$	1067.85	25·05
Ca	427·14	10·02	Al_2O_3	3·60	·08
Mg	277·32	6·51	SiO_2	12·40	·29
Na	680·71	15·97			
	4262·31	100·00		4262.31	100·00

WATER OF SOAP LAKE, WASHINGTON.

[Stated in parts per million. Analysis by George Steiger.]

	Found.	Per cent total solids.	Hypothetical combination.		Per cent total solids.
SiO_2	113·00	.40	NaCl	5810·80	20·61
SO_4	4362·40	15·47	Na_2SO_4	6452·76	22·89
CO_3	9624·59	34·13	Na_2CO_3	11339·99	40·22
Cl	3526·20	12·50	$NaHCO_3$	4412·02	15·65
Ca	trace	trace	$MgH_2C_2O_6$	66·00	·23
Mg	10·85	·04	SiO_2	113·00	·40
Na	10504·11	37·27			
H (bicarbonate)	53·42	·19			
	28194·57	100·00		28194·57	100·00

Water strongly alkaline. Contains about four parts per million of sediment, containing carbonate of lime with a little sulphur and organic matter. A good deal of organic matter is in the water.

WATER FROM OJO CALIENTE, NEW MEXICO.

A thermal spring near Taos. Sp. Gr., 1·00273, 18° ·4.

[Analysis by W. F. Hillebrand. In parts per million.]

	Found:	Hypothetical combination.		Per cent total solids.
SiO_2	60·2	LiCl	20·9	·62
SO_4	151·0	KCl	59·9	1·76
PO_4	·2	NaCl	305·5	9·01
CO_3	2153·5	$Na_2B_4O_7$	5·4	·16
B_4O_7	4·2	Na_2SO_4	223·3	6·59
Cl	231·4	Na_2CO_3	1846·9	54·49
F	5·2	$Ca_3P_2O_8$	·3	·01
Fe_2O_3*	1·6	CaF_2	10·7	·32
Al_2O_3	·5	$CaCO_3$	43·0	1·27
Ca	22·8	$SrCO_3$	2·4	·07
Sr	1·4	$MgCO_3$	33·2	·98
Mg	9·5	SiO_2	60·2	1·78
K	31·4	Fe_2O_3	1·6	·05
Na	995·1	Al_2O_3	·5	·01
Li	3·4	CO_2 bicarb	775·6	22·88
	3671·4		3389·4	100·00

*State of oxidation unknown. Fe_2O_3 all in sediment.

The water also contains traces of arsenic, nitrates, iodine (?), barium, and ammonium. No organic matter. Titamium, bromine, manganese, and sulphides were looked for but not found.

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